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Polymerization in the Crystalline State. X. Solid-State Conversion of 6-Aminocaproic Acid to Oriented Nylon 6

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Synopsis

When single crystals of 6-aminocaproic acid (ACA) are heated about 30°C below their melting point, polycondensation to nylon 6 takes place. The polymer crystallites are biaxially oriented towards each other and the relation between their orientation and that of the parent monomer crystal has been clarified. The kinetics of the process are characterized by three stages, (*a*) an induction period, (*b*) a stage in which monomer disappears at a constant rate while polymer of relatively low molecular weight is formed, and (*c*) a slow polycondensation of the polyamide chains after exhaustion of the monomer. Oligomer concentrations were below detectable limits at all stages of the process. Addition of monomer to the polyamide was retarded when ACA was kept from reaching its equilibrium vapor pressure (0.12 mm Hg at 170°C) by condensation on a cool surface or when an inert gas was admitted to the system. This was interpreted as suggesting that ACA is transported through the vapor phase to the propagating polyamide. A number of surfaces catalyzed the polycondensation of ACA vapor, but nylon 6 formed in this way on KCl crystals exhibited no preferred orientation. The linear dimer and trimer of ACA were also found to condense to nylon 6 in the crystalline state, although at a slower rate than the monomer. The solid-state polycondensation of these oligomers was accelerated when they were exposed to the vapor of the monomer. Solid-state polycondensation of single crystals of the linear dimer led also to biaxially oriented nylon 6.

INTRODUCTION

The reactivity of organic compounds in the crystalline state has become only in recent years a subject of systematic investigation.[1-3] Among such studies, particular interest attaches to the question whether it is possible to make use of the orientation of reagent molecules in a single crystal of a polymerizable substance to produce chemically specimens with oriented polymer chains, without need of the usual mechanical orientation process. Such production of oriented polymer chains has been shown to occur in the solid-state polymerization of trioxane[4,5] and trithiane[6,7] as well as in the polymerization of a variety of vinyl monomers contained in urea[8] or thiourea[9] clathrate complexes. In the absence of the constraints imposed by inclusion in a channel complex, the solid-state polymerization of vinyl monomers may still be characterized by partial orientation effects. These lead to an anisotropy of the electron spin resonance spectrum in the initial stages of the polymerization of barium methacrylate dihydrate[10] and acrylamide,[11] infrared dichroism of the polymer obtained from *p*-benzamidostyrene,[12] and an x-ray diffraction pattern which proves that the side chains of vinyl stearate retain their original orientation during the polymerization process.[13]

It has also been reported by various investigators that some polycondensation reactions may take place in the crystalline state.[14] Since such a reaction requires the diffusion of the eliminated molecules through the partially polymerized specimen and a substantial contraction in the direction of the fiber axis, it seemed unlikely that oriented chain growth could be achieved in this way. Yet, in a note previously published from this laboratory,[15] clear crystallographic evidence was presented that single crystals of 6-aminocaproic acid (ACA) heated well below their melting point are converted into an assembly of crystallites of polycapramide (nylon 6) which are highly oriented towards each other in all crystallographic directions.

The x-ray evidence for the production of oriented polycapramide from single crystals of ACA and the correlation of the orientation of the polymer crystallite with the parent monomer crystal are now discussed in more detail. The existence of an oriented polycondensation process raises many questions which we were trying to clarify by studies of the kinetics of the process, analysis for oligomeric products, electron-microscopic observations, and a comparison of the polymerizability of crystals of ACA and its oligomers.

EXPERIMENTAL

Materials

Commercial 6-aminocaproic acid (Columbia Organic Chemical Co.) was recrystallized three times from 5 ml ethanol and 1.5 ml water per gram of ACA at 50°C, raising the melting point from 205°C to 207°C. The crystals were sifted through standard sieves, selecting the fraction with an average size of 0.3 mm for studies of the polycondensation kinetics. Single crystals for crystallographic studies were grown from a mixture of 4 ml water and 40 ml *n*-butanol per gram ACA. Monoclinic needles about 3 mm long were obtained.

To synthesize the ACA dimer, the following steps were employed: (*a*) ACA was carbobenzoxylated,[16a] yielding a product melting at 55.5–56.5°C in 89% yield; (*b*) the carbobenzoxy-ACA was coupled with free ACA by the mixed anhydride technique[17] to yield the carbobenzoxylated dimer (m.p. 106.5–107°C) in 69% yield; (*c*) the free dimer was obtained by palladium-catalyzed reduction of the carbobenzoxy-derivative[16b] and recrystallized from aqueous *n*-butanol (m.p. 202°C). The x-ray powder diagram of the product agreed with data in the ASTM powder file. Single crystals of the dimer were grown from 9:1 mixtures of *n*-butanol with water. They were obtained as monoclinic needles 1 mm long.

A similar procedure was used to obtain the ACA trimer (m.p. 209–210°C).

4-Aminobutyric acid (Calbiochem, A Grade) was recrystallized from ethanol–water, yielding a product melting at 206.5°C.

5-Aminovaleric acid (Aldrich Chem. Co.) was recrystallized from a mixture of 20 ml of 95% ethanol and 5 ml of ethyl acetate. The product melted at 157°C.

11-Aminoundecanoic acid (Aldrich Chem. Co.) was recrystallized from ethanol containing 30 vol-% of water. The product melted at 188°C.

Kinetic Studies

Samples of ACA (or the other compounds under investigation) were weighed in micro test tubes which were placed into glass ampules. The ampules were evacuated for at least 4 hr at 10^{-4} mm Hg, sealed, and placed in a constant temperature bath containing Dow Corning 200 Fluid at 170 ± 0.1°C. In one series of experiments, nitrogen under fixed pressure was admitted before sealing the ampules. In another series, weighed amounts of water were placed in separate microtubes which were placed into the ampules together with the sample of ACA. The ampules were cooled in a Dry Ice–acetone bath and evacuated to 10^{-2} mm Hg for 4 hr before sealing. For any given kinetic run, ampules were removed from the thermostatic bath after varying reaction times and their contents were analyzed as described below.

Analytical Procedures

The extent of the polycondensation reaction was determined by conductometric amine titration[18] with the use of a dipping cell with platinum electrodes with a surface area of 2 cm^2 at a distance of 1.7 mm from each other. The titrant was $0.1N$ aqueous HCl administered from a microburet with a precision Teflon plunger operated by a manual micrometer. The volume of the buret was 2 ml graduated in 0.001 ml. The resistance was measured with an Industrial Instruments Co. RC-1682 bridge. In a typical experiment, 10–20 mg of sample was dissolved at 50°C in phenol, adding subsequently 5 ml of 95% ethanol and 5 ml of water. The titration was run well past the end point and the conductances were plotted against the volume of titrant. The points were found to lie on two straight lines whose intersection defined the equivalence point. ACA, its dimer and trimer yielded titration values within ±2% from theoretical. Similar reproducibility was attained in the estimation of the number-average degree of polymerization of commercial nylon 6 ($\bar{P}_n = 190$). Denoting by b the number of milliequivalents of amine per gram of sample, $\bar{P}_n = (8.85/b) - 0.16$. The degree of conversion is given by $p = (\bar{P}_n - 1)/\bar{P}_n = (7.62 - b)/(7.62 - 0.14b)$.

To determine the water-insoluble fraction (i), 100 mg of sample obtained from the polymerization experiments were stirred with 5 ml of water at

50°C for 15 min, transferred to a fritted glass filter (medium size), washed with water, vacuum-dried, and weighed. The filtrate was reserved for chromatographic analysis.

Thin-layer chromatography of the water-soluble fraction was carried out according to general guidelines of Stahl[19] and Bobbitt.[20] Adsorbent layers (20 μ thick) were made from a slurry of 30 g of Silica Gel H (Merck) with 70 ml of distilled water. The developing solution contained 150 ml butanol, 50 ml pyridine, 120 ml acetic acid, and 50 ml water. The chromatographic spots were rendered visible by spraying with a solution of 0.3 g ninhydrin in 100 g *n*-butanol and 3 g acetic acid. After spraying, the chromatogram was dried at room temperature for 1 hr and heated in an oven at 110°C for 15 min. The method was standardized with ACA and its oligomers, yielding $R_f = 0.31$ for monomer, $R_f = 0.42$ for dimer, $R_f = 0.53$ for trimer, and 0.61 for tetramer. The intensities of the spots were proportional to the concentration of endgroups. As little as 3% dimer could be detected in a monomer–dimer mixture.

X-Ray Diffraction

All x-ray diffraction photographs were taken with the use of nickel-filtered copper radiation.

Specimen Preparation for Electron Microscopy

To obtain a replica of the surface of a polymerized ACA crystal, a 5% acetone solution of parlodion (Mallinckrodt purified cellulose nitrate) was evaporated slowly at low temperature to give a film thickness of about 50 μ. The film was slightly swollen with a 1:1 mixture of ethyl acetate and *n*-pentane, and the crystals to be studied were applied to it. After 15–20 hr the crystals were carefully removed with a needle, the operation being checked under a stereo microscope by using polarized light. The parlodion replica was then shadowed with platinum at an angle of 30° and backed by a film of carbon. The surface of the parlodion was covered with a 5% solution of gelatin in water at 50°C. After 24 hr the gelatin film, with the carbon–platinum replica adhering to it, was peeled off and the gelatin was dissolved in water at 50°C, leaving the carbon–platinum replica to be picked up on a copper grid.

For electron microscopy of films prepared by surface-catalyzed polycondensation, the reaction time was so adjusted as to produce a film thickness of about 300 Å (16 hr at 170°C). The film with the underlying substrate was shadowed as described above, squares of 2 mm × 2 mm were scratched on its surface with a sharp needle, and the little squares of polymer film shadowed with platinum and backed with carbon were detached from the catalytic surface by immersion in water.

Infrared Spectroscopy

A Perkin-Elmer Model 21 spectrophotometer was used. For studies of infrared dichroism, a pile of 0.02 in. silver chloride plates was used as polarizer.

Determination of the Vapor Pressure of ACA

Isooctane (bp 99.3°C), toluene (bp 111°C), xylene (bp 139°C), cumene (bp 153.3°C) and *p*-cymene (bp 176°C) were carefully dried over metallic sodium, and 1500 ml of the solvent was distilled with 50 mg of finely ground ACA. A 1000 ml portion of the distillate was extracted four times with 5 ml of deionized water. The ACA in the aqueous extract was determined by conductometric titration and the extraction was repeated to make sure that no amino acid remained in the organic layer. The vapor pressure of ACA was then calculated, complete immiscibility of ACA with the organic solvent being assumed.

RESULTS AND DISCUSSION

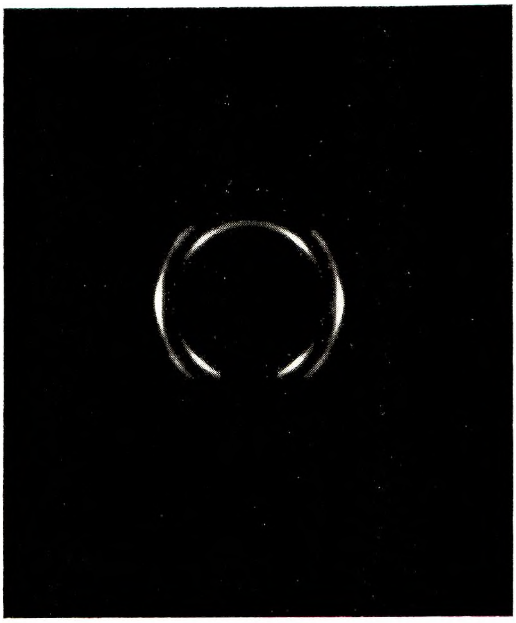
Crystallographic Study of Nylon 6 Obtained by Solid-State Polycondensation of 6-Aminocaproic Acid

Single crystals of ACA heated *in vacuo* for 16 hr at 168°C were found to be converted quantitatively to highly oriented nylon 6. An x-ray photograph of polymerized crystal rotated about the *b* axis of the monomer precursor is shown in Figure 1*a*. It contains three intense reflections. Two, corresponding to a spacing of 3.7 Å, appear on the zero layer and the first layer, while a third reflection corresponding to 4.4 Å is seen on the first layer. These strong reflections are characteristic of the monoclinic α form of nylon 6 as described by Holmes et al.[21] This identification was confirmed by the observation of weaker reflections for spacings of 2.4, 2.2, 1.98, and 1.84 Å.

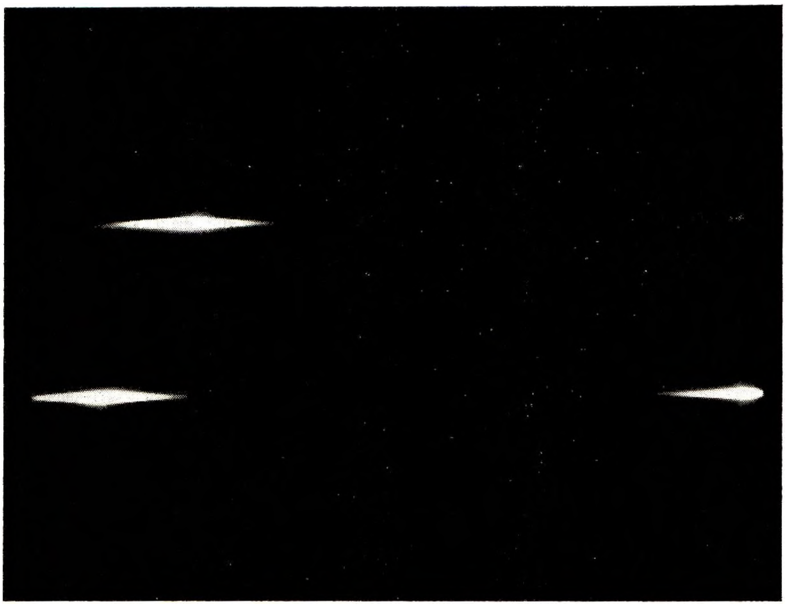
A Weissenberg photograph of the same sample is shown in Figure 1*b*, and it proves in conjunction with the rotation photograph that the nylon 6 is biaxially oriented. The extent of the orientation about axes normal to the axis of rotation may be judged from the length of the streak on the 0-layer Weissenberg photograph, which corresponds to an angular range of 20° for each of the intense reflections. Similar biaxial orientation of the polymer formed in a solid-state polymerization process has previously been reported for the conversion of single crystals of trioxane into polyoxymethylene[22] and of trithiane into polymethylene sulfide.[6,7]

The monomer crystal is monoclinic, space group $P2_1/c$, with $a = 8.555$ Å, $b = 5.872$ Å, $c = 15.274$ Å, $\beta = 103.1$ Å, and four molecules per unit cell. The structure has been determined recently by Bodor et al.[23]

The amino acid molecules are in the zwitterionic form (this is also confirmed by the infrared absorption at 1400 cm^{-1}, characteristic of ionized carboxyl) and lie in layers approximately parallel to the *ab* plane. Each of the four molecules per unit cell belongs to a different layer and the nitrogen atom of each molecule forms three hydrogen bonds. Of these, two serve to bind molecules together in the *ab* layers while the third serves to link the layer at $z = {}^1/_8$ and the layer at $z = {}^5/_8$ to that at $z = {}^7/_8$, forming strongly bonded double layers. It should be noted that these double layers are held together by relatively weak intermolecular interactions and



(*a*)



(*b*)

Fig. 1. X-ray diffraction from nylon 6 produced from a single crystal of 6-aminocaproic acid rotated around the *b* axis of the parent monomer: (*a*) rotation photograph; (*b*) zero-layer Weissenberg photograph.

also that if molecules at $z = {}^3/_8$ are oriented parallel to the [110] direction, those at $z = {}^7/_8$ will be parallel to the [1$\bar{1}$0] direction. It would be expected that disordering processes (mechanical stress, melting, sublimation) would be propagated within the double layers but would not be transmitted easily from one double layer to the next. This would leave the surface of the double layer as the predominant ordered exposed surface in the crystal.

The polymer crystal structure belongs to space group $P2_1$, $a = 9.56$ Å, $b = 17.2$ Å, $c = 8.01$ Å, $\beta = 67.5°$, with the chain axis parallel to b and nearest neighbor chains, antiparallel to each other, forming a hydrogen-bonded network parallel to the *ab* plane.

Weissenberg photographs of partially converted monomer crystals showed that the (200) reflection of the polymer lies parallel to the $(11\bar{2})$ monomer reflection. Beyond that, the data allowed two alternative interpretations, either $(202)_{\text{pol}} \parallel (112)_{\text{mon}}$ with $(002)_{\text{pol}} \parallel (004)_{\text{mon}}$, or, $(202)_{\text{pol}} \parallel (004)_{\text{mon}}$ with $(002)_{\text{pol}} \parallel (112)_{\text{mon}}$. [The interplanar spacings are 3.70 Å for $(002)_{\text{pol}}$ and 3.59 Å for $(202)_{\text{pol}}$; these values are too close to one another to distinguish unambiguously between the two correlations given above.] Since the three polymer reciprocal lattice vectors are perpendicular to the b axis of the polymer, while the three monomer reciprocal lattice vectors are perpendicular to the intersection of the (110) or (1$\bar{1}$0) planes with the (004) planes of the monomer, it may be concluded that the b axis of the polymer unit cell must lie parallel to the (110) and (1$\bar{1}$0) directions in the monomer. The polymer crystallites were, in fact, found to be twinned with the preferred orientation of the polymer b axis at ±55° to the b axis of the monomer. Such twinning is a necessary consequence of the space group of the monomer which requires chain growth to be equally probable in two alternative directions symmetrical about the *ac* plane. A similar twinning phenomenon was previously encountered in the solid-state polymerization of trioxane.[22]

The conclusions reached on the basis of crystallographic studies were supported by electron-microscopic observation of the surface of an ACA crystal after conversion to nylon 6. The electron micrograph shown on Figure 2 reveals two alternative directions of fiber crystal orientation inclined to each other at 110°.

It may be noted that the direction of fiber growth is almost identical to the orientation of the molecules in the monomer crystal. However, interpretation of the polycondensation as a solid-state reaction poses some serious problems. The reaction involves a contraction of 17% in the direction of the polymer chain axis and a 18% reduction of volume and it is not at all clear how this could be accomplished in a topotactic process. In addition, we have to account for the fact that all the chains in the polymer crystal are either parallel or antiparallel to each other, while the orientations of the molecules in alternate layers of the monomer crystal subtend an angle of 55°, so that the solid-state polycondensation would have to involve considerable rotation of the monomer residues.[23] These difficulties may be avoided if we assume that we are dealing with an epitactic process in

Fig. 2. Electron micrograph of a replica of the surface of a 6-aminocaproic acid crystal converted to nylon 6.

which vapor of the monomer reacts at the (001) crystal surface to form oriented nuclei of the polymer crystallites. The orientation of these nuclei would then occur with equal probability in the two directions characterizing the orientation of alternate layers of the monomer molecules, thus leading to the observed twinning of the polymer crystallites. We shall see later that observations of the kinetics of the polycondensation process also support this interpretation.

Polymerization of a single crystal of the ACA dimer led also to nylon 6 specimens with biaxial orientation. The complete crystal structure of the dimer is not available at this time but infrared spectroscopic evidence shows that here, too, the endgroups are ionized. The monoclinic unit cell, space group $P2_1/c$, a = 17.50 Å, b = 4.92 Å, c = 17.40 Å, β = 106.8° contains four molecules which again seem to lie approximately parallel to the 110 direction.

Kinetics of ACA Polycondensation

The kinetic pattern was characterized by three clearly distinct stages of the polycondensation process. In the first stage, polymer formation was negligible. This induction period was followed by a period when the degree of conversion increased rapidly at a constant rate essentially up to the complete disappearance of monomer. Finally, the degree of polymerization of the polyamide continued to increase slowly for a long time. Data from a typical kinetic run are listed in Table I; we may see that under the conditions of this experiment no reaction is observed for the first 2 hr, while 52% of the amine groups reacted in the following 9 hr. From the overall degree of conversion p, the water-insoluble fraction i, and the number-average degree of polymerization of the water-insoluble fraction $\bar{P}_{ni}$, we may calculate the amine content of the water-soluble fraction, and that is given as b_s in the last column of Table I. The values deviate little from $b_s = 7.62$ corresponding to pure monomer. Thin-layer chromatography also led to the conclusion that no detectable amounts of dimer, trimer or tetramer are present in the aqueous extracts at any stage of the solid-state polycondensation. In this respect, the product obtained in the polycondensation of crystalline ACA differed strikingly from that obtained when the reaction was carried out in molten ACA. In the latter case, the same chromatographic procedure revealed large concentrations of dimer, trimer, and tetramer. Assuming that the reactivity of a functional group is independent of the length of the chain to which it is attached,[24] the mole fraction $N(P)$ of an oligomer with P units is given by $N(P) = p^{P-1}(1 - p)$, so that for high degrees of conversion, monomer and low oligomers should be present in nearly identical molar concentrations. The color intensities of the spots due to monomer, dimer, trimer, and tetramer in an aqueous extract from melt-polymerized ACA were, in fact, found to be approximately equal in accordance with expectation, since the color reaction is proportional to the endgroup concentrations. The fact that in solid-state polycondensation the molar concentration of the oligomers is negligibly small compared to that of the monomer results from the heterogeneous character of the solid-state reaction which segregates the polymer in a separate phase. Thus, even if the chain-length distribution in the polymer phase corresponds to the classical distribution functions, the oligomer will

TABLE I

Solid-State Conversion of 6-Aminocaproic Acid to Nylon 6 at 170°C[a]

Time, hr	Amine, meq/g	$\bar{P}_n$	p	Fraction water-insoluble (i)	$\bar{P}_{ni}$	b_s
1	7.62	1.0	0.00	0.00	—	7.62
2	7.70	1.0	0.00	0.00	—	7.70
5	7.10	1.1	0.08	0.06	16.5	7.52
6	6.25	1.26	0.20	0.18	18	7.50
9	4.75	1.70	0.41	0.32	22	6.83
11	3.90	2.11	0.52	0.41	27	6.42
13	3.25	2.72	0.61	0.57	32	7.23
16	2.20	3.82	0.74	—	—	—
20	0.17	52	0.98	—	—	—

[a] 230 mg ACA in 25-ml ampules with a surface of 48 cm^2.

be below detectable limits in the presence of the large amount of monomer in the separate monomer phase.

On the basis of our data, the solid-state polycondensation of ACA can be described in the following terms. In the initial stages, the polymer phase has to be nucleated. The formation of such nuclei is readily observable under the polarizing microscope. An induction period corresponding to the time required to produce nuclei of a polymer phase has previously been observed in the solid-state polymerization of *N*-carboxy-α-amino acid anhydrides to polypeptides.[25] The rate of nucleation of a new phase is highly sensitive to the perfection of a crystal,[26] but in polycrystalline samples a fair degree of reproducibility can be achieved by statistical averaging. In the second stage, monomer disappears at an approximately constant rate, while polymer of relatively low molecular weight is formed. Finally, after exhaustion of the monomer, polycondensation involving terminal groups of the polymer chains leads to a slow increase of the molecular weight of the product, even though the system is kept below the melting point of the polymer. (The existence of such a process was described in the patent literature almost thirty years ago.[27]) We shall now consider the characteristics of these three stages in somewhat more detail.

It was suspected that the length of the induction period might be sensitive to the vapor pressure of water to which the monomer crystals are exposed.[25] This was varied in the following way. When the monomer was sealed *in vacuo*, the aqueous vapor pressure built up gradually owing to the water eliminated during the polymerization process, and this pressure could be varied by varying the ratio of the size of the monomer sample to the available vapor space. Since it was invariably noted that a thin film formed on the surface of the glass tubes (this film being identified spectroscopically as nylon 6), the question arose whether the polymerization rate of the bulk of the ACA would be significantly affected if this initial surface-

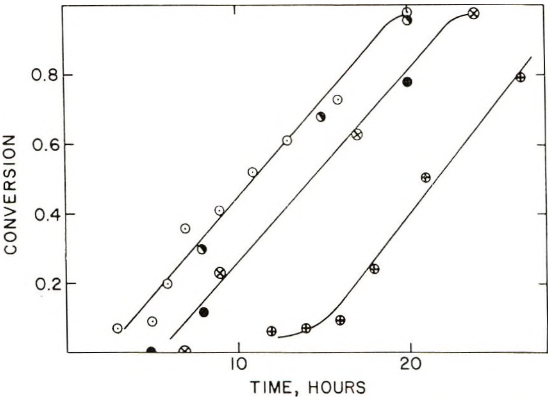


Fig. 3. Dependence of polycondensation on experimental conditions: (○) 230 mg ACA in a 25 ml ampule; (⊗) 200 mg ACA in 230 ml; (⊕) 670 mg ACA in 230 ml; (◑) 200 mg ACA in 25 ml, ampule surface silicone-coated; (●) 200 mg ACA in 25 ml, initial aqueous vapor pressure 410 mm Hg.

catalyzed polymerization, with its attendant water elimination, could be prevented. It was found that the catalytic effect of the glass on the ACA vapor could be suppressed by coating with silicone oil and baking for 1 hr at 170°C before introducing the monomer, and a kinetic run was carried out under these conditions. Finally, a run was carried out with a weighed amount of water added to the reaction tube so as to provide a relatively high aqueous vapor pressure at the outset of the experiment.

The results obtained under these various conditions are given in Figure 3. It may be seen that the reaction rate in its rapid phase is quite independent of the variables investigated (0.06 hr^{-1} at 170°C), while the length of the induction period is subject to wide variations. When the monomer sample was enclosed in 25 ml ampules, the induction period was not altered by silicone treatment of the glass surface so as to prevent the surface-catalyzed reaction. Moreover, the introduction of water at the beginning of the experiment yielded results very similar to those obtained in one of the runs in which the space above the monomer was initially highly evacuated. We are, at present, unable to define the factors determining the length of the induction period.

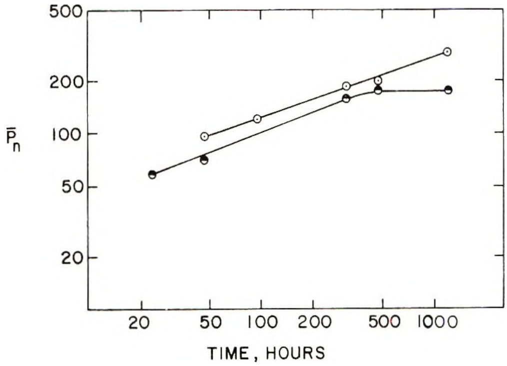


Fig. 4. Polycondensation of nylon 6 after exhaustion of the monomer: (○) final aqueous vapor pressure 180 mm Hg; (◓) final aqueous vapor pressure 1680 mm Hg.

Once the polymer phase has been nucleated, the growth of polymer chains appears to be relatively rapid. We see, for instance, in Table I that at a point where only 8% of the reactive groups had disappeared, the system consisted of unchanged monomer and a water-insoluble fraction constituting 6% by weight and containing polymer with a degree of polymerization of 16.5. As monomer gradually disappears, the polymer chain length increases, but the degree of polymerization increases much more slowly than in proportion to the weight of the water-insoluble fraction. Thus, the growth of new polyamide chains must be initiated while monomer adds to extend the length of existing chains. For instance, an almost tenfold increase in the water-insoluble fraction from 6% to 57% was accompanied by about a doubling of the polymerization degree, from 16.5 to 32.

The last stage of the process, i.e., the polycondensation of the polyamide following monomer disappearance, was also followed as a function of the ambient aqueous water pressure (varied by the space provided per unit weight of monomer at the outset of the experiment). In view of the highly restricted mobility of the reactive groups in the semicrystalline polymer sample, one would not expect the reaction to follow, in this case, conventional second-order kinetics.[28]

In fact, plots of $\bar{P}_n$ against time and even plots of $(\bar{P}_n)^2$ against time (corresponding to third-order kinetics) are strongly concave towards the time axis. A double logarithmic plot of the degree of polymerization against reaction time was found to be linear (Fig. 4), with the higher aqueous vapor pressure leading to somewhat lower chain length at long reaction times. Under these conditions, $\bar{P}_n$ did not increase between 20 and 50 days, suggesting that a state of equilibrium[29,30] may have been reached.

Mechanism of the Reaction

The high orientation of the polymer obtained in the polymerization of crystalline ACA suggests that the process takes place in the solid state and that the direction of chain propagation is governed by the crystal structure of the monomer. Yet, the high contraction in the direction of the fiber axis, which we have referred to previously, renders it rather difficult to visualize such a process, and alternative possibilities have to be considered.

First we should consider the possibility that the reaction occurs in a small volume of a liquid phase. Let us note that the reaction takes place more than 30°C below the melting points of either monomer or polymer, but that we do not know to what extent the semicrystalline polymer may be swollen by ACA and how much the polymer melting point might be lowered by such dilution. In addition, the relatively high pressure of water vapor built up when sizable amounts of ACA undergo a polycondensation in a closed space (between 180 and 1930 mm Hg under the conditions of the experiments illustrated in Fig. 3) might, in principle, lead to formation of a liquid phase at temperatures close to the melting point of the monomer.

It was found that the addition of water to provide an initial aqueous vapor pressure of 410 mm Hg led to no detectable reduction in the orientation of the polyamide formed. This can be reconciled with polymerization in a disordered phase only by assuming oriented deposition of polymer crystallites on the underlying monomer crystal. Such epitactic polymer crystal growth has been observed even on chemically quite dissimilar substrates,[31,32] and an analogous oriented crystallization of a polyamide on the surface of an ACA crystal would appear to be quite feasible. However, if the presence of a liquid phase is essential for the reaction to proceed, the initial addition of water should lead to a marked acceleration and the elimination of the induction period. No such effect was observed and it appears that the role of a liquid phase in the process studied in the present investigation may be safely excluded.

The other possibility to be considered involves the transport of monomer through the vapor phase to the reaction site. We have already noted that during the polycondensation of crystalline ACA a film of nylon 6 was deposited on the surface of the glass ampules in which the monomer was contained. Control experiments, in which the ampules contained caprolactam, produced no such film, proving that the glass surface catalyzed the polycondensation of ACA, rather than the polymerization of caprolactam which might have been formed by dehydration of ACA in the vapor phase. Since the film could be grown to a thickness of several microns, it is clear that only the initiation of the chain growth could have been affected by the specific properties of the glass and that addition of ACA vapor to the polyamide can continue independently of the nature of the underlying surface. It may then be conjectured that a similar process is responsible for the growth of polymer nuclei formed on the ACA crystals. The vapor pressure of ACA at five temperatures ranging from 99.3 to 176°C was determined as described in the experimental section, yielding the values listed in Table II. From these data, the vapor pressure at the reaction temperature of 170°C is estimated as 0.12 mm Hg. This value is easily sufficient to account for the transport of monomer to the reaction site.

TABLE II
Vapor Pressure of 6-Aminocaproic Acid

Temperature, °C	Vapor pressure, mm Hg
99.3	0.00025
111.0	0.00095
139.0	0.0069
153.0	0.034
176.0	0.197

Two experiments were carried out to test the role of monomer transport through the vapor phase in the polymerization of crystalline ACA. In the first, a sample of ACA was placed in one leg of a U tube, while some water was placed in the other leg. The system was frozen at −78°C and sealed under a pressure of 10^{-3} mm Hg. The leg containing the monomer was then placed in a thermostat at 170°C while the other leg was maintained at 26°C. In this fashion it was insured that the vapor pressures of water and of ACA would not exceed their equilibrium values at 26°C, i.e., $p_{H_2O} = 24$ mm Hg and an estimated $p_{ACA} = 10^{-7}$ mm Hg. Under these conditions, only 5% of the amine groups of ACA had reacted in 21 hr, a time corresponding to 50–98% conversion in the runs plotted in Figure 3. In a second experiment in which the water in the cold leg of the U tube was omitted, no detectable reaction was observed after heating the ACA for 21 hr at 170°C. These results may be interpreted as signifying that crystalline ACA cannot be converted to polyamide in the absence of ACA vapor. When the cold leg of the U tube contains water, the aqueous vapor reduces the diffusion rate of the gaseous ACA so that the steady-state concentration of the reactive gas molecules in contact with the ACA crystals is no longer negligible. Thus, the rate of polycondensation is reduced, but the reaction is not entirely suppressed with this experimental arrangement. Admission of an inert gas, i.e., nitrogen, to the vapor space above the ACA crystals was found to retard very significantly the polycondensation process. Data illustrating this effect are presented in Figure 5. The retardation was found to be independent of the nitrogen pressure in the range of 170–820 mm Hg. This is interpreted as signifying that the reactive surface is shielded by an adsorbed layer of nitrogen from attack by ACA molecules in the gas phase. (Note that the nitrogen was, in these experiments, at a pressure 1500–7000 times as high as the ACA.)

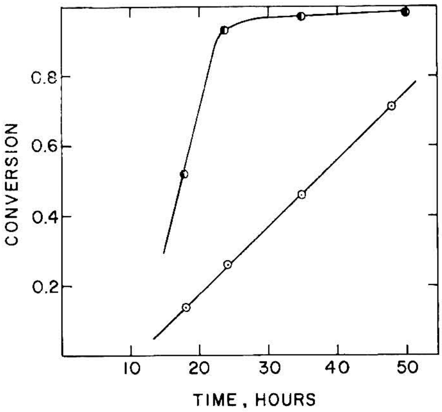


Fig. 5. Effect of inert gas on polycondensation of crystalline ACA: (◐) ampules initially under vacuum; (○) ampules initially under a nitrogen pressure of 800 mm Hg.

The above evidence leaves little doubt that the process during the rapid period of polyamide formation involves transport of monomer through the vapor phase. We have already noted that in this stage the number of polymer chains increases, while the individual chains grow slowly. Even though the monomer vapor pressure remains constant as long as crystalline monomer is present, the constancy of the reaction rate is not easily accounted for. The rate of monomer addition seems to drop off sharply with increasing polymer chain length. The constant reaction rate would then imply a constant rate at which the growth of new polyamide chains is being initiated, although the area of the interface of the polymer and monomer phases, which is believed to represent the reaction site, cannot be assumed to remain fixed.

Surface-Catalyzed Polycondensation

A number of surfaces, crystalline or amorphous, were found to catalyze the polycondensation of ACA vapor at 170°C. Among these, studies were carried out on Pyrex glass (thickness 0.1 mm), mica (0.07 mm), and single crystals of NaCl, KCl, and KBr. A reaction time of 48 hr was found to be required to build up a polymer film of 20 μ thickness. Since the monomer was essentially exhausted after 24 hr by solid-state polycondensation, the ampules were opened, the monomer replenished, the system sealed again, and the process continued.

In all cases, the polymer gave the characteristic infrared spectrum of nylon 6. In the case of films deposited on the 100 faces of KCl, the spectrum was also observed with polarized infrared radiation. The intensity of the N—H stretching band at 3300 cm^{-1}, the amide I band at 1648 cm^{-1}, and the amide II band at 1540 cm^{-1} were all found to be independent of the orientation of the plane of polarization. It was concluded that polymer crystallites exhibit no epitaxial orientation on this substrate. This conclusion was substantiated by electron microscopy which revealed spherulites with fibers about 170 Å thick and several thousands of Angstroms in length.

Behavior of Oligomers of ACA

The linear dimer and trimer of ACA behaved in a manner qualitatively similar to that of ACA. With 70 mg samples in 25 ml ampules at 170°C, the dimer was characterized by a maximum rate of 0.024 hr^{-1} and an induction period of 10 hr, while for the trimer the maximum rate was 0.01 hr^{-1} and the induction period 17 hr. While these rates are distinctly lower than that characterizing the monomeric ACA, it should be noted that the reduction in the rate is much less than that which would be expected from the change in the vapor pressure of the reagent which must decrease by many orders of magnitude as we pass from the monomer to the dimer and the trimer.

Interesting results were obtained when separate vials containing ACA (120 mg) and dimer (18 mg) were sealed in a 25-ml ampule and heated, so that the oligomer was exposed to ACA vapor. Under these conditions, the polycondensation of the dimer sample was characterized by an induction period of 6 hr and a maximum conversion rate of 0.05 hr^{-1}. The dimer sample was also found to increase in weight by 10%, but all of this gain was completed at the time the conversion had attained 16%. It appears then that the monomer vapor reacts with the dimer surface and helps to initiate the polycondensation reaction, increasing the number of chains whose propagation characterizes the period of maximum reaction rate.

Exposure to ACA vapor had a much more dramatic effect on the polycondensation of crystalline trimer. This material, when contained alone in the ampule, reached degrees of polymerization of only 3.2 and 3.7 after 19 and 34 hr, respectively. If the ampule also contained monomer, the polycondensation of the trimer reached P_n values of 8.7 in 13 hr and 101 in 19 hr. In all experiments involving crystalline dimer or trimer, chromatographic analysis of aqueous extracts of partially converted samples revealed only the oligomer present originally.

Behavior of ACA Homologs

Attempts to carry out a polycondensation of 4-aminobutyric acid (mp 206°C) at 170°C and 5-aminovaleric acid (mp 157°C) at 120°C failed, since only the low-melting lactams were obtained. With 11-aminoundecanoic acid (mp 186–187°C), a slow polycondensation was observed at 145°C, leading to a degree of conversion of 0.23 in 476 hr. Polycondensation of this substance has been studied previously at temperatures closer to the melting point.[33,34] Unfortunately, we were unable to grow suitable single crystals so as to determine whether oriented polyamide is formed in this process.

In the crystallographic investigation we have been greatly aided by the advice of Professor B. Post of the Department of Physics, Polytechnic Institute of Brooklyn. For the Weissenberg photograph reproduced in Figure 1*b* we are indebted to Dr. P. N. Kasai of the Department of Applied Chemistry, Osaka University. The electron microscopic studies were performed under the direction of Prof. E. Fischer of the University of Mainz. We are greatly indebted to Prof. G. Palade of the Rockefeller University for offering us the use of his electron microscope for this work.

This paper is abstracted from Ph.D. theses submitted by N. Morosoff in 1965 and by E. M. Macchi in 1967 to the Graduate School of the Polytechnic Institute of Brooklyn.

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Inorganic Esters of Novolacs*

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Synopsis

Reaction of conventional novolacs with polyfunctional materials is known to yield crosslinked infusible products. Surprisingly, high proportions of polyfunctional phosphorus derivatives can be esterified with *o,o'*-linked novolacs without encountering gelation. Soluble, fusible resins of high phosphate content, which possess improved flame retardance, are conveniently obtained. We attribute this result to the formation of cyclic esters in preference to crosslinking, as evidenced by the formation, in good yield, of the eight-membered heterocyclic compound $C_{27}H_{31}O_4P$ from *o,o'*-methylenebis(*p-tert*-butylphenol) and phenyl phosphorodichloridate. Relatively large amounts of polyfunctional derivatives of boron and silicon can also be reacted with *o,o'*-linked novolacs, presumably in a similar manner. Novolacs partially reacted with phosphorus, boron, or silicon derivatives and retaining some phenolic hydroxyl cure readily with hexamethylenetetramine, yielding products exceptionally low in volatile loss at 400°C.

INTRODUCTION

Esterification of novolacs is a potential means of modifying and improving their properties. Of particular interest is esterification with inorganic polybasic acids, such as phosphoric, boric, and phosphorus acids, since these modifiers offer special promise for increasing heat or flame resistance as well as for modification of electrical and mechanical properties. Similarly, modification of novolacs by conversion to silanediol derivatives is also of potential value.

However, because the OH functionality of novolac molecules is usually high (typically about 5 in many commercial novolacs), esterification with polybasic acids, such as phosphoric acid, tends to yield crosslinked, insoluble products. Several investigators[1-3] have studied such systems, and some[1,2,4-6] have obtained linear polymers using diphenols and difunctional derivatives of phosphoric acid.

We wish now to report that novolacs having appropriate structure can be esterified with relatively large amounts of inorganic acids to yield soluble, fusible products having unusual and useful properties.

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*Presented in part at the 153rd Meeting of the American Chemical Society, Miami Beach, Fla., April 9-14, 1967.

RESULTS AND DISCUSSION

Effect of Novolac Structure on Esterification

Two structurally different types of novolacs have been used in this work: (*a*) those in which the methylene linkages are located more or less randomly in the *o*- and *p*- positions,[7] hereafter called random novolacs, and (*b*) those in which practically all methylene linkages are located in the *o*-positions, hereafter called *o,o'*-novolacs.[8-11]

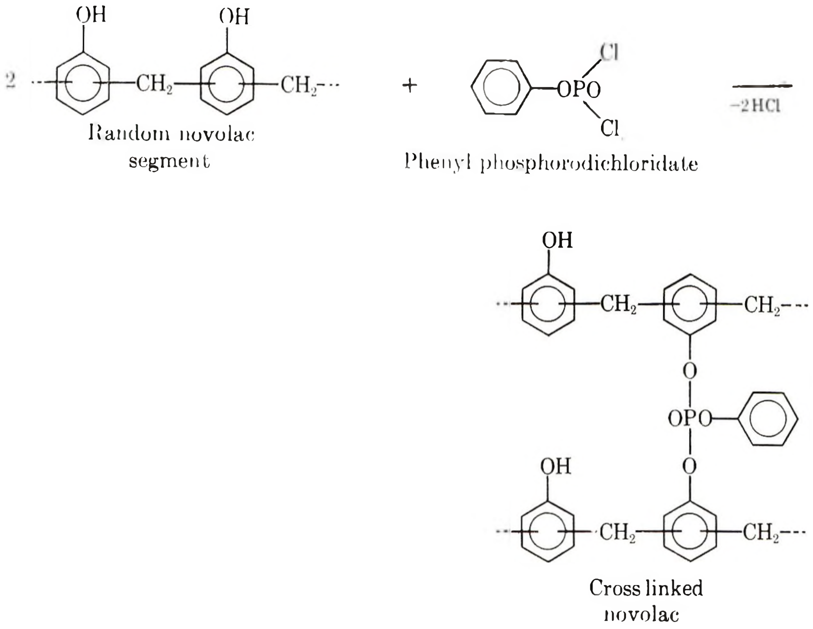
These two novolac types behave quite differently on esterification, as shown in Table I. Runs 1, 2, and 3 compare formation of phosphate esters from *o,o'*- and random novolacs by reaction with phenyl phosphorodichloridate, while runs 9 and 10 show the behavior of the same novolacs in their alkali-catalyzed transesterification with triphenyl phosphate to yield the same type of product. In both cases, the *o,o'*-novolac can be quite extensively esterified, while the random novolac gels at a low level of esterification. Similar differences are also seen between runs 6, 7, and 8, where reactions with diphenyl silyl dichloride are compared, and between runs 11 and 12, where direct esterifications with boric acid were conducted.

TABLE I
Novolac Esterifications

Run	Kind	$\bar{M}_n$	Ester with	Equivalents phenolic OH/ reactive group	Product
1	Random	510	$C_6H_5OPOCl_2$	18	Fusible
2	Random	510	$C_6H_5OPOCl_2$	6.7	Gel
3	*o,o'*-	560	$C_6H_5OPOCl_2$	1.8	Fusible
4	*o,o'*-	560	$Cl_2C_6H_3OPOCl_2$	1.9	Fusible
5	*o,o'*-	560	$Br_2C_6H_3OPOCl_2$	1.8	Fusible
6	Random	510	$(C_6H_5)_2SiCl_2$	20	Fusible
7	Random	510	$(C_6H_5)_2SiCl_2$	17	Gel
8	*o,o'*-	560	$(C_6H_5)_2SiCl_2$	2.2	Fusible
9	Random	510	$(C_6H_5)_3PO_4$	1.2	Gel; 19% reaction
10	*o,o'*-	600	$(C_6H_5)_3PO_4$	1.2	Fusible; 73% reaction
11	Random	510	H_3BO_3	12	Fusible, very viscous
12	*o,o'*-	560	H_3BO_3	1.9	Fusible

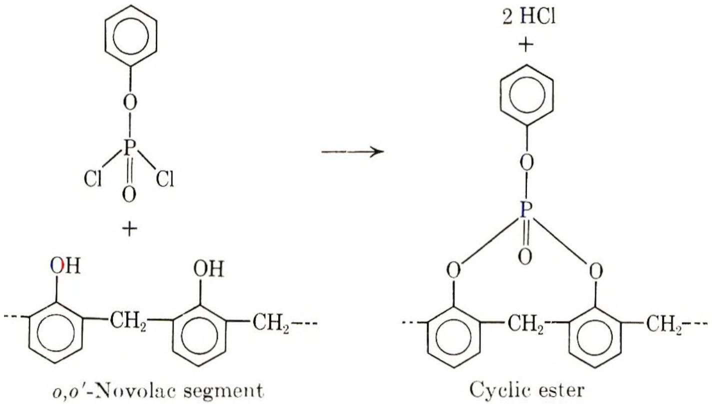
Formation of Cyclic Esters

A possible explanation for the distinct difference between *o,o'*- and random novolacs in the foregoing esterifications is that the random novolacs undergo the expected intermolecular esterification as suggested by Cass[3] [eq. (1)], while in contrast we have



(1)

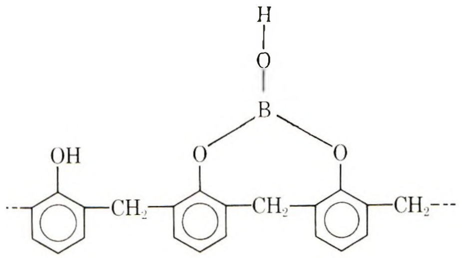
found that *o,o'*-novolacs have an unusually strong tendency to form stable cyclic esters by intramolecular esterification [eq. (2)]. In this connection,



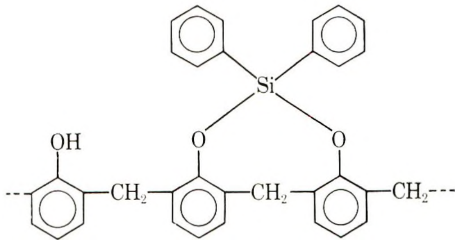
(2)

it is noteworthy that recent patents[12–14] describe cyclic carbonates and other esters obtained from *o,o'*-novolacs or *o,o'*-methylene-linked diphenols under mild reaction conditions; but these cyclic carbonates are metastable and resinify on heating.

In the reactions with boric acid or diphenyl silyl dichloride a similar situation may also exist, with the *o,o'*-novolac being prone to form intramolecular compounds, some possible types of which are the cyclic borate ester (I) and the cyclic silanediol derivative (II).



(I)

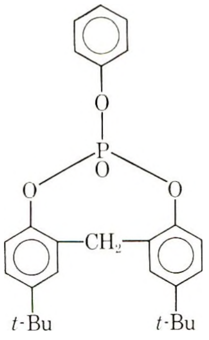


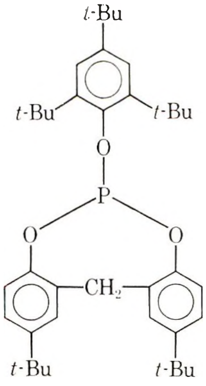
(II)

Simple Cyclic Esters

In support of this explanation, we have found that an *o,o′*-methylene-linked diphenol gives good yields of the cyclic phosphate (III). A related cyclic phosphite (IV) has also been obtained in an analogous reaction between the same diphenol and a phenyl phosphorodichloridite.

(III)

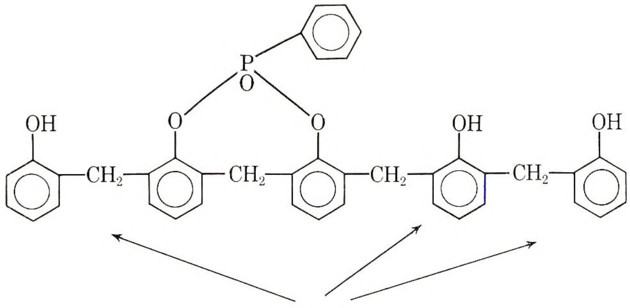




(IV)

Application for Novolac Esters

Of various possible uses for the esters, some of the more interesting stem from novolacs which are only partially esterified. Phenol–formaldehyde novolacs in which 25–50% of the original phenolic hydroxyls remain unesterified still remain curable with conventional novolac curing agents as illustrated in structure V.



(V)

Available for hexa cure

With hexamethylenetetramine (hexa) in particular, the curability of the novolacs is preserved to a large degree. This makes available phenolics which behave more or less normally in processing and molding, yet which contain substantial amounts of such modifying elements as phosphorous or boron.

Also, as shown in Table I, runs 4 and 5, stably bound halogen is easily incorporated in novolac phosphate molecules through the use of halogenated phenyl phosphorodichloridates.

These curable modified phenolics can be used in the formulation of flame-retardant or self-extinguishing materials. More significantly, however, these modified phenolics can have outstanding heat resistance under drastic conditions. Several examples of this are shown in Table II. The lower weight losses from the modified *o,o′*-resins are quite striking, and it is considered that this type of heat resistance should be useful in many phenolic applications.

In the case of the random novolac, the degree of modification approaches the maximum which can be obtained without gelation.

TABLE II
400°C. Weight Losses

Base Novolac	Modifier	Run no. (Table I)	4-hr. weight loss, %
Random	None	—	60–90
Random	0.3% B	11	58
Random	0.7% Si	6	56
Random	0.8% P	1	48
o,o′-	4.5% Si	8	39
o,o′-	1.7% B	12	34
o,o′-	6.0% P	3	28

EXPERIMENTAL

Novolac Esters

The general procedure[3] used in obtaining the data of Table I was to react a mixture of novolac and esterifying agent at temperatures up to about

200°C. Where phosphorus or silicon halide derivatives were used, reaction was carried out at atmospheric pressure and was continued till hydrogen chloride formation subsided and over 90% of reactive chlorine had been eliminated.

In the transesterifications, mixtures of triphenyl phosphate, novolac and sodium hydroxide (0.5% of 50% aqueous sodium hydroxide on the novolac) were warmed to 90°C., water being removed under vacuum. The mixtures were then more strongly heated, phenol being distilled off at 180 mm. over a period of up to 45 min. and a pot temperature up to 220°C. Boric acid esterifications were conducted by heating novolac–boric acid mixtures for about 1 hr. at 150–210°C., water being distilled off as it formed.

$\bar{M}_n$ values were determined in tetrahydrofuran and/or methyl ethyl ketone with a Mechrolab Model 301 vapor pressure osmometer.[15]

Simple Cyclic Esters

The cyclic phosphate 2,10-di-*tert*-butyl-6-phenoxy-12-di-H-dibenzo(d,g)(1,3,2)-dioxaphosphocin-6-oxide (III) was prepared by dropwise addition of 10.6 g. (0.05 mole) of phenyl phosphorodichloridate to a solution of 15.6 g. (0.05 mole) of 2,2′-methylenebis(4-*tert*-butylphenol) and 11 g. (0.1 mole) triethylamine in 20 ml. of diethylene glycol dimethyl ether. The mixture was kept below 50°C. during the addition and was then cooled and kept at room temperature overnight. Product was recovered by pouring the mixture into 2 liters of cold water, separating the resulting white solid, and washing it with water and with hot hexane; yield 19 g. crude, (84% of theory) m.p. 171–178°C. Repeated crystallization from hexane yielded 10 g. of colorless crystalline ester, m.p. 179.5–181°C.

ANAL. Calcd. for $C_{27}H_{31}O_4P$: P, 6.88%; mol. wt. 450. Found: P, 7.00%; mol. wt. 446.

The cyclic phosphite 2,10-di-*tert*-butyl-6-(2,4,6-tri-*tert*-butyl phenoxy)-12-di-H-dibenzo(d,g)(1,3,2)-dioxaphosphocin, (IV) was obtained as follows. A solution of 13.1 g. (0.05 mole) of 2,4,6-tri-*tert*-butylphenol and 17 g. (0.175 mole) triethylamine in 65 ml. diethylene glycol dimethyl ether was added dropwise to 6.9 g. (0.05 mole) phosphorus trichloride at 10°C. After 2 hr. at 10°C., the mixture was heated to 90°C. and 15.6 g. (0.05 mole) of 2,2′-methylene-bis(4-*tert*-butylphenol) dissolved in 45 ml. diethylene glycol dimethyl ether was added and heating continued for 20 hr. at 95°C. The mixture was cooled, poured into 300 ml. water, and the separated solids were extracted with hexane and crystallized from ethanol. The colorless crystalline product, m.p. 181–6°C., amounted to 13 g. Further purification by repeated crystallizations from ethanol yielded 8 g. cyclic phosphite, m.p. 188–189°C.

ANAL. Calcd. for $C_{39}H_{55}O_3P$: P, 5.15%; mol. wt. 602. Found: P, 5.11%; mol. wt. 585.

The eight-membered heterocyclic structures assigned to the phosphate and phosphite are supported by infrared spectra and by ^{31}P and ^{1}H NMR. Neither compound absorbs in the OH stretching region of the infrared.

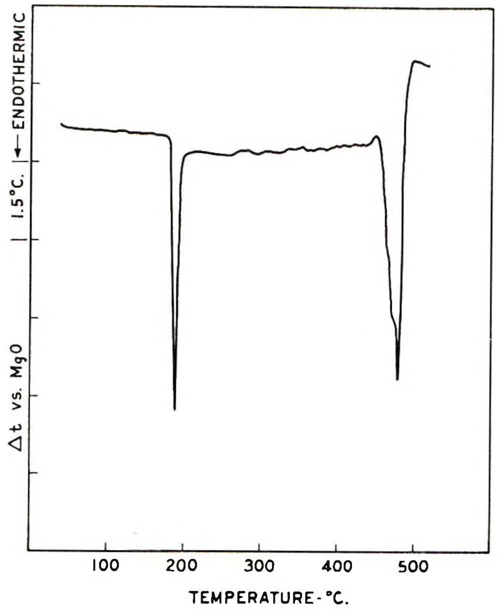


Fig. 1. DTA plot for cyclic phosphate III.

The phosphate shows a chemical shift in the ^{31}P spectrum of +17.3 ppm upfield from phosphoric acid and in excellent agreement with triphenyl phosphate at +17.2 ppm. In the ^{1}H spectrum its tertiary butyl protons are magnetically equivalent while the methylene protons, as expected from molecular models, are non-equivalent, and the low field member of this pair is further split. The phosphite exhibits a ^{31}P shift at −136 ppm comparable to −127 ppm for triphenyl phosphite. The ^{1}H spectrum of the phosphite shows three tertiary butyl moieties, in a ratio of 2/1/2, and two magnetically non-equivalent methylene protons of which the low field member is further split.

The cyclic phosphate examined by DTA in N_2 gave no indication of rearrangement or polymerization at temperatures up to 400°C. (Fig. 1).

Existence of related simple heterocyclic ring systems has been proposed, though not substantiated, by others.[16,17]

400°C. Weight Losses

In obtaining these data, resin samples were cured with 11% of their own weight of hexamethylenetetramine, reduced to 100–400 μ particle size, weighed, baked in air for 4 hr. at 400°C., and reweighed to determine weight loss.

The advice and assistance of Messrs. M. E. Hull, III, D. W. Hoch, J. J. Pullano, and Mrs. L. M. Kaderabeck are gratefully acknowledged. Thanks are also due to Dr. J. G. Colson for interpretation of NMR spectra, and to the Hooker Chemical Corporation for permission to publish this paper.

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Synthesis of Ordered Copolyamides by the Interfacial Polycondensation of the Hydrolyzate of Bisimidazoline with Diacid Chloride

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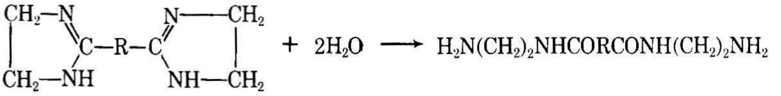
Synopsis

Ordered copolyamides were prepared by the interfacial polycondensation of the hydrolyzate of bisimidazoline in the aqueous solution with diacid chloride in chloroform solution; bisimidazolines used were 1,4-bis(imidazoline-2-yl)butane and 1,4-bis(imidazoline-2-yl)-octane; diacid chlorides used were adipoyl chloride, sebacoyl chloride, and terephthaloyl chloride. The aqueous solutions of the hydrolyzates of bisimidazolines were prepared by heating the aqueous solutions of imidazolines at 70°C. It was shown by infrared spectra and paper electrophoresis of the hydrolyzates that bisimidazolines were hydrolyzed to give quantitatively diamines containing amides linkages of the type $H_2N(CH_2)_2NHCORCONH(CH_2)_2NH_2$. The regularity in the sequence of the copolyamide of nylon 26 and nylon 2T prepared from the hydrolyzate of 1,4-bis(imidazoline-2-yl)butane and terephthaloyl chloride was studied by NMR spectrometry; it was concluded that the copolyamide was highly ordered.

INTRODUCTION

Preston has reported the synthesis of aromatic ordered copolyamides of high thermal stability by the interfacial polymerization of aromatic diamines containing amide linkages with diacid chloride.[1] It has been shown that the ordered copolyamides had characteristic properties different from those of corresponding homopolymers and those of random copolyamides. Little attention has, however, been paid to the preparative method and the properties of aliphatic ordered copolyamides.

As has been reported by the present authors,[2] copolyamides are synthesized by the polyaddition of bisimidazolines with dicarboxylic acids at 220°C. in bulk. The regularity in the sequence of these copolyamides was studied by means of x-ray analysis and melting-point measurement; it was concluded that the regularity was low because of the occurrence of the transamidation reaction between polyamides formed and carboxylic acid unreacted. In view of preparing ordered copolyamides from bisimidazolines, the authors have carried out the interfacial polyaddition reaction of bisimidazolines with diacid chloride at a low temperature. The polymers formed in this case were, however, crosslinked; therefore, the regularity could not be determined. In carrying out this study, the authors have found that bisimidazolines are easily hydrolyzed by heating the aqueous solution to give quantitatively diamines containing amide linkages [eq. (1)]



(1)

By carrying out the interfacial polycondensation of the hydrolyzate with diacid chloride, the authors have prepared ordered copolyamides. The regularity in the sequence of these copolyamides was confirmed by NMR study.

EXPERIMENTAL

Materials

Imidazoline. 2-Ethyl-2-imidazoline, 1,4-bis(imidazoline-2-yl)butane, and 1,4-bis(imidazoline-2-yl)octane were prepared according to the method reported in a patent.[3] Physical constants were: 2-ethyl-2-imidazoline, b.p., 92–93°C./13 mm. (lit.:[3] 109–110°C./15 mm.); 1,4-bis(imidazoline-2-yl)butane, m.p. 218–219°C. (lit.:[3] 215–216°C.); 1,4-bis(imidazoline-2-yl)-octane, m.p. 192–193°C.

ANAL. Calcd. for $C_{10}H_{18}N_4$: C, 61.82%; H, 9.34%; N, 28.84%. Found: C, 61.92%; H, 9.33%; N, 29.02%.

ANAL. Calcd. for $C_{14}H_{26}N_4$: C, 67.26%; H, 10.40%; N, 22.10%. Found C, 66.98%; H, 10.55%; N, 22.10%.

Acid Chloride. Commercial (G.R. grade, Nakarai Chemicals, Ltd.) propionyl chloride and benzoyl chloride were used without purification. Adipoyl chloride and sebacoyl chloride (G.R. grade, Nakarai Chemicals, Ltd.) were purified by vacuum distillation before use. Commercial (G.R. grade, Nakarai Chemicals Ltd.) terephthaloyl chloride was purified by recrystallization from dry hexane.

Diamide. *N*,*N*′-Dipropionylethylenediamine and *N*,*N*′-dibenzoylethylenediamine were prepared by the interfacial reactions of ethylenediamine in the aqueous solution with propionyl chloride and benzoyl chloride in chloroform solution, respectively. *N*-Propionyl-*N*′-benzoylethylenediamine was prepared by the interfacial reaction of benzoyl chloride in chloroform solution with *N*-propionylethylenediamine in aqueous solution which was prepared by the hydrolysis of 2-ethyl-2-imidazoline.[4] Physical constants were: *N*,*N*′-dipropionylethylenediamine, m.p. 191–192°C. (lit.:[5] 191–192°C.); *N*,*N*′-dibenzoylethylenediamine, m.p. 240–251°C. (lit.:[5] 246–247°C.); *N*-propionyl-*N*′-benzoylethylenediamine, m.p. 157–158°C.

Hydrolysis of Bisimidazoline

Bisimidazoline dispersed in 30 ml. of water was heated at 70°C. (The concentration of bisimidazoline was 0.15–0.35 mole/l.). The aqueous solution of the hydrolyzate prepared by heating for 1 hr. in the case of 1,4-bis(imidazoline-2-yl)butane and for 4 hr. in the case of 1,4-bis(imidazoline-2-yl)octane was used for the polycondensation. The consumption of bisimidazoline by the hydrolysis was followed by measuring the infrared spectrum of the hydrolyzate isolated from the aqueous solution by a freeze-drying method, on a KBr pellet; the characteristic peaks of imidazoline at 1610 and 995 cm.$^{-1}$ were used for the determination. In order to check the formation of ethylenediamine by the second-stage hydrolysis (see Results and Discussion), paper electrophoresis was used under the following conditions: 1500 v.; 33 ma.; pH 4.49 ($M/15$ KH_2PO_4 aqueous solution); Toyo Filter No. 2. A ninhydrin–n-butanol solution was used for the coloration.

Interfacial Polycondensation

A 50 ml. portion of a chloroform solution of diacid chloride was charged into a 200 ml. flask; then, 30 ml. of the aqueous solution of the hydrolyzate prepared from bisimidazoline and sodium hydroxide as an acid acceptor were charged into the flask. (The feed molar ratio of diacid chloride, bisimidazoline, and sodium hydroxide was 1:1:2; the concentration of diacid chloride was 0.15–0.35 mole/l.) Immediately, the mixture was stirred vigorously. After 10 min., the stirrer was stopped, and 100 ml. of water was poured into the flask. The reaction product was separated by suction filtration, washed with water and ethanol, and subsequently washed with hot water under reflux for a $^1/_2$ hr. The solid product was dried at 60°C. for 24 hr. under vacuum.

Characterization of the Polymers

The infrared spectra were determined with a Shimadzu Infracord, Model IR-27, on KBr pellets. The viscosity of the formic acid or the trifluoroacetic acid solution of the polymer was measured at 35°C. in an Ubbelohde-type viscometer. The melting point of the polymer was determined visually from the softening point to the liquefaction point in a sealed capillary under a nitrogen atmosphere with a Yanagimoto melting point measuring apparatus, Model MP-S2. The differential thermal analysis was performed with the use of a Rigaku Denki DTA apparatus. The NMR spectrum was run at 23.5°C. in a formic acid solution for diamides and at 70°C. in a trifluoroacetic acid for polymers on a Japan Electron Optics high resolution spectrometer, Model 4H-100, at 60 Mc./sec. with tetramethylsilane as a standard.

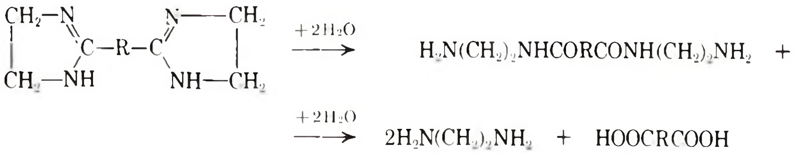
RESULTS AND DISCUSSION

Hydrolysis of Bisimidazolines

1,4-Bis(imidazoline-2-yl)butane and 1,4-bis(imidazoline-2-yl)octane were slightly soluble in water and were not hydrolyzed at the room temperature.

They were readily soluble and hydrolyzed in hot water, however. The hydrolysis of 2-methyl-2-imidazoline was studied by Aspinal,[4] and he reported that 2-methyl-2-imidazoline was readily hydrolyzed in boiling water to yield *N*-acetylethylenediamine.

The hydrolysis of bisimidazolines was followed by means of infrared spectrometry to determine the concentration of the unreacted bisimidazoline and by means of paper electrophoresis to determine the concentration of ethylenediamine formed by second-stage hydrolysis [eq. (2)]:



(2)

The hydrolyses of 1,4-bis(imidazoline-2-yl)butane and 1,4-bis(imidazoline-2-yl)octane in water were carried out at 70°C. over the concentration range of 0.15–0.35 mole/l. The characteristic peaks of imidazoline at 1610 and 995 cm.$^{-1}$ disappeared in the infrared spectrum of the hydrolyzate of 1,4-bis(imidazoline-2-yl)butane after 1 hr. hydrolysis and in that of the hydrolyzate of 1,4-bis(imidazoline-2-yl)octane after 4 hr. hydrolysis, while the spectra displayed the characteristic peaks of secondary amide at 1640 and 1550 cm.$^{-1}$.

The results of the paper electrophoresis of the aqueous solutions of the hydrolyzate of 1,4-bis(imidazoline-2-yl)butane prepared by heating for 1 hr. and that of 1,4-bis(imidazoline-2-yl)octane prepared by heating for 4 hr. are shown in Table I. Each hydrolyzate gave one spot which was not assignable to ethylenediamine. A faint spot assignable to ethylenediamine appeared after heating the aqueous solution for 16 hr. at 100°C. It is, therefore, concluded that diamines which have amide linkages were obtained by the hydrolysis of bisimidazolines.

TABLE I

Paper Electrophoresis of the Hydrolyzate of Bisimidazoline[a]

Hydrolyzate	Mobilities to cathode[b]		
Ethylenediamine	1.0		
BBD[c]		0.72	
BOD[d]			0.64
BOD[e]	1.0 (Trace)		0.64

[a] Conditions: 1500 v.; 33 ma.; pH 4.49 (M/15 KH_2PO_4 aqueous solution); 70 min.; Toyo Filter No. 2.

[b] Mobilities relative to that of ethylenediamine.

[c] Hydrolyzate of 1,4-bis(imidazoline-2-yl)butane. (Conditions of hydrolysis: 70°C.; 1 hr.; 0.25 mole/l.)

[d] Hydrolyzate of 1,4-bis(imidazoline-2-yl)octane. (Conditions of hydrolysis: 70°C.; 4 hr.; 0.25 mole/l.)

[e] Hydrolyzate of 1,4-bis(imidazoline-2-yl)octane. (Conditions of hydrolysis: 100°C.; 16 hr.; 0.25 mole/l.)

Interfacial Polycondensation of the Hydrolyzate of Bisimidazoline with Diacid Chloride

Interfacial reaction of an aqueous solution of hydrolyzate of bisimidazoline with a chloroform solution of diacid chloride, such as adipoyl chloride, sebacoyl chloride, and terephthaloyl chloride, gave a white solid product in a good yield. The results are listed in Table II. It is considered that these products are represented by the structure I:

$$-\!\!\left[NH(CH_2)_2NHCORCONH(CH_2)_2NHCOR'CO\right]\!\!-_n,$$

I

where R represents an alkylene group in the hydrolyzate of bisimidazoline, and R′ is an alkylene group in diacid chloride.

The products possessed the following characteristics of polyamide: (*1*) the infrared spectra were very similar to that of polyamide; (*2*) the products were soluble in formic acid, but insoluble in hot water and in common organic solvents; (*3*) the reduced viscosities in formic acid solution at 35°C. were 1.0–1.6.

When R and R′ are different, it is suggested that the product would be an ordered copolyamide if the transamidation reaction were not to take place.

TABLE II
Interfacial Polycondensation of the Hydrolyzate of Bisimidazoline with Diacid Chloride

	Polymer code	Reactants[a]	Yield, wt.-%	Melting Point, °C.	η_{sp}/c, dl./g.
Polymer A	262–6	BBD + A	72.2	314–315	0.98
Polymer B	262–10	BBD + S	69.1	301–302	1.06
Polymer C[b]	262–10	BB + SA	86.0	233–234	0.24
Polymer D	2102–6	BOD + A	69.7	301–302	1.21
Polymer E	2102–10	BOD + S	82.1	279–280	1.60
Polymer F	262–T	BBD + T	84.6	390[c]	1.16
Polymer G[d]	26	E + A	80.8	315[c]	0.96
Polymer H[d]	2T	E + T	79.9	451[c]	1.20
Polymer I[d]	26–2T	E + $^1/_2$A + $^1/_2$T	78.3	388[c]	1.08

[a] BBD = hydrolyzate of 1,4-bis(imidazoline-2-yl)butane; BB = 1,4-bis(imidazoline-2-yl)butane; BOD = hydrolyzate of 1,4-bis(imidazoline-2-yl)octane; A = adipoylchloride; S = sebacoyl chloride; T = terephthaloyl chloride; E = ethylenediamine; SA = sebacic acid.

[b] Prepared by the polyaddition of 1,4-bis(imidazoline-2-yl)butane with sebacic acid in bulk (conditions: 220°C.; 6 hr.).[2]

[c] The position of a melting peak in the thermogram measured by DTA.

[d] Prepared by the usual interfacial polycondensation.[6]

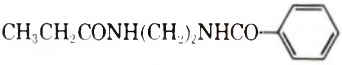
Determination of the Regularity of Copolyamides by Means of NMR Spectrometry

Recently, it was reported[7] that the order of monomer units in the reaction product of poly(ethylene terephthalate) and poly(ethylene sebacate) had been determined by means of NMR spectrometry by measuring the τ values of the methylene protons in ethylene glycol units in the copolyester. To the best knowledge of the present authors, however, regularity in the sequence of copolyamides has never been studied by means of NMR spectrometry.

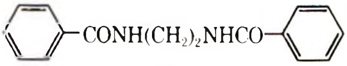
In order to examine whether regularity in the sequence of a copolyamide is determined by NMR measurement, NMR spectra of three diamides (I–III) were measured:

$CH_3CH_2CONH(CH_2)_2NHCOCH_2CH_3$

II



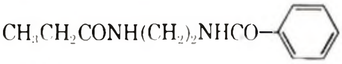
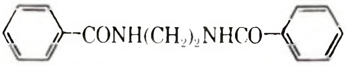
III



IV

The singlets at 6–7 ppm (Fig. 1) are assignable to the methylene protons of ethylenediamine units. The τ values of these chemical shifts are listed in Table III. The symmetrical diamides, II and IV, exhibited singlets at different τ values; the difference is due to the difference in the shielding effects of acid components. The unsymmetrical diamide III also exhibited a singlet which lay between those of II and IV; this result means that the chemical shifts of two methylene groups of the ethylenediamine unit of III are nearly equal, but distinctly different from those of II and IV.

TABLE III
Chemical Shifts of the Methylene Protons of Ethylenediamine Units of Diamines

Unit	τ, ppm[a]
$CH_3CH_2CONH(CH_2)_2NHCOCH_2CH_3$	6.58
	6.42
	6.35

[a] 5% formic acid solution; 23.5°C.; 60 Mc./sec.; tetramethylsilane as a standard.

From these results, it was suggested that the regularity in the sequence of the copolyamide of nylon 26 and nylon 2T, the unit structures of which are similar to the diamides, II, III, and IV, be determined by NMR spectrometry.

The NMR spectra of polymer F which is expected to be an ordered copolyamide, nylon 26, nylon 2T, and the random copolyamide (polymer I) of nylon 26 and nylon 2T are shown in Figure 2; τ values of singlets at 6–7 ppm assigned to the methylene protons of the ethylenediamine units

TABLE IV
Chemical Shift of the Methylene Protons of Ethylenediamine Units of Polymers

	τ, ppm[a]
Polymer G (nylon 26)	6.67
Polymer H (nylon 2T)	6.39
Polymer F (ordered copolyamide)	6.51
Polymer I (random copolyamide)	6.39
	6.50
	6.66 (shoulder)

[a] 5% trifluoroacetic acid solution; 70°C.; 60 Mc./sec.; tetramethylsilane as a standard.

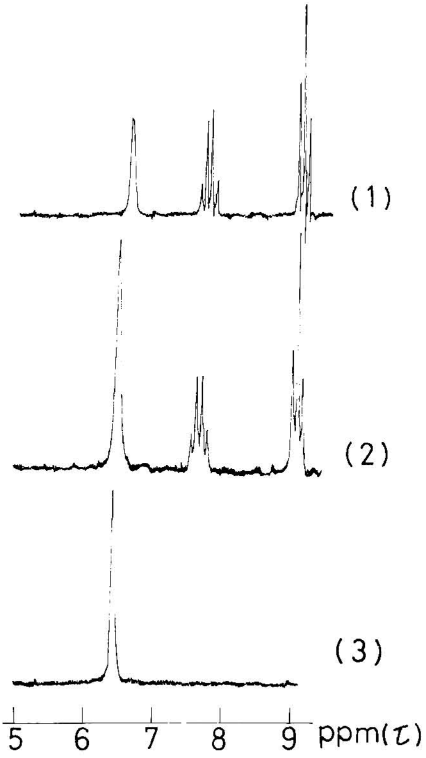


Fig. 1. NMR spectra of (*1*) *N,N'*-dipropionylethylenediamine, (*2*) *N*-propionyl-*N'*-benzoylethylenediamine, and (*3*) *N,N'*-dibenzoylethylenediamine. Conditions: 5% formic acid solution; 23.5°C.; 60 Mc./sec.; tetramethylsilane as a standard.

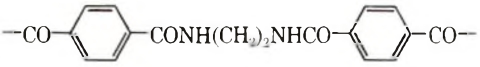
are listed in Table IV. Ethylenediamine groups in these polymers are contained in the following unit structures.

For nylon 26:

$$-CO(CH_2)_4CONH(CH_2)_2NHCO(CH_2)_4CO-$$

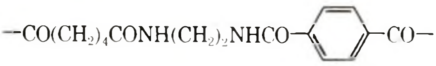
V

For nylon 2T:



VI

For polymer F (expected formula):



VII

For polymer I:

V + VI + VII

As is seen in Figure 2, the peak assignable to the methylene protons of the ethylenediamine units of nylon 26 as well as that of nylon 2T was a singlet, but the spectrum of the random copolyamide exhibited three peaks assignable to the methylene protons of the ethylenediamine units; these three peaks at a higher field, at the middle field, and at a lower field were assigned, respectively, to the unit structures of V, VII, and VI. On the

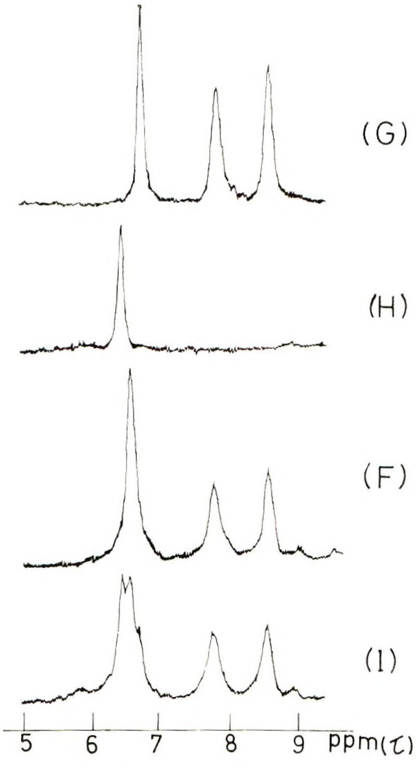


Fig. 2. NMR spectra of polymers: Symbols (*F*)-(*I*) stand for the polymers (F)-(I) in Table II. Conditions: 5% trifluoroacetic acid solution; 70°C.; 60 Mc./sec.; tetramethylsilane as a standard.

other hand, the spectrum of polymer F exhibited one singlet assignable to the methylene protons of the ethylenediamine units, and the τ value was identical with that of the middle peak of the random copolyamide (polymer I), i.e., the peak assigned to the unit structure VII.

From these results, it was concluded that the copolyamides prepared by the interfacial polycondensation of the hydrolyzate of bisimidazoline with diacid chloride possessed highly ordered structures, and that the regularity in the sequence of the copolyamide of nylon 26 and nylon 2T can be determined quantitatively by measuring the relative areas of three peaks assignable to the unit structures V, VI, and VII.

Melting Points of Ordered Copolyamides

Generally, properties such as polymer melt temperature of the random copolyamides pass through a minimum at a certain composition between the homopolymers, and the properties of a random copolyamide of a 1:1 composition show lower values than the corresponding homopolymers. An exception is found in those copolyamides having constituents which are isomorphous, i.e., are capable of occupying interchangeably the same crystal lattice.[8] Such copolymers show a linear dependence of physical properties on composition.

The melting points of ordered copolyamides (Table II) lay between those of the corresponding homopolymers. The melting point of the ordered copolyamide, nylon 2,6,2,10, was higher than that of the copolyamide prepared by the polyaddition of 1,4-bis(imidazoline-2-yl)butane with sebacic acid in bulk at 220°C.[2] whose sequence was disordered by the transamidation reaction. On the other hand, the melting point of the ordered copolyamide, nylon 2,6,2,T, was close to that of the random copolyamide prepared by the interfacial polycondensation of the equimolar mixture of adipoyl chloride and terephthaloyl chloride with ethylenediamine. It is considered that this result is due to the isomorphism.

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Effect of Alcohols on the Gamma-Radiation-Induced Polymerization of Ethylene

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Synopsis

Gamma-radiation-induced polymerization of ethylene in alcohols such as methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *tert*-butyl, and *n*-pentyl alcohols was carried out under a pressure of 400 kg./cm.^{2} at 30°C. at a dose rate of 1.4×10^5 rad/hr. in a batch reactor of 100 ml. capacity. The yield and molecular weight of polymer formed in the alcohols (except *tert*-butyl alcohol) were much lower than those of the bulk polymerization under the same conditions, whereas the addition of *tert*-butyl alcohol increased the yield and reduced the molecular weight. From the infrared spectra of the polymers and those of the bromination products it was concluded that only primary OH exists in the polymer formed in methyl alcohol and that both primary and secondary OH are in the polymer formed in other primary alcohols. Both secondary and tertiary OH were observed in the polymer when the secondary alcohols were used, and only tertiary OH in the case of *tert*-butyl alcohol. These polymers were found to contain small amounts of vinylidene unsaturation and methyl group. On the basis of these results the roles of the alcohols in the polymerization are discussed.

INTRODUCTION

The gamma-radiation-induced polymerization of ethylene in the presence of various solvents under relatively low pressure, below 50 kg./cm.^{2}, has been reported by Henley et al.,[1] Medvedev et al.,[2] and Wiley et al.[3] Recently, Machi et al. studied this subject with several kinds of organic solvent[4,5] and liquid carbon dioxide[6] as an inorganic solvent under the intermediate pressure region of 70–400 kg./cm.^{2} and reported that the polymerization rate and molecular weight of polymer are lower than those of the bulk polymerization under the same conditions.

In the present paper the effects of the addition of various alcohols on the polymer yield, molecular weight, and polymer structure are reported, and the roles of alcohols in the polymerization are discussed on the basis of these results.

EXPERIMENTAL

The reaction vessel was a stainless-steel autoclave of 100 ml. capacity with a magnetic agitator. The ethylene used was 99.9% pure (free from

CO and H_2S), containing less than 3 ppm O_2. Reagent-grade alcohols were purified by distillation before use. Reagent-grade bromine was also used for the bromine treating of polymer.

Ethylene was fed to the vessel containing a definite amount of an alcohol to about 20 kg./cm.^{2}, agitation was then made for several minutes, and the ethylene was purged. After this operation was repeated five times, ethylene was fed to the desired reaction pressure at 30°C. During the course of the reaction the temperature was maintained constant within ±1.0°C., and no agitation was made. Cobalt-60 (5000 curie) was used as a gamma-ray source. Residual gas was exhausted after irradiation. The reaction product was poured into 200 ml. of methyl alcohol. The solid polymer was filtered off, washed with methyl alcohol, and dried to constant weight in a vacuum oven at room temperature.

The number-average molecular weight of the polymer in tetralin solution was determined from an intrinsic viscosity at 130°C. by means of Tung's equation.[7] Bromine-treating of polymer was carried out as follows. A polymer film of 0.2 mm. thickness was treated with bromine vapor for 2 days at room temperature. The infrared spectrum of the polymer was measured with a Nippon Bunko Ltd. (Model DS 301) spectrophotometer with NaCl optics. Assignment of the absorption bands of polymer was made according to the literature.[8] The methyl content of the polymer was determined by the method of Bryant and Voter[9] and the unsaturation by that of Cernia et al.[10] The density of the polymer was determined by the gradient tube method at 25°C.

RESULTS AND DISCUSSION

Effects of Alcohols on Polymer Yield and Molecular Weight

The experimental results are summarized in Table I. It is clear that the polymer yield and molecular weight are remarkably reduced by the addition of alcohols except *tert*-butyl alcohol. When *tert*-butyl alcohol is solvent, the yield increases, and the molecular weight reduces to about one-half of the bulk polymerization. It can be seen that the rates of polymerization are accelerated in methyl alcohol and in *tert*-butyl alcohol but are almost constant in other alcohols during the course of the reaction. Since the number of moles of polymer chains (defined as the ratio of polymer yield to number-average molecular weight) in alcohols per unit time is several times to several tens of times as many as that of the bulk polymerization, alcohols are considered to act as a transfer agent.

Effects of Alcohols on Polymer Structure

Hydroxyl Groups in Polymers. The infrared spectra of the polymers formed in alcohols and of the polymers treated with bromine are shown in Figure 1. Several absorption bands that may be assigned to alcohols are observed besides typical polyethylene bands. The bromine-treating of polymer was made in order to ensure the assignment of these bands. It is

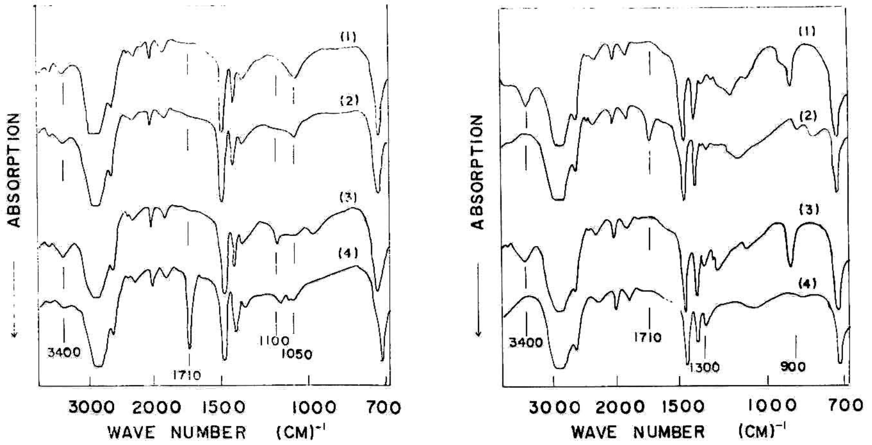
TABLE I
Polymer Yield, Molecular Weight, and Number of Polymer Chains[a]

Reaction time, hr.	Solvent	Polymer yield, g./l.	Avg. rate of polymzn., g./hr.-l.	Mol. wt. ×10⁻⁴	No. of polym. chains ×10⁴, mole/l.
1.0	None	14.0	14.0	28.0	0.50
1.0	Methyl alcohol	8.7	8.7	2.6	3.35
2.0		20.4	10.2	2.1	9.72
1.0	Ethyl alcohol	7.5	7.5	0.57	13.2
2.0		14.4	7.2	0.60	24.0
0.5	*n*-Propyl alcohol	3.6	7.2	—	—
1.0		6.5	6.5	0.81	8.03
1.0	Isopropyl alcohol	6.1	6.1	0.38	16.0
2.0		12.4	6.2	—	—
0.5	*n*-Butyl alcohol	3.9	7.8	—	—
1.0		8.4	8.4	0.98	8.57
0.5	Isobutyl alcohol	4.0	8.0	—	—
1.0		8.1	8.1	1.05	7.71
1.0	*sec*-Butyl alcohol	4.9	4.9	0.60	8.17
2.0		9.0	4.5	—	—
0.5	*tert*-Butyl alcohol	6.9	13.8	—	—
1.0		18.8	18.8	15.5	1.21
1.0	*n*-Pentyl alcohol	8.0	8.0	1.18	6.78

[a] Reaction conditions: 30°C., 400 kg./cm.^{2}, 1.4 × 10^5 rad/hr., solvent 30 ml., reactor 100 ml.

known that the OH group in primary alcohols is not affected by bromine, the group in secondary alcohols is oxidized to form ketone, and the group in tertiary alcohols is substituted by bromine atom.[11,12]

In the spectrum of the polymer formed in methyl alcohol the band near 3400 cm.$^{-1}$, ascribed to associated OH stretching vibration, and that near 1050 cm.$^{-1}$, which may be assigned to C—O stretching and O—H deformation vibrations of primary alcohols, are observed (curve 1 in Fig. 1*a*). These bands are not affected by bromine-treating (curve 2 in Fig. 1*a*). Only the primary OH groups, therefore, are shown to exist in this polymer. The spectrum of the polymer formed in *n*-propyl alcohol shows the absorption band near 1100 cm.$^{-1}$ that may be attributed to C—O stretching and O—H deformation vibrations of secondary alcohols, together with the bands near 3400 and 1050 cm.$^{-1}$ (curve 3 in Fig. 1a). When the polymer was treated with bromine, the band near 3400 cm.$^{-1}$ decreased remarkably, and that near 1100 cm.$^{-1}$ disappeared, whereas the strong absorption band near 1710 cm.$^{-1}$, assigned to the carbonyl groups, appeared, and that near 1050 cm.$^{-1}$ remained (curve 4 in Fig. 1*a*). Consequently, the polymer is shown to contain both primary and secondary OH groups. In the spectrum of the polymer formed in isopropyl alcohol several bands in the range 900–1300 cm.$^{-1}$, which may be due to the C—C skeletal vibrations and/or the C—O stretching and O—H deformation vibrations of secondary and tertiary



(*a*) (*b*)

Fig. 1. (*a*) Infrared spectra of polymer: (*1*) formed in methyl alcohol; (*2*) treated with bromine; (*3*) formed in *n*-propyl alcohol; (*4*) treated with bromine. (*b*) Infrared spectra of polymer: (*1*) formed in isopropyl alcohol; (*2*) treated with bromine; (*3*) formed in *tert*-butyl alcohol; (*4*) treated with bromine.

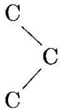
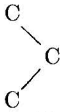
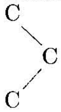
alcohols, are observed together with that near 3400 cm.$^{-1}$ (curve 1 in Fig. 1*b*). When the polymer was treated with bromine, the band near 3400 cm.$^{-1}$ vanished, those in the range 900–1300 cm.$^{-1}$ changed remarkably, and a weak absorption band appeared near 1710 cm.$^{-1}$ (curve 2 in Fig. 1*b*). This means that both secondary and tertiary OH groups exist in this polymer. The spectrum of the polymer formed in *tert*-butyl alcohol displays several absorption bands in the range 900–1300 cm.$^{-1}$ together with the band near 3400 cm.$^{-1}$ (curve 3 in Fig. 1*b*). The polymer treated with bromine displays the disappearance of the band near 3400 cm.$^{-1}$, the remarkable change of the bands in the range 900–1300 cm.$^{-1}$, and no appearance of the band near 1710 cm.$^{-1}$ (curve 4 in Fig. 1*b*). Therefore, only tertiary OH groups are shown to exist in this polymer.

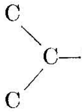
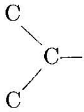
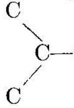
The results in this section are summarized in Table II. The bands in the range 900–1300 cm.$^{-1}$ observed in the spectra of the polymers formed in isopropyl alcohol and in *tert*-butyl alcohol will be assigned in the following section.

TABLE II
Hydroxyl Groups in Polymers Formed in Various Alcohols

Solvent	OH groups in polymers
Methyl alcohol	Primary
n-Propyl alcohol	Primary and secondary
Isopropyl alcohol	Secondary and tertiary (1-methyl alcohol and 1,1-dimethyl alcohol)
tert-Butyl alcohol	Tertiary (1,1-dimethyl alcohol)

TABLE III
Assignment of Absorption Bands (cm.$^{-1}$)
Ascribed to C—C Skeletal Vibrations

2-Methyl alkanes[13,14]	Isopropyl alcohol[16]		Polymer 1[a]	Polymer 2[b]
	Band	Assignment[c]		
1172–1170	1162	 sym. v. − C—O v.	1190	none
1150–1143	1130	 asym. v.	1150	none
922– 919	953	rocking v. of CH_3	950	none
—	818	 sym. v. + C—O v.	none	none

2,2-Dimethyl alkanes[13,14]	*tert*-Butyl alcohol[16]		Polymer 1[a]	Polymer 2[b]
	Band	Assignment[c]		
1253–1235	1242	—C d. v.	1250	1240
1208–1173	1201	—C sym. v. − C—O v.	1200	1200
932– 926	915	rocking v. of CH_3	910	910
—	750	—C sym. v. + CO— v.	none	none

[a] Polymer formed in isopropyl alcohol.
[b] Polymer formed in *tert*-butyl alcohol.
[c] Sym., symmetrical; asym., asymmetrical; d. degenerate; v., vibration.

Structure of Terminal Groups of Polymer Formed in Isopropyl Alcohol and in *tert*-Butyl Alcohol. As described before, the spectra of the polymers formed in isopropyl alcohol and in *tert*-butyl alcohol show several bands that may be ascribed to C—C skeletal and OH vibrations. The structure of the terminal groups of the polymers is determined by assigning these bands. The characteristic absorption bands for C—C skeletal vibrations are well known and are attributed to isopropyl, $(CH_3)_2CH$—, and *tert*-butyl, $(CH_3)_3C$—, structures.[13,14] The mass of the CH_3 group is nearly equal to that of the OH group, and the force constant of the C—C bond in the C—CH_3 structure is nearly equal to that of the C—O bond in the C—OH structure.[15] Consequently, with respect to the skeletal vibrations the absorption bands

TABLE IV
Molecular Structure of Polymers[a]

Solvent	Mol. wt., ($\times 10^{-4}$)	Dens., g./ml.	Methyl content per 1000 C		Double bond per 1000 C		
			CH_3	CH_3 cor.[b]	$RHC{=}CH_2$	$RHC{=}CR'H$ (*trans*)	$RR'C{=}CH_2$
None	28.0	0.931	1.0	1.0	0	0	0.024
Methyl alcohol	2.6	0.942	1.1	0.6	0	0	0.040
Ethyl Alcohol	0.57	0.955	3.8	0	0	0	0.039
n-Propyl alcohol	0.81	0.952	2.7	0	0	0	0.041
Isopropyl alcohol	0.38	0.964	19.2	8.6	—	0	0.038
n-Butyl alcohol	0.98	0.954	3.0	0.5	0	0	0.047
Isobutyl alcohol	1.05	0.953	4.1	0.2	0	0	0.14
sec-Butyl alcohol	0.60	0.963	9.8	2.8	—	0	0.037
tert-Butyl alcohol	15.5	0.933	6.0	5.7	—	0	0.029
n-Pentyl alcohol	1.18	0.954	3.7	1.3	0	0	0.039

[a] Reaction conditions: 30°C., 400 kg./cm.^{2}, 1 hr.; 1.4 × 10^5 rad/hr., solvent 30 ml. reactor 100 ml.

[b] Values corrected for terminal groups.

are considered to be not markedly changed, even if the CH_3 group in the $(CH_3)_2CH$— and $(CH_3)_3C$— groups is replaced with the OH group.[15] Therefore, the absorption bands ascribed to the $(CH_3)_2CH$— group (in 2-methyl alkanes) are considered to be similar to those of isopropyl alcohol (generally, 1-methyl alcohols). The same relation between the $(CH_3)_2CH$— group and isopropyl alcohol may be found between the bands ascribed to the $(CH_3)_3C$— group (in 2,2-dimethyl alkanes) and those ascribed to *tert*-butyl alcohol (generally, 1,1-dimethyl alcohols).

On the basis of these considerations the bands in the range 900–1300 cm.$^{-1}$ in the spectra of the polymers formed in isopropyl alcohol and in *tert*-butyl alcohol are assigned to the structures shown in Table III and may be compared with the structures of 2-methyl alkanes, 2,2-dimethyl alkanes,[13,14] isopropyl alcohol, and *tert*-butyl alcohol.[16] That is, in the spectrum of the polymer formed in isopropyl alcohol the bands corresponding to both 2-methyl alkanes (or isopropyl alcohol) and 2,2-dimethyl alkanes (or *tert*-butyl alcohol) are observed; this polymer therefore is found to contain both the structures of 1-methyl alcohol and 1,1-dimethyl alcohol. Only the latter structure is found in the polymer formed in *tert*-butyl alcohol, according to the bands corresponding to 2,2-dimethyl alkanes or *tert*-butyl alcohol.

These results are summarized in Table II.

Methyl Content and Unsaturation in Polymers. As shown in Table IV, the methyl content of the side chains of the polymer formed in alcohols is 0–3 CH_3 groups per 1000 carbon atoms, which is almost equal to that of the polymer obtained by bulk polymerization.[17,18] The methyl content of the polymers formed in isopropyl alcohol and in *tert*-butyl alcohol is high.

The polymers formed in alcohols lack both terminal vinyl and *trans*-vinylene types and contain only a small amount of vinylidene unsaturation (0.02–0.05 double bonds per 1000 carbons), like the polymer formed in

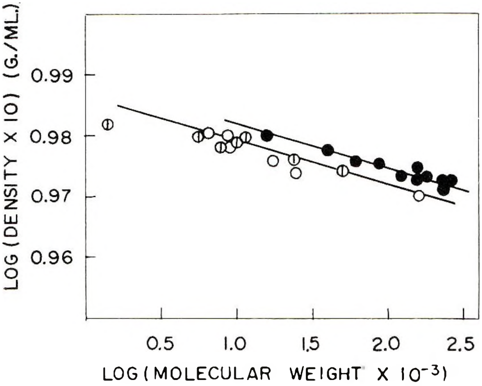


Fig. 2. Logarithmic plots of density versus molecular weight of polymer formed: (○) in various alcohols present work, CH_3 per 1000 C = 2.7–4.4, average 3.5; (⦶) in methyl alcohol, lit.,[18] CH_3 per 1000 C = 2.2–4.4, average 3.4; (●) in bulk, lit.,[17,18] CH_3 per 1000 C = 2.1–4.6, average 3.7.

bulk.[18] The amount of vinylidene unsaturation of the polymer formed in isobutyl alcohol is high.

Effects of Alcohols on Arrangement of Polymer Chains

Since the OH groups in the polymers formed in alcohols are associated as described before, they may affect the arrangement of the polymer chains. It is considered that the arrangement of the polyethylene molecules is affected by the molecular weight and degree of branching and that it determines the density. As shown in Figure 2, the logarithmic plots of density versus molecular weight are on a straight line, and density decreases with increase in molecular weight. In the polymer with same molecular weight the density of the polymer formed in alcohols is lower than that in bulk. This fact may be ascribed to a hydrogen bond of the terminal OH group in the polymer formed in alcohols.

Roles of Alcohols in Polymerization

From the results on the telomerization between alcohols and ethylene[4,19] it is considered that initiation and transfer may occur that are mainly induced by a dissociation of the C—H bond at the α-position with respect to OH group, in the case of ethylene polymerization in alcohols. As shown in Table II, in the polymer formed in methyl alcohol only primary OH group is observed. This means that the initiation and/or the transfer may occur in the polymerization:

$$\text{Initiation:}\quad CH_3OH \rightsquigarrow \cdot CH_2OH \tag{1}$$

$$\text{Transfer:}\quad CH_3OH + R_n\cdot \rightarrow \cdot CH_2OH + R_nH \tag{2}$$

The polymer formed in n-propyl alcohol contains both primary and secondary OH groups. This fact indicates that the initiation and/or the transfer induced by dissociation of the C—H bond at the β position of n-propyl alcohol may occur [reactions (3) and/or (4)] besides its dissociation at the α position [reactions (5) and/or (6)]:

$$\text{Initiation:}\quad CH_3CH_2CH_2OH \rightsquigarrow CH_3\dot{C}HCH_2OH \tag{3}$$

$$\text{Transfer:}\quad CH_3CH_2CH_2OH + R_n\cdot \rightarrow CH_3\dot{C}HCH_2OH + R_nH \tag{4}$$

$$\text{Initiation:}\quad CH_3CH_2CH_2OH \rightsquigarrow CH_3CH_2\dot{C}HOH \tag{5}$$

$$\text{Transfer:}\quad CH_3CH_2CH_2OH + R_n\cdot \rightarrow CH_3CH_2\dot{C}HOH + R_nH \tag{6}$$

The existence of both secondary and tertiary OH groups in the polymer formed in isopropyl alcohol is considered to show the occurrence of initiation and/or transfer: [reactions (7), (8), (9), and (10)]:

$$\text{Initiation:}\quad (CH_3)_2CHOH \rightsquigarrow (CH_3)_2\dot{C}OH \tag{7}$$

$$\text{Transfer:}\quad (CH_3)_2CHOH + R_n\cdot \rightarrow (CH_3)_2\dot{C}OH + R_nH \tag{8}$$

$$\text{Initiation:}\quad (CH_3)_2CHOH \rightsquigarrow \cdot CH_2(CH_3)CHOH \tag{9}$$

$$\text{Transfer:}\quad (CH_3)_2CHOH + R_n\cdot \rightarrow \cdot CH_2(CH_3)CHOH + R_nH \tag{10}$$

When *tert*-butyl alcohol is solvent, only tertiary OH group is observed in the polymer. This means that the following initiation and/or transfer may occur:

$$\text{Initiation:}\quad (CH_3)_3COH \rightsquigarrow \cdot CH_2(CH_3)_2COH \qquad (11)$$

$$\text{Transfer:}\quad (CH_3)_3COH + R_n\cdot \rightarrow \cdot CH_2(CH_3)_2COH + R_nH \qquad (12)$$

From the viewpoint of radiolysis products of alcohols (since the G values of the formation of methane in isopropyl alcohol and in *tert*-butyl alcohol are comparable to those of the formation of hydrogen)[20] the dissociation of the C—C bond and also that of the C—H bond takes place, which is considered to be the initiation shown in the following reactions in the case of polymerization in *tert*-butyl alcohol and in isopropyl alcohol:

$$\text{Initiation:}\quad (CH_3)_3COH \rightsquigarrow (CH_3)_2\dot{C}OH \qquad (13)$$

$$\text{Initiation:}\quad (CH_3)_2CHOH \rightsquigarrow \cdot CH(CH_3)OH \qquad (14)$$

On the other hand, in the case of methyl alcohol and n-propyl alcohol, the G value of hydrocarbon formation is much lower than that of hydrogen formation.[20] The initiation shown in reactions (1), (3), and (5), which are brought about by dissociation of the C—H bond mainly occur, therefore, in methyl alcohol and in n-propyl alcohol.

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Free-Radical Copolymerization of 9-Vinylanthracene

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Synopsis

Free-radical copolymerization of methyl acrylate, ethyl acrylate, butyl acrylate, and methyl methacrylate with 9-vinylanthracene was studied, and the reactivity ratios r_1 and r_2 were calculated. In the light of earlier data on copolymerization of 9-vinylanthracene with styrene results show that the difference in polarity of the monomers participating in the copolymerization has an insignificant influence compared with that of the steric factors involved in the reaction.

INTRODUCTION

Free-radical polymerization of 9-vinylanthracene (9-VAn) and its copolymerization with styrene were reported earlier.[1,2] In view of the good scintillation properties of 9-VAn,[3] the interesting behavior of the monomer in polymerization processes,[2–9] and the possibilities of using its copolymers as plastic scintillators[2] and organic semiconductors,[10] the free-radical copolymerization with additional vinyl monomers was studied.

In the copolymerization process with styrene 9-VAn showed low reactivity, mainly attributed to the aplanarity of the 9-VAn molecule with steric hindrance of the exocyclic double bond by the bulky anthracene system.[2] As styrene and 9-VAn are of the same polarity, the present study was undertaken in order to ascertain whether copolymerization of 9-VAn would proceed more readily with monomers of opposite polarity. The monomers used were methyl acrylate (MAc) ethyl acrylate (EAc), butyl acrylate (BAc), and methyl methacrylate (MM).

EXPERIMENTAL

Preparation of 9-Vinylanthracene

The synthesis of 9-VAn, based on acetylation of anthracene in the 9 position, reduction of the acetylanthracene, and dehydration of the carbinol were described earlier.[1] Small modifications in the original acetylation procedure,[11] such as lowering of the temperature range from about 5–0° to about $-10°$ to $-5°$ and heating of the reaction mixture after addition of the $AlCl_3$ to $+5°$ instead of $+10°$ increased the efficiency of this step from 57–60 to 73%. The methyl acrylate, ethyl acrylate, and methyl methacrylate were obtained from British Drug Houses, Ltd., the butyl acrylate from Rohm & Haas Company, and the di-*tert*-butyl peroxide from the Lucidol Division, Wallace & Tiernan Inc. After removal of the inhibitor with a 5% solution of NaOH the monomers were purified by additional distillation.

Copolymerization

Four series of experiments were conducted for the study of copolymerization of 9-VAn with each of the other monomers. In each series six test tubes containing 9-VAn, the other monomer, and the catalyst were sealed under reduced pressure in an atmosphere of dry N_2, the pressure at the moment of sealing being about 1 mm. Hg. The ratio of 9-VAn to the other monomer differed in each test tube, ranging from 10 to 60 mole-% 9-VAn. The amount of polymerization initiator (di-*tert*-butyl peroxide) used in the reaction was 3 mole-% per mole of monomer. The test tubes were kept in a thermostatic bath (76 ± 0.5° for 9-VAn methyl acrylate and 78 ± 0.5° for the other systems) for different lengths of time. The polymerization process was interrupted before conversion reached 15% by opening the test tubes, dissolving their contents in methyl ethyl ketone, and precipitating the copolymers with *n*-heptane. Dissolution and precipitation of each polymer were repeated several times up to a constant weight of the dry polymer, after which the percentage of conversion was determined.

The composition of the copolymers was determined by measuring their specific extinction coefficients in chloroform solutions at 261/mμ. The equation used for calculation was

$$X = (E^* - E_B^*)/(E_A^* - E_B^*) \qquad (1)$$

where X is the fraction of monomer A in the copolymer and E_A^*, E_B^*, and E^* are the specific extinction coefficients of homopolymer A, homopolymer B, and copolymer, respectively. This method, first used by Meehan in determining the composition of GR-S rubbers,[12] was also applied earlier in the study of the 9-VAn styrene copolymerization.[2] The specific extinction coefficients measured at 261/mμ for the different polymers relating to

TABLE I

Copolymerization of Methyl Acrylate (M_1) with 9-Vinylanthracene (M_2)
(76 ± 0.5°, 3 mole-% di-*tert*-butyl peroxide)

No.	$[M_2]$ in init. monomer mixt., mole-%	Polymn. time, hr.	Convsn., %	E^* at 261 mμ	$[m_2]$ in copolymer, mole-%
1	10	166	1.84	7.65	3.43
2	20	210	1.21	16.10	7.61
3	30	234	1.13	23.30	11.59
4	40	258	1.02	29.60	15.45
5	50	261	0.96	38.80	21.65
6	60	330	1.13	46.51	27.52

this work were *p*-9-VAn 98.0, *p*-MAc 0.05, *p*-EAc 0.03, *p*-BAc 0.034, *p*-MM 0.08. Experimental results and calculated values of the 9-VAn content in the copolymers are listed in Tables I–IV.

TABLE II
Copolymerization of Ethyl Acrylate (M_1) with 9-Vinylanthracene (M_2)
(78 ± 0.5°, 3 mole-% di-*tert*-butyl peroxide)

No.	$[M_2]$ in init. monomer mixt., mole-%	Polymn. time, hr.	Convsn., %	E^* at 261 mμ	$[m_2]$ in copolymer, mole-%
1	10	193	1.65	6.10	3.10
2	20	330	0.95	12.41	6.63
3	30	333	0.78	20.04	11.16
4	40	380	0.75	27.68	16.26
5	50	476	1.24	36.91	22.92
6	60	499	1.27	45.10	29.54

TABLE III
Copolymerization of Butyl Acrylate (M_1) with 9-Vinylanthracene (M_2)
(78 ± 0.5°, 3 mole-% di-*tert*-butyl peroxide)

No.	$[M_2]$ in init. monomer mixt., mole-%	Polymn. time, hr.	Convsn., %	E^* at 261 mμ	$[m_2]$ in copolymer, mole-%
1	10	280	1.73	4.34	2.86
2	20	329	1.31	9.19	6.10
3	30	350	0.95	14.73	10.03
4	40	449	1.21	21.00	14.60
5	50	504	1.18	27.43	19.57
6	60	543	1.24	33.62	24.67

TABLE IV
Copolymerization of Methyl Methacrylate (M_1) with 9-Vinylanthracene (M_2)
(78 ± 0.5°, 3 mole-% di-*tert*-butyl peroxide)

No.	$[M_2]$ in init. monomer mixt., mole-%	Polymn. time, hr.	Convsn., %	E^* at 261 mμ	$[m_2]$ copolymer, mole-%
1	10	110	14.7	5.50	2.78
2	20	115	7.5	11.20	5.94
3	30	139	5.3	17.00	9.32
4	40	161	2.6	23.76	13.57
5	50	221	1.9	30.30	18.03
6	60	245	1.5	38.69	24.13

Data on the initial composition of the monomer mixtures (M_1, M_2) and on the amount of monomers found in the copolymers (m_1, m_2) were used for calculating the relative reactivities of 9-VAn and other monomers (r_1, r_2). The copolymerization equation derived by Alfrey and Goldfinger[13] and by Mayo and Lewis[14] was applied in its graphic representation:

$$r_2 = [M_1]/[M_2]\{[m_1]/[m_2](1 + [M_1]/[M_2]\,r_1) - 1\} \qquad (2)$$

For each copolymerization series a family of six straight lines (one for each experiment) was obtained in the r_1–r_2 system of coordinates. Theoretically, each family of lines should have a single intersection point, but no concurrence could be obtained, owing to experimental errors, and mean values of r_1 and r_2 had to be calculated, allowing for different weights of the intersection points (nearly right-angled intersections being more important than acute-angled ones).

The equations used were:

$$r_2 = (m_1x_1 + m_2x_2 + \ldots + m_nx_n)/\Sigma m_n \qquad (3)$$

$$r_1 = (m_1y_1 + m_2y_2 + \ldots + m_ny_n)/\Sigma m_n \qquad (4)$$

where x_n and y_n are coordinates of the nth point of intersection, and m_n is the sine of the angle between the intersecting lines. This approach was already used by one of the authors in an earlier work.[2] The relative reactivities of the monomers obtained are listed in Table V.

TABLE V

Copolymerization of Methyl Acrylate, Ethyl Acrylate, Butyl Acrylate, and Methyl Methacrylate (M_1) with 9-Vinylanthracene (M_2)

No.	M_1	M_2	r_1	r_2	Temp., °C.	di-*tert*-butyl peroxide, mole-%
1	Methyl acrylate	9-Vinylanthracene	2.97	0.082	76 ± 0.5	3
2	Ethyl acrylate	"	3.43	0.274	78 ± 0.5	3
3	Butyl acrylate	"	3.76	0.163	78 ± 0.5	3
4	Methyl methacrylate	"	3.81	0.071	78 ± 0.5	3

CONCLUSIONS

In the light of earlier data on the copolymerization of styrene with 9-VAn[2] the present results show that the difference in polarity of the monomers participating in the copolymerization has an insignificant influence compared with that of the steric factors involved in the reaction.

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Determination of Theoretical Plates in Gel Permeation Chromatography by Using Polydisperse Materials (Polymers)*

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Synopsis

The need for an improved method of expressing performance of GPC columns and operating conditions is discussed. It is shown that theoretical plates can be calculated from chromatograms of high molecular weight materials (polymers) if the curve widths are normalized for polydispersity. The resulting value N, where $N = 16d^2(v/W)^2$, is a useful measure of the real plate count afforded by the columns to polymers and is useful for comparison purposes. Since N does not provide absolute data on separation, it is better to use formulas for resolution and fractionation when such data are needed.

Introduction

Gel permeation chromatography (GPC), a rapid, new method for determining molecular weight distributions of polymers,[1] is a column chromatographic technique which sorts molecules according to their sizes in solution.[2,3] Two methods are generally used to evaluate the performance of the columns and operating conditions in GPC: the determination of theoretical plates N by means of a low molecular weight, monodisperse (single molecular size) material and the establishment of a calibration curve relating molecular weight to the peak elution volume v of the GPC curve.[3,4] In addition, this author has described formulas which can be used as tests for performance by calculating and predicting resolution and fractionation in GPC,[5] and Giddings has discussed the maximum number of components resolvable by GPC.[6]

Although the calibration curve is a useful measure of quality for the GPC operator, it depends specifically on polymer type and cannot be used easily to communicate quality between laboratories. Plate count, or number of theoretical plates, is a well-defined quantity used extensively in some areas of chromatography, but as presently determined it is not properly descriptive for GPC.[5] The very low molecular weight, monodisperse material (such as acetone) is the last of the molecular sizes, except perhaps water and air, to be eluted from the column. The size exclusion/diffusion mechanism[7,3] suggests that this material has taken the longest possible

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* Contribution No. 1389.

equilibrium route through the column and thus can be used to measure the maximum plate count affordable by the column. Unfortunately the maximum plate count does not very well describe the real plate count available to much larger, more slowly diffusing polymer molecules which see a smaller column volume. Because monodisperse polymer standards do not exist, polymers have not been used to determine plate count. The curve width W varies with dispersity, and it has been assumed that eq. (1)[8] cannot be used when polydisperse materials are employed.

$$N = 16(v/W)^2 \tag{1}$$

This paper describes a simple normalization technique for permitting the use of polydisperse materials to determine realistic N values for polymer fractionations.

Materials and Experimental Conditions

The polystyrenes used were purchased from commercially available stocks. Specifications and suppliers are listed in Table I. The anionically polymerized polycaprolactams were prepared by methods described by

TABLE I

GPC Data for Standard Samples

Sample	$\bar{M}_w \times 10^{-3}$ reported	d reported	V, counts	W, counts	W/d	N calc'd. as $16d^2 (v/W)^2$
Polystyrenes[a]						
P-18M	1800	1.20	16.22	2.47	2.05	993.5
W-4190037	411	1.05	17.44	2.23	2.12	1079
N-705	185	1.10	18.35	2.08	1.89	1507
P-7a	51	1.06	19.73	1.93	1.82	1875
P-2a	19.8	1.06	21.01	2.14	2.02	1733
P-12a	2.03	1.10	23.63	2.14	1.95	2360
PMMA						
1 (containing 4% ethyl acrylate)	169[b]	2.00[c]	18.39	3.90	1.95	1423
2 homopolymer	75[b]	1.95[c]	19.30	3.81	1.95	1561
3 (containing 4% ethyl acrylate)	100[b]	1.86[c]	18.95	3.63	1.95	1508
Nylons (anionically prepared Polycaprolactam)						
1	175	3.51	18.38	6.86	1.95	1415
2	100	2.56	18.51	4.99	1.95	1443
3	26	2.5	19.66	4.91	—	1600
Acetone	—	—	25.77	1.22	—	7120

[a] Sources: P = Pressure Chemical Company; W = Waters Associates, Inc.; N = National Bureau of Standards.

[b] From light-scattering data.

[c] From GPC.

Gechele and Stea[9] with slight modifications in temperature and time. The PMMA samples were prepared for characterization purposes by routine, free-radical solution or emulsion polymerization using techniques similar to those described by Sorenson and Campbell.[10] Samples 1 and 3 were copolymers with 4% ethyl acrylate while 2 was a homopolymer.

The $\bar{M}_w$ values for polycaprolactam in Table I were obtained by light scattering in 95% formic acid containing 0.2 mole-% sodium formate. The refractive increments were 0.143 at 5461 A. and 0.144 at 4358 A. The Zimm method of extrapolation to zero angle and zero concentration was employed. The instrument has been described by Baum and Billmeyer.[11] The PMMA samples were measured in acetone at 90° only. The usual extrapolation to zero angle was made but there was no dissymmetry correction. Refractive increments were 0.129 for both wavelengths. Osmotic pressure measurements were made on the PMMA samples in acetone with a Stabin-Shell Automatic Osmometer. The light-scattering/osmometry ratios agree with the GPC d values for $\bar{M}_w/\bar{M}_n$ within 10%. All GPC experiments were carried out in freshly distilled m-cresol at 100°C. at 1 ml./min. flow rate, 0.25–0.5% polymer concentration with nominal $10^6 + 10^5 + 10^3$ A. columns in series.

Development

This author has shown that the width W of a GPC curve divided by the sample polydispersity d is a constant for a fixed set of operating conditions provided the sample distribution is continuous and composed of linear molecules, and the elution curve falls within the linear portion of the "linear-log calibration."[5] In this case W is the curve width in volume units, defined as the width of the base line of the curve between two tangents drawn on the inflection points of the GPC curve and extended to the base line. W should be measured very carefully and converted into volume by a factor relating inches to volume (counts or milliliters) across the full curve. The polydispersity d is $\bar{M}_w/\bar{M}_n$. Since many polymers, including commercially available standards, fit these criteria, this principle is very useful. The GPC curve width W can be normalized by dividing it by d, and eq. (1) is transformed into eq. (2).

$$N = \left[16\frac{v}{W/d}\right]^2 = 16d^2\left(\frac{v}{W}\right)^2 \tag{2}$$

it follows that

$$N^{1/2} = 4dv/W \tag{3}$$

and since

$$W/d = \text{Constant}$$

then

$$d/W = \text{Constant}$$

and

$$N^{1/2} = CV \tag{4}$$

Thus $N^{1/2}$ as calculated from eq. (2) or (3) should vary linearly with the peak elution volume and should be independent of polymer type. These hypotheses are confirmed and the equations are satisfied by the data in Figure 1 and Table I which relate $N^{1/2}$ to the peak elution volumes obtained for polystyrene, nylon, and poly(methyl methacrylate) samples of various molecular weights and polydispersities. The constant C will vary with columns and operating conditions. Although the data points of Figure 1 appear to be considerably scattered, the data are quite good considering the strong

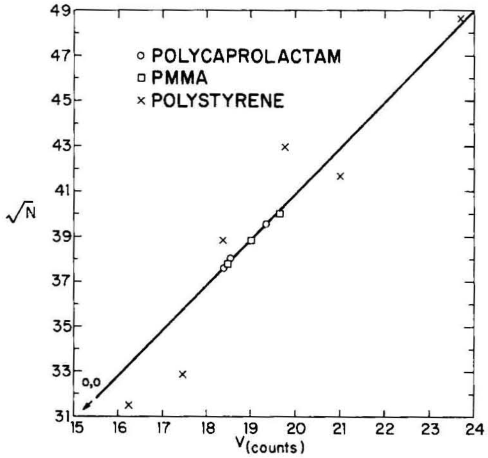

Fig. 1. Square root of theoretical plates N vs. peak elution volume V as an independent function of polymer type in GPC.

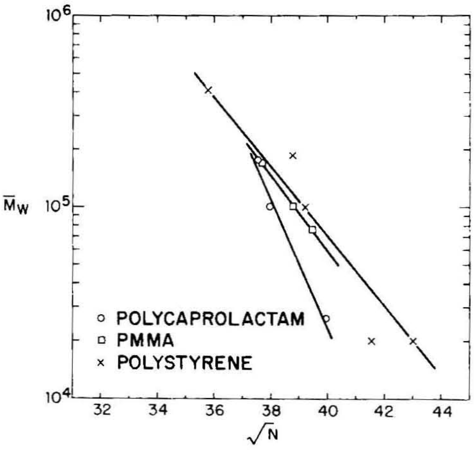

Fig. 2. Square root of theoretical plates N vs. log molecular weight as a function of polymer type in gel permeation chromatography.

dependence on d which is difficult to determine to better than 10% by absolute means. Note that the line extrapolates to zero N at zero V. The high result for acetone is thought to be related to diffusion rate.

Moore has described a linear log calibration in GPC by eq. (5).[1]

$$\log \bar{M}_w = A - BV \tag{5}$$

From eq. (4)

$$N^{1/2} = C[A - \log \bar{M}_w]/B$$

or

$$N^{1/2} = k - K \log \bar{M}_w \tag{6}$$

Equation (6) predicts that $N^{1/2}$ will vary with $\log \bar{M}_w$ and for this equation will be dependent on polymer type. Indeed as shown in Figure 2, three separate relationships are found for polystyrene, nylon, and poly(methyl methacrylate), respectively. The closeness of the polystyrene and PMMA curves agrees with our calibration data for these materials.

In summary, we propose that plate count, calculated from polymer curves via eq. (2) is often useful to describe the performance of a column or series of columns in fractionating polymers. Plate count so obtained is more realistic in polymer work than the values found from monomers. Since the calculated N depends on elution volume, the volume or volume range used to calculate N should be noted so that the various laboratories can compare numbers.

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Coordinated Radical Polymerization and Redox Polymerization of Acrylamide by Ceric Ammonium Nitrate

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Synopsis

The ceric salt-initiated polymerization on acrylamide and graft copolymerization of acrylamide onto cellulose were studied. The mechanism of the ceric salt-initiated polymerization of acrylamide in the homopolymerization system can be explained by a radical mechanism based upon Ce^{4+}-coordinated acrylamide, and the mechanism of the ceric salt-initiated graft copolymerization of acrylamide onto cellulose can be explained in two ways: a free-radical mechanism with the ceric–cerous redox system, and a radical mechanism based upon Ce^{4+}-coordinated acrylamide. The velocities of initiation, propagation, and termination in the redox mechanism are quite different from those in the coordinated radical mechanism. From the infrared absorption and nuclear magnetic resonance spectra measurements it is concluded that the structure of the ceric-coordinated acrylamide is the π-complex.

INTRODUCTION

Since Mino and Kaizerman[1] made a study of some vinyl monomer polymerizations initiated by ceric ammonium nitrate, many other reports have been published. They were mainly connected with graft copolymerization onto cellulose. The mechanism of the initiation of graft copolymerization has been generally reported as a free-radical mechanism based upon the cellulose radical formed.[2–4] In addition to this, another mechanism of initiation reaction was reported.[5–7]

As previously reported,[7] the existence of two polymerization mechanisms is recognized in the present system. One is a free-radical mechanism based upon the ceric–cerous redox system; the other cannot be interpreted as a mechanism based upon the ceric–cerous redox system, but it should be concluded that the radical mechanism is based upon the ceric-coordinated vinyl monomer. The structure or polymerizability of this coordinated compound has not been sufficiently elucidated, however.

EXPERIMENTAL

Acrylamide (a commercially available sample, Nitto Chemical Industry Company, Japan) was used after recrystallization from benzene.

Iodine double bond determination indicated 99.3% purity. Ceric ammonium nitrate was obtained from Showa Chemical Company (Japan), and ferrosimetric analysis indicated 99.05% purity. Acrylamide and ceric ammonium nitrate will be denoted by AM and Ce^{4+}, respectively.

The cellulose film was used as a wet sheet not undergoing drying to cellophane; the crystallinity was 30–32% (x-ray method); the weight-average molecular weight ranged between 48,000 and 50,500; the thickness of the wet sheet was 100–105 μ (after dryup 20 μ).

The polymerization was carried out in nitrogen in a round-bottomed flask equipped with a stirrer.

The concentrations of Ce^{4+} and AM were kept at 0.0069 and 0.42 mole/l., respectively. Nitric acid was not added in this solution.

The yield of monomer polymerized was assessed by the use of the iodine double bond determination. The number-average molecular weight of polyacrylamide was determined by using an Ostwald viscometer at 30°C. for aqueous solution and was calculated from the viscosity data by using the equation:[8]

$$[\eta] = 6.80 \times 10^{-4}\bar{M}_n^{0.66}$$

The grafting yield was determined by nitrogen analysis or by direct weighing of the graft copolymer produced. The polyacrylamide making up the branches was extracted from the graft copolymer by the depolymerization of cellulose chain, and the number-average molecular weight of branched polymer was determined viscometrically.

RESULTS AND DISCUSSION

Ceric Salt-Initiated Homopolymerization of Acrylamide

The initiation of this polymerization is accompanied by an induction period. It can be seen that the polymer yield increased slowly with reaction time. The rate of polymerization shows a decrease with reaction time in this polymerization.

The molecular weight of polymer formed increases in proportion to the polymer yield, as shown in Figure 1. It should be noted that the life of the growing polymer chain is quite long, and the rate of propagation is very slow. And, since the molarity of the growing polymer chain is nearly constant during reaction, it is presumed that the rate of initiation is much smaller than that of propagation.

The rate of polymerization was accelerated with increasing temperature. But, since the relationship between the molecular weight of polymer and the polymer yield at the higher temperature (50°C.) agreed with that at the lower temperature as shown in Figure 2, it is presumed that primarily the rate of propagation is affected by the temperature.

When nitric acid, in concentration of 0.010 mole/l., was added to the solution in which the polymerization was proceeding, the increase of molecular weight soon stops, as shown in Figure 3.

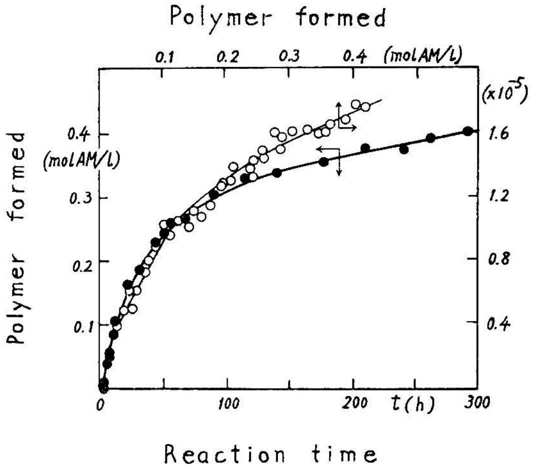


Fig. 1. Plots of (●) polymer yield vs. reaction time and (○) molecular weight in the Ce^{+4}-initiated homopolymerization of acrylamide. Reaction temperature 20°C.

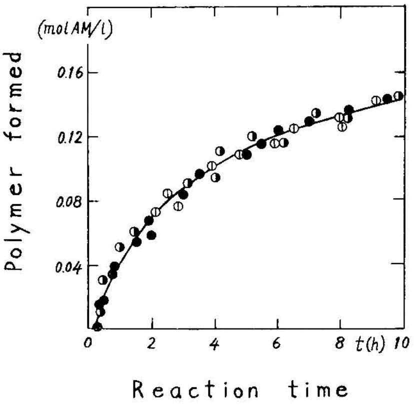


Fig. 2. Plots of polymer yield vs. reaction time: (●) no HNO$_3$; (⦶) 0.010 mole/l. HNO$_3$ added after monomer conversion of 0.072 mole/l.; (◑) system with HNO$_3$.

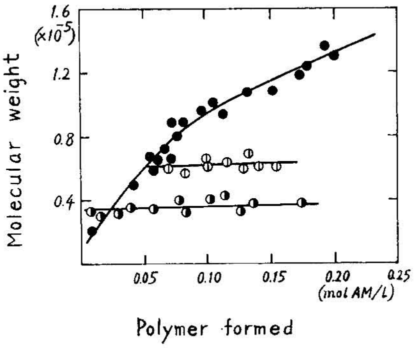


Fig. 3. Plots of molecular weight vs. polymer yield in the Ce^{+4}-initiated homopolymerization of acrylamide. Symbols as for Fig. 2. Reaction temperature 50°C.

TABLE I
Relation between HNO_3 Concentration in the System and $\bar{M}_n$ of Polymer Formed

HNO_3, mole/l.	Homopolymer $\bar{M}_n \times 10^{-5}$
(0)	(10.2)
0.005	5.2
0.0075	3.9
0.010	3.1
0.015	2.3
0.019	1.5
0.023	1.1

On the other hand, when nitric acid (0.010 mole/l.) was added to the solution at the time the Ce^{4+}–AM aqueous solution was prepared, the same induction period was observed, and the rate of polymerization was comparable with the system without nitric acid and with that in the system at the initial stage. The molecular weight of the polymer in the system with nitric acid was almost unchanged during the polymerization, as shown in Figure 3. It should be noted that the nitric acid is an excellent chain transfer agent. The relationship between the molecular weight of polymer and the concentration of nitric acid in the system is given in Table I. When the monomer in this system had been almost completely consumed by polymerization, AM was replenished in this system without nitric acid. As soon as AM was replenished, the rate of polymerization began to increase again, and the molecular weight increased proportionally to the polymer yield. But shortly after the addition of monomer, the molecular weight of polymer showed a sharp increase; this presents a great contrast to the relationship between molecular weight and polymer yield before the addi-

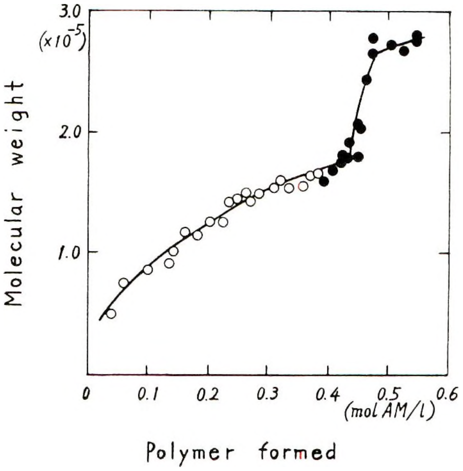


Fig. 4. Plots of molecular weight vs. polymer yield: for systems without HNO_3: (●) 0.20 mole/l. acrylamide added after 0.395 mole/l. monomer conversion; (○) before replenishment of acrylamide. Reaction temperature 20°C.

tion of monomer, as shown in Figure 4. Thereafter, the rate of polymerization was observed to decrease rapidly. These results are presumed to be related to the termination reaction by the recombination of polymer radicals.

The behavior of Ce^{4+} in the system was also studied. The change of Ce^{4+} concentration with the progress of polymerization was determined by ferrosimetric analysis with excess orthophosphoric acid. The result shows that cerous ion formation is not detected extending over a long time, no matter what the polymer produced may be. This covered every case of polymerization.

These results cannot be interpreted on the basis of a mechanism based upon the ceric–cerous redox polymerization.

Ceric Salt-Initiated Graft Copolymerization of Acrylamide onto Cellulose Film

First graft copolymerizability in the case of freshly prepared Ce^{4+}–AM aqueous solution was studied. As soon as the Ce^{4+}–AM aqueous solution was prepared, a given weight of cellulose film was introduced in the solution for a given time, and copolymerization took place. The concentration of cellulose was kept at 1.80 g./l. grafting solution. After various treatment times (1, 2, 3, or 4 hr.), the treated film was removed from the solution, and homopolymer in the grafted film was extracted in boiling water for many hours. The grafting yields were plotted against reaction time (Fig. 5). The grafting yield shows a maximum value (about 20%) in a short reaction time. As soon as the cellulose film was introduced, the Ce^{4+} showed a slight decrease in concentration, and it then showed the maximum value within a short reaction time, and a decrease of 2×10^{-4} mole/l., and in terms of mole ratio, a decrease of about 5.39 of Ce^{4+} per unit cellulose chain.

The mechanism of the initiation of graft copolymerization has been reported quite generally as a free-radical mechanism based upon the cellulose radical formed; the same holds for this grafting reaction in the case of the Ce^{4+}–AM aqueous solution, either freshly prepared or shortly after preparation.

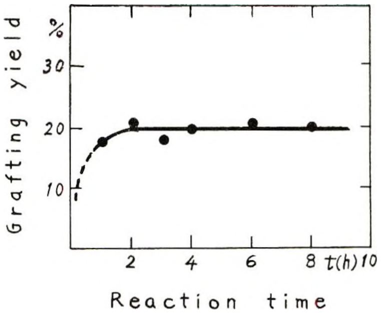


Fig. 5. Plot of grafting yield vs. reaction time with freshly prepared Ce^{4+}–AM solution.

Another experiment was carried out to study the graft copolymerizability as a function of ripening of the Ce^{4+}–AM aqueous solution.

The freshly prepared Ce^{4+}–AM aqueous solution was stored for 2 hr. at 20°C. in nitrogen. Then, a given weight of cellulose film (1.80 g./l.) was introduced in the ripened solution and graft copolymerization was carried out. After various treatment times, the film was taken out from the solution. In this case, the grafting yield increased substantially proportional to the reaction time, and the molecular weight of polyacrylamide making up the branches showed a considerable increase in parallel with the grafting

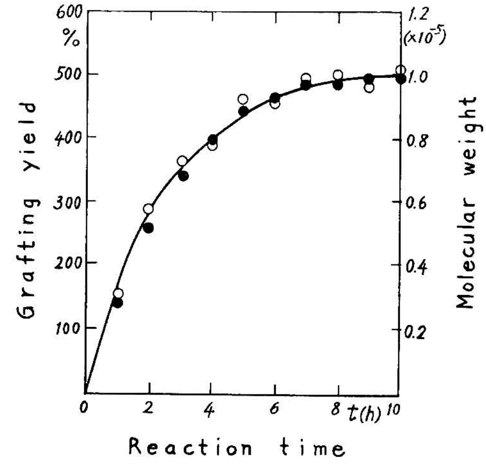


Fig. 6. Plot of (○) grafting yield and (●) molecular weight of polyacrylamide making up branches of copolymer vs. reaction time. The grafting was carried out 2 hr. after preparation of Ce^{4+}–AM solution.

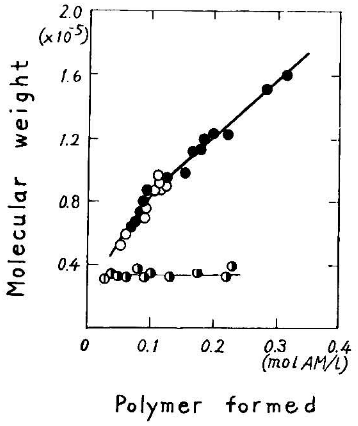


Fig. 7. Molecular weight of both branched and homopolymer vs. graft polymer and homopolymer yield on acrylamide graft copolymerization onto cellulose: (○) grafted polyacrylamide, no HNO_3; (●) homopolymer, no HNO_3 in system; (◐) grafted polyacrylamide, 0.010 mole/l. HNO_3; (◑) homopolymer, 0.010 mole/l. HNO_3.

yield value as shown in Figure 6. The formation of homopolymer was also observed in parallel with the graft copolymerization. The molecular weights of both branched polymer and homopolymer in the solution were plotted versus monomer conversion by homopolymerization and graft copolymerization in the same solution (Fig. 7). This agrees closely with Figure 1.

The rate of propagation of graft copolymerization shows a rapid decrease as the grafting yield value approaches about 500%. According to another experiment, the maximum grafting yield depends on the structure of cellulose film. That is, the volume extension of the cellulose structure reaches its limit: as a consequence, it follows that the cellulose film is unable to house a branched polymer above some percentages, about 500%. Little concentration decrease in Ce^{4+} was detected during the grafting reaction, no matter what the graft copolymer is produced.

In another series of experiments, nitric acid (0.010 mole/l.) was added to the solution as soon as the Ce^{4+}–AM aqueous solution was prepared. This solution was stored for 2 hr. at 20°C. in nitrogen. Then the same weight of cellulose film was introduced to the ripened solution, and graft copolymerization was allowed to take place. After varying treatment times, the films were taken out of the solution. In this case, the grafting yield value increased proportionally to the reaction time but the increase of grafting value terminated at the time amounts to about 150%. The molecular weight of branched polymer at this time was $3.6 \pm 0.2 \times 10^4$, and this value agreed with the molecular weight of polyacrylamide in the homopolymerization system containing 0.010 mole/l. nitric acid (Fig. 3). Little concentration decrease in Ce^{4+} was detected during this grafting reaction.

The relationship between nitric acid concentration in the system and both grafting yield and molecular weight of polyacrylamide making up the branches was examined by the same method: results are given in Table II. It can be seen that the molecular weights in Table II agree closely with those in Table I. These results seem to suggest that the termination mechanism of graft copolymerization is the same as that of homopolymer-

TABLE II

Relation between HNO_3 Concentration in the System and Both Grafting Yield and $\bar{M}_n$ of Branched Polyacrylamide

HNO_3, mole/l.	Branched polymer	
	Grafting, %	$\bar{M}_n \times 10^{-4}$
(0)	(493)	—
0.005	245	4.9
0.0075	207	4.1
0.010	159	3.4
0.015	124	2.2
0.019	81	1.6
0.023	56	1.2

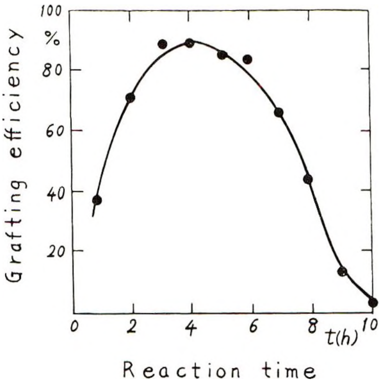


Fig. 8. Grafting efficiency vs. reaction time.

ization. However, the rates of initiation and propagation reaction of the two are different. The rates of initiation and propagation reaction of graft copolymerization are proportionately larger than those of homopolymerization at the initial stage of polymerization, as shown in Figure 8.

The behavior in the cases of the experiments described above cannot be interpreted on the basis of a mechanism based upon the ceric–cerous redox polymerization.

Interaction between Ce^{4+} and AM

There is no sufficient reason for the polymerization behavior without the formation of cerous ion. It may, however, be presumed that there is some relationship to the ripening of the Ce^{4+}–AM aqueous solution. Some experiments were therefore carried out to study the interaction between Ce^{4+} and AM at varying times after preparation of the Ce^{4+}–AM aqueous solution.

The behavior of Ce^{4+} during the reaction was followed by two methods: volumetric analysis by the ferrosimetric method and an iodometric method. They differ in oxidation–reduction potential. When no cellulose film was

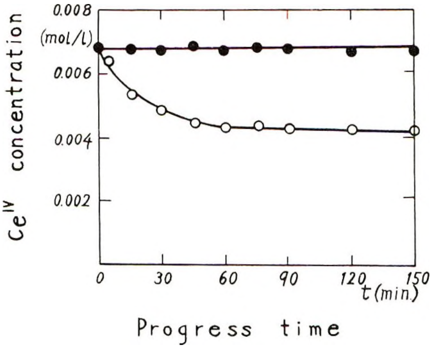


Fig. 9. Ce^{4+} concentration vs. time: (●) ferrosimetric method; (○) iodometric method.

introduced in the solution, no change in Ce^{4+} concentration was detected by the ferrosimetric method for many hours. However, a change of Ce^{4+} concentration with time was noted by means of the iodometric method. For the same solution without AM, the Ce^{4+} concentration as obtained by the ferrosimetric method agreed with that obtained by the iodometric method. The difference in the Ce^{4+} concentration obtained by these two methods thus may be due to formation of complex between Ce^{4+} and AM. The relation between Ce^{4+} concentration by two methods and the lapse of time after preparation of Ce^{4+}–AM aqueous solution is given in Figure 9. Formation of Ce^{3+} ion and polyacrylamide were not recognized during these experiments. The Ce^{4+}–AM complex was resolved into Ce^{4+} ion and AM monomer by adding excess orthophosphoric acid. It seems that the C═C bond retains most of its double-bond character, and Ce^{4+} retains most of its Ce^{4+} character in the compound.

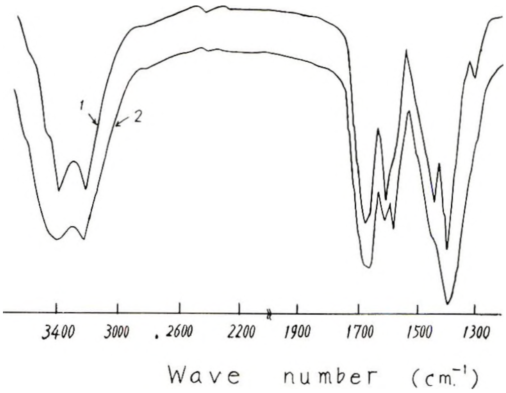


Fig. 10. Typical infrared spectra of Ce^{4+}–AM mixtures: (*1*) immediately after preparation; (*2*) after 15 min. ripening.

When a mixture of Ce^{4+} and AM in the crystal state was crushed in the mortar it acquired a slightly glutinous and deliquescent character. The infrared absorption spectrum of such a mixture was determined by the KBr disk method. AM and Ce^{4+} were mixed at a molar ratio of $AM/Ce^{4+} = 10$. Typical infrared spectra are given in Figure 10. The C═C stretching (1616 cm.$^{-1}$) and the C═O stretching (1670 cm.$^{-1}$) bands of AM were shifted to frequencies about 20 and 10 cm.$^{-1}$ lower, respectively, by the action of Ce^{4+}. The strong band at around 3400 cm.$^{-1}$, which is assigned to the —NH_2 group, broadened as a consequence of bringing the Ce^{4+} molecule into close proximity with AM. The shift of C═C stretching band is especially marked.

The data from the infrared spectra may be interpreted as follows. The red shift of the C═C stretching band may be considered indicative of π-complex. The small red shift and broading of the C═O stretching band may be interpreted as a σ-complex. Broading of the strong band at

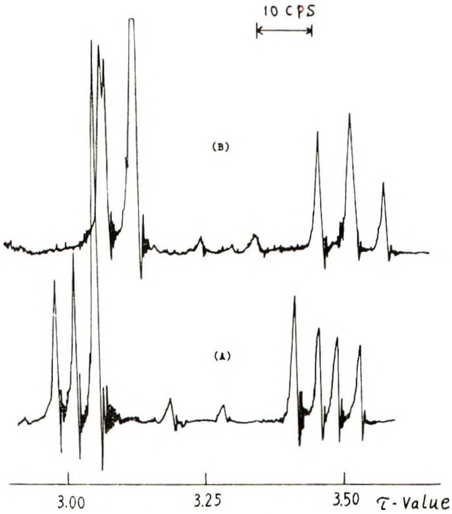


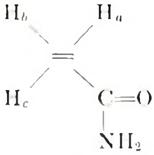
Fig. 11. Typical NMR spectra of acrylamide: (*A*) in absence of Ce^{4+}; (*B*) in presence of Ce^{4+} (acrylamide/Ce^{4+} = 1).

approximately 3400 cm.$^{-1}$, which is associated with the $-NH_2$ group, may be interpreted as a σ-complex.

The correct structure may be roughly deduced from information on the vinyl proton. Therefore the nuclear magnetic resonance spectra (NMR) of monomer and Ce^{4+}-attacked monomer were obtained. All measurements were made with a high-resolution spectrometer with a 100 Mc. oscillator with super stabilizer and field homogeneity control. AM and Ce^{4+} were mixed at a molar ratio AM/Ce^{4+} of 9.9–10 D_2O at a monomer concentration of 1.0 mole/l. The typical spectra are given in Figure 11. The NMR spectrum for AM in the presence of Ce^{4+} is significantly different from that of AM in the absence of Ce^{4+}; the centers of the quartet assigned to H_a,

TABLE III

NMR Data for Acrylamide in the Presence of Ce^{4+}



Mole ratio AM/Ce^{4+}	Chemical shift, τ			Coupling constant, cps		
	H_a	H_b	H_c	J_{trans}	J_{cis}	J_{gem}
Only AM	3.01	3.47	3.16	13.0	7.5	4.3
10	3.01	3.47	3.16	12.8	7.4	4.5
5	3.02	3.48	3.16	12.4	7.4	4.9
2	3.05	3.50	3.17	12.2	6.8	5.0
1	3.08	3.52	3.19	11.7	5.7	5.7

H_b, and H_c of AM in the presence of Ce^{4+} are shifted approximately 0.05 ppm to higher field than those of AM in the absence of Ce^{4+}, and a change has been effected in the spin–spin coupling, as shown in Table III.

This seems to suggest that the positive electric charge on the carbon atom of the C—H bond has decreased, that the degree of electron delocalization, where it extends from $C—H_a$ to the $C—H_b$ and $C—H_c$ bonds, shows a slight decrease, and that electrons are attracted to Ce^{4+} from the $C—H_a$ and $C—H_c$ bonds as a consequence of the interaction between Ce^{4+} and AM.

The x-ray diffraction patterns of the glutinous mixture AM–Ce^{4+} are consistent with a lengthening of the C=C bond length of AM and thus with a slight increase[9] in the electron density by the Ce^{4+}.

These results lend support to the concept of formation of a π-type structure. It is a phenomenon of some interest that, although Ce^{4+} does not have an incomplete *5d* electron shell and is a hard Lewis acid, it forms a π-complex with AM. This may be explained as follows. The hydration of Ce^{4+} occurs in aqueous solution. As a result, the Ce^{4+} behaves as if it had an unpaired electron in a vacant orbital (probably the *5d* orbital). The formation of aqueous ion is suspected from measurements of the ultraviolet and visible absorption spectra. Ce^{4+}-coordinated AM is obtained in systems without nitric acid or at low concentration of nitric acid (0.015*M* or less), and hydrated Ce^{4+} is also obtained under these particular conditions. It may be that the hydrated nucleus in the immediate formation has chemical peculiarities. When AM molecules approach hydrated Ce^{4+}, a π-electron orbital of AM overlaps the *dsp* vacant hybrid orbital of hydrated Ce^{4+}, and an unpaired electron of hydrated Ce^{4+} overlaps a vacant antibonding orbital of AM. This has great resemblance in structure to Ziese's salt,[10,11] but the stability of the present coordinated compound is quite different.

It is presumed that formation of Ce^{4+}-coordinated AM is directly involved in the initiation of homopolymerization in the system, and while graft copolymerization is entirely different in behavior from redox polymerization. The mechanism of the ceric salt-initiated polymerization of AM in the homopolymerization system, without nitric acid, can be explained by a radical mechanism based upon Ce^{4+}-coordinated AM, and the mechanism of the ceric salt-initiated graft copolymerization of AM onto cellulose can be explained in two ways: a free-radical mechanism involving the ceric–cerous redox system, and in addition a radical mechanism based upon Ce^{4+}-coordinated AM. The induction period for polymerization must reflect the time necessary for activating the comparatively stable Ce^{4+}–AM π-complex in order to initiate the polymerization, and after the activation, the Ce^{4+}-coordinated AM initiates both graft and homopolymerization.

In the case of redox polymerization, the remaining unhydrated Ce^{4+} ion, acts as an attack reagent for cellulose, while the case of coordinated radical polymerization is attributable to a hydrated Ce^{4+}.

The rates of initiation, propagation, and termination in the redox mechanism are quite different from those in the coordinated radical mechanism.

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Silicon-Containing Amide, Benzimidazole, Hydrazide, and Oxadiazole Polymers

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Synopsis

This study reports the synthesis of new silicon-containing amide, benzimidazole hydrazide, and oxadiazole polymers. Procedures are described for the preparation of several intermediate compounds. The silicon-containing polymers are soluble in organic solvents. Solution-cast films from the polymers generally are flexible and exhibit good adhesion to glass and metal surfaces. Preliminary examination indicates that the polymers are heat-stable at elevated temperatures.

INTRODUCTION

A considerable number of aromatic and heterocyclic polymers have been reported,[1-5] some of which show good thermal resistance. The relation of the molecular structure of Schiff base and acid amide polymers to their resistance to thermal decomposition was investigated at this laboratory.[6] These products are generally insoluble in organic solvents and, therefore, they have limited end-item application.

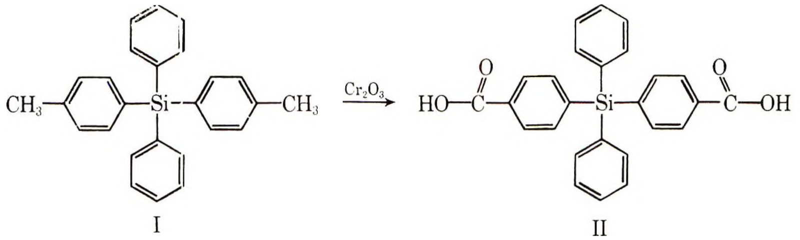
A recent study[7] covering the synthesis and heat-stability properties of silicon-containing Schiff base and benzimidazole derivatives indicated that polymers based on such structures might possess good thermal resistance and exhibit other useful characteristics. In continuation of this work, this paper reports the results of investigations leading to the development of novel silicon-containing acid amide, benzimidazole, and oxadiazole polymers.

DISCUSSION

Synthesis of Intermediate Compounds

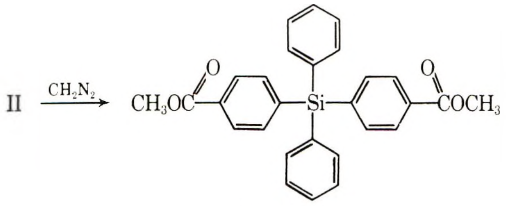
Intermediate compounds had to be synthesized before the desired polymers were prepared. Di(*p*-tolyl)diphenylsilane (I) was oxidized with chromic acid in a mixture of acetic acid and acetic anhydride to produce white crystalline bis(*p*-carboxyphenyl)diphenylsilane (II) in 96% yield, m.p. (uncorr.) 266–268°C. This method is based on that described by Lewis and Gaines[8] for the oxidation of alkarylsiloxanes. Speck[9] prepared II, m.p. 250–257°C., by oxidation of I with potassium permanganate.

The diacid II was treated with excess of diazomethane to prepare bis(*p*-carbomethoxyphenyl)diphenylsilane (III). Efforts to prepare polymers by reaction of III with phenylenediamines were unsuccessful.



I II

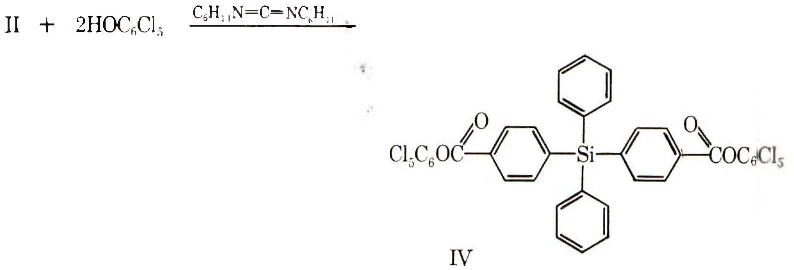
(1)



III

(2)

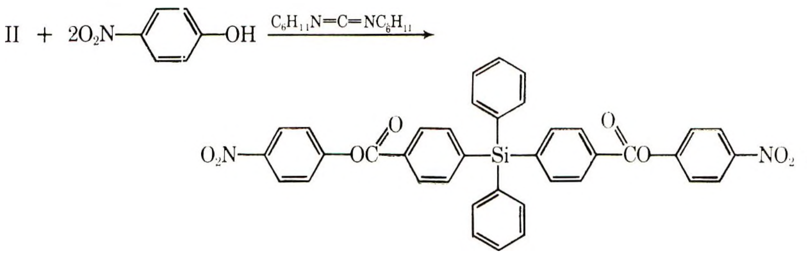
Previous studies involving the synthesis of polypeptides from pentachlorophenyl esters[10,11] suggested that such reactions might be applicable in this case. Thus, II was converted by reaction with pentachlorophenol in the presence of dicyclohexylcarbodiimide as coupling agent to produce bis(*p*-carbopentachlorophenoxyphenyl)diphenylsilane (IV) in 81.4% yield.



(3)

IV

Since *p*-nitrophenyl esters of amino acids are used as intermediates for polymerizations, bis[*p*-carbo-(*p*-nitrophenoxy)phenyl]diphenylsilane (V) was similarly prepared in yields of 18–42%.

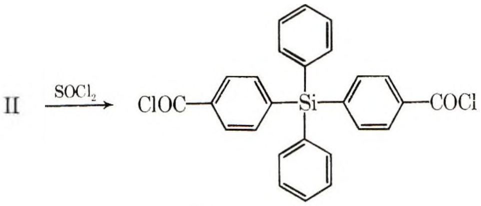


(4)

V

Optimum yields of IV and V were obtained when dicyclohexylcarbodiimide and pentachlorophenol or *p*-nitrophenol were used in large excess. When equivalent weights of reactants were employed, the yields of IV and V were much lower and the *N*-acylurea derivative of their half-esters were isolated as additional by-products.

The reaction of II and thionyl chloride gave white crystalline bis(*p*-chlorocarbonylphenyl)diphenylsilane (VI) in 91% yield.



VI

(5)

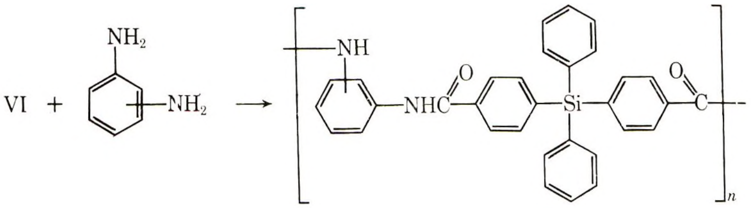
The infrared spectrum from the dicarboxylic acid II showed a carboxyl group absorption band at 5.9 μ. After esterification, the peak disappeared and was replaced by a new vibration mode at 5.80, 5.72, and 5.71 μ for III, IV, and V, respectively. The spectrum of diacid chloride VI exhibited two peaks in the carbonyl region at 5.64 and 5.76 μ. The location of these absorption bands is identical with that found in the spectrum of benzoyl chloride.[13] Vibration frequencies at 7.0 and 8.9 μ that are characteristic of phenyl–silicon bonds were present in the spectra of all of the intermediate compounds.

Synthesis of Silicon-Containing Polymers

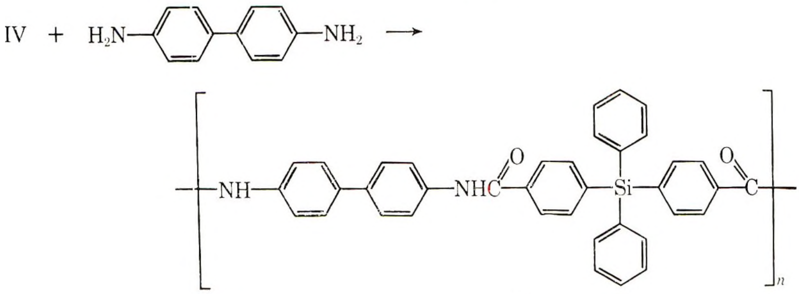
Polyamides. Polyamides VII and VIII were prepared by interfacial[14] and solution polycondensation[15] techniques with the use of equimolar quantities of acid chloride VI with *m*-phenylenediamine and *p*-phenylenediamine, respectively. In the interfacial polymerization method methylene chloride was employed as the organic solvent and sodium carbonate as the base.

Polymers VII and VIII prepared by the interfacial condensation method gave inherent viscosities of 0.95 and 1.86, respectively. Viscosities of 0.69 and 0.79 were obtained from specimens of polymers VII and VIII, respectively, that were synthesized by polycondensation of the reactants in chloroform solution. Similar polycondensation reactions in dimethylacetamide produced polymers VII and VIII with viscosities of 0.27 and 0.26, respectively.

While polymers VII and VIII were successfully prepared from the diacid chloride VI, no polymers could be obtained from the dimethyl ester III. Low yields of polymer VII were isolated after the dipentachlorophenyl ester IV was refluxed with *m*-phenylenediamine for 30 hr. in toluene or for 50 hr. in dimethylformamide.


(6a)

VII and VIII


(6b)

IX

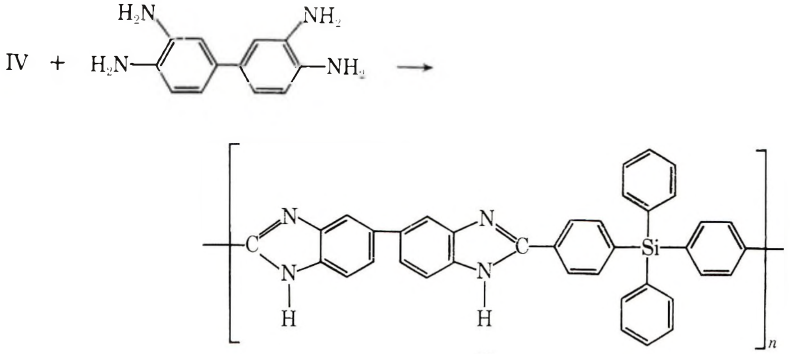
Contrary to this, when IV was refluxed with benzidine in *N*,*N*-diethylaniline for 52 hr. the silicon-containing polyamide IX was produced in 64% yield. The inherent viscosity of the polymer was determined to be 0.20. A number-average molecular weight of about 20,000 (approximately 34 recurring units) was calculated on the basis of chlorine analysis, assuming an average of one pentachlorophenyl endgroup per polymer chain. The reaction of benzidine and the *p*-nitrophenyl ester V for 11 hr. produced polymer IX with an inherent viscosity of 0.38, but the yield was only 19%.

The infrared spectra of polymers VII, VIII, and IX were consistent with their structure.

Speck[16] reported the preparation of silicon-containing polyamides from alkyl and alkaryl diamines. These polymers softened at about 200°C. On the other hand, polymers VII, VIII, and IX that were derived from aromatic diamines do not melt before they start to decompose at about 400°C. On this basis, the polymers produced in this study are more heat-stable.

Polybenzimidazole. Brinker and Robinson[17] introduced benzimidazoles into polymer chemistry by reacting bis-*o*-diaminophenyl compounds with aliphatic dicarboxylic acids. More recently, Marvel and co-workers[1] prepared fully aromatic polybenzimidazoles that exhibited high thermal stability in inert atmospheres, but were insoluble in organic solvents. Improved solubility properties were achieved by incorporating aryl ether linkages[18] or disiloxane units[19] into the polybenzimidazole structure. The polymers with the disiloxane group, however, showed much more lower resistance to thermal decomposition than the fully aromatic polybenzimidazoles.

In this study a new type of benzimidazole polymer containing silarylene groups in the repeating unit was synthesized. The reaction of the dipentachlorophenylester IV with 3,3′-diaminobenzidine in boiling *N*,*N*-dimethylaniline or *N*,*N*-diethylaniline at a temperature about 200°C. for 3–11 hr. produced yellow polymeric precipitates having inherent viscosities of 0.38–0.71. The higher viscosities were exhibited by the polymers obtained from the longer reaction periods. However, some tar formed when the reactants were heated for 11 hr. in dimethylaniline.



X (7)

Several experiments also were carried out at 235°C. for 4–11 hr. in quinoline from which solvent the polymer did not separate. The dark products thus obtained had inherent viscosities of 0.33–0.57.

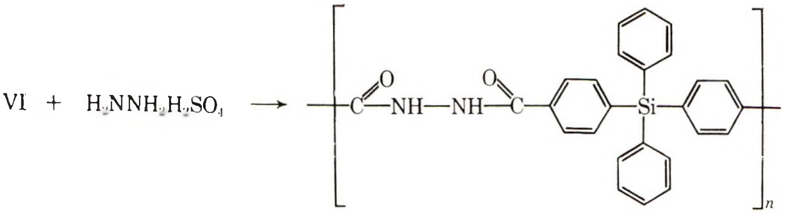
When a polymer prepared in *N*,*N*-dimethylaniline was refluxed for 37 hr. in tetralin, the inherent viscosity of the product increased from 0.57 to 1.23. Comparison of elemental analysis results before and after the tetraline treatment showed that the carbon–hydrogen values increased while the chlorine content of the polymer decreased. Assuming one pentachlorophenyl endgroup per molecule, the number-average molecular weight of the polymer before and after the tetralin treatment can be calculated from the chlorine analysis to be about 11,000 and 126,000, respectively.

The infrared spectrum of X showed absorption peaks at 2.92, 3.25, 6.14, 6.23, 6.50, 7.00, and 8.90 μ. Similar vibration frequencies have been observed in the spectra of a silarylenebenzimidazole model compound[7] and aromatic polybenzimidazoles.[1]

All of the silicon-containing polybenzimidazoles prepared with the different solvents were soluble in dimethylformamide, dimethyl sulfoxide, dimethylacetamide, and pyridine. After heating at 340–350°C. for 4 hr. under vacuum, about 30% of a polymer prepared with *N*,*N*-dimethylaniline became insoluble in these solvents. Comparison of the C=N/C=C (6.14/6.23 μ) absorption ratio in the spectra of X before and after heating indicates that the insoluble fraction may have formed because of the partial rupture of phenyl groups. Inherent viscosity measurements showed that the molecular weight of the soluble polymer fraction was essentially unchanged.

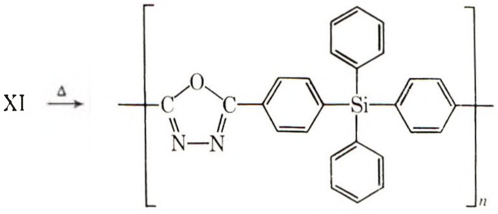
Polyoxadiazole. Huisgen and co-workers[20] were the first to report the synthesis of 1,3,4-oxadiazole oligomers through a series of reactions involving the thermolysis of 5-substituted 2-acyltetrazoles at 60–110°C. Low molecular weight oxadiazole polymers were made by Abshire and Marvel[21] by refluxing bistetrazoles with dicarboxylic acid chlorides in pyridine. On the basis of Stelle's earlier work,[22] Frazer and co-workers[2] prepared high molecular weight poly-1,3,4-oxadiazoles through the thermal cyclodehydration of aliphatic[23] and aromatic[24] polyhydrazides. The latter fully aromatic infusible polyoxadiazoles were thermally stable but insoluble in organic solvents and, therefore, could not be fabricated into films and fibers by conventional means.

From the behavior of the silicon-containing polyamides and polybenzimidazoles described above, it was considered feasible that the incorporation of a silicon atom into the recurring structure of aromatic polyoxadiazoles would improve their solubility properties. Thus, interfacial polycondensation methods[14] were used to synthesize a new silicon-containing polyhydrazide (XI) from the diacid chloride VI and hydrazine sulfate.



(8a)

XI



(8b)

XII

The silicon-containing polyhydrazide XI was converted to XII by heating under vacuum. The temperature was gradually raised to 285°C. and maintained there for several hours. The polyhydrazide XI was soluble in dimethylacetamide and insoluble in benzene and chloroform. After the ring formation, the new polyoxadiazole XII was readily soluble in these solvents also. The inherent viscosity of XII was 0.23.

The infrared spectrum of polyhydrazide XI showed absorption peaks at 3.08, 6.08, 6.45, 7.00, and 8.90 μ that are consistent with its structure. After the thermal cyclodehydration of XI, the spectrum no longer exhibited absorption bands at 3.08, 6.08, and 6.45 μ. Instead, a doublet was present at 6.40 and 6.50 μ and a new peak appeared at 10.40 μ that is characteristic of the oxadiazole ring structure.[2,25]

Flexible films were produced from solutions of the silicon-containing polymers VII–XII. The films generally showed good adhesion to metals and glass. The polymers also exhibited good resistance to decomposition when heated in air at elevated temperatures. Results of the heat-stability studies will be presented in another paper.[26]

EXPERIMENTAL

Viscosity

Inherent viscosity measurements were made at 30°C., from dimethyl acetamide solutions containing 5% of lithium chloride, except in the case of the silicon-containing polyoxadiazole where the solvent was chloroform.

Infrared Spectroscopy

Spectra from solution cast films and Nujol mulls of the products were recorded in the 2.5–15.0 μ region with a Perkin-Elmer model 337, grating infrared spectrophotometer equipped with sodium chloride windows.

Elemental Analysis

The products were analyzed by the Schwarzkopf Microanalytical Laboratories, Woodside, New York.

Purification of Materials

Chloroform was purified and dried as described by Morgan and coworkers.[27] The remainder of the solvents used in the polymer synthesis procedures were freshly distilled.

The aromatic amines, *m*-phenylenediamine, *p*-phenylenediamine, benzidine, and 3,3′-diaminobenzidine were recrystallized from ether–petroleum ether, methylene chloride at −20°C., acetone–cyclohexane, and methyl alcohol, respectively.

Synthesis of Intermediate Compounds

Diphenyldi(p-tolyl)silane (I). The method of Maienthal and coworkers[28] was used to prepare I.

Bis(*p*-carboxyphenyl)diphenylsilane (II). To a well stirred suspension of 10.92 g. (0.03 mole) of I in a mixture of 450 ml. of glacial acetic acid, 150 ml. of acetic anhydride, and 18 ml. of concentrated sulfuric acid was added 120 g. (1.2 mole) of chromic acid over 55 min. while maintaining the temperature at 15°C. The reaction mixture was stirred for an additional 10 min., poured onto ice and stirred vigorously for about 30 min. After filtering, the residue was washed thoroughly with water and air-dried to produce 12.3 g. (96% yield) of colorless, crude product; m.p. 258–264°C. (uncorr.). The crude material was dissolved in acetone, treated with activated charcoal, filtered, and reprecipitated with water. The precipitate was separated, dried, and dissolved in 250 ml. of ether. The insoluble material was removed by filtration and the ether solution was concentrated until crystals started to form. Then an equal volume of petroleum ether was added and 9.65 g. of white crystalline product was recovered, m.p. (uncorr.) 266–268°C. (lit.:[9] 250–257°C.).

ANAL. Calcd. for $C_{26}H_{20}O_4Si$: C, 73.56%; H, 4.75%; Si, 6.62%. Found: C, 73.57%; H, 4.76%; Si, 6.57%.

Bis(*p*-carbomethoxyphenyl)diphenylsilane (III). This compound was prepared by adding 4.25 g. (0.01 mole) of II in small portions to an ice-cooled yellow solution of excess diazomethane in ether. The pure dicarboxylic acid II, which was not easily soluble in ether, dissolved readily in the diazomethane solution and bubbles of nitrogen gas evolved immediately. This indicated that the esterification reaction was very rapid. The yellow ether solution was evaporated to dryness under vacuum. The residue, m.p. (uncorr.) 168–169°C., was recrystallized from a mixture of methyl alcohol and ethyl acetate (9:1) to recover 4.1 g. (90% yield) of white crystalline III, m.p. (uncorr.) 169–170°C. (lit.:[9] 169–170°C.).

ANAL. Calcd. for $C_{28}H_{24}O_4Si$: C, 74.31%; H, 5.35%; Si, 6.21%. Found: C, 74.30%; H, 5.35%; Si, 5.70%.

Bis(*p*-carbopentachlorophenoxyphenyl)diphenylsilane (IV). To a solution of 10.64 g. (0.04 mole) of pentachlorophenol in 50 ml. of dry ethyl acetate was added 8.24 g. (0.04 mole) of dicyclohexylcarbodiimide in 50 ml. of the same solvent. After standing at room temperature for 10 min., 4.24 g. (0.01 mole) of dicarboxylic acid II suspended in 100 ml. of ethyl acetate was added to the clear solution. The acid dissolved immediately and, after a few seconds, crystal formation was observed. The reaction mixture was allowed to stand at room temperature for 15 hr., and then refluxed for 2.5 hr. The mixture was concentrated under vacuum to a volume of about 100 ml. and cooled in an ice bath for several hours. The crystalline mixture was separated by filtration and washed in sequence with ice-cold ethyl acetate, acetone, and ether to remove unreacted materials. Then the 12.5 g. of residue was washed with 300 ml. of benzene to dissolve the diester IV and leave 4.1 g. of insoluble dicyclohexylurea, m.p. (uncorr.) 228–230°C. The benzene solution was concentrated under vacuum to a volume of 50 ml. diluted, with 250 ml. of dry acetone, and cooled in an ice bath for 1 hr. to give 6.5 g. of IV, m.p. (uncorr.) 269–271°C. An additional 1 g. of IV, m.p. (uncorr.) 264–266°C. was recovered from the mother liquor to produce a total yield of 81.4%. A sample for analysis was recrystallized from benzene and ethyl acetate (1:10) and dried in vacuum over boiling water, m.p. (uncorr.) 269–271°C.

ANAL. Calcd. for $C_{36}H_{18}Cl_{10}O_4Si$: C, 49.55%; H, 1.97%; Cl, 38.49%; Si, 3.05%. Found: C, 49.94%; H, 1.95%; Cl, 38.14%; Si, 2.91%.

When the molar ratio of dicarboxylic acid IV, pentachlorophenol, and dicyclohexylcarbodiimide was 1:2:2, the *N*,*N*′-dicyclohexylurea derivative of the pentachlorophenyl half-ester, $C_6Cl_5OOC_6H_4Si(C_6H_5)_2C_6H_4CON(C_6H_{11})CONHC_6H_{11}$, m.p. (uncorr.) 142–145°C. was isolated in 39% yield. The infrared spectrum of the half-ester was consistent with its structure.

ANAL. Calcd. for $C_{45}H_{41}Cl_5N_2O_4Si$: C, 61.48%; H, 4.7%; N, 3.18%; Cl, 20.16%; Si, 3.19%. Found: C, 61.54%; H, 4.81%; N, 3.04%; Cl, 19.32%: Si, 3.28%.

Bis-*p*-carbo-(*p*-nitrophenoxy)phenyldiphenylsilane (V). A solution of 1.4 g. (0.01 mole) of *p*-nitrophenol and 2.06 g. (0.01 mole) dicyclohexylcarbodiimide dissolved in 50 ml. of dry ethyl acetate was allowed to stand for 10 min. Then, 1.06 g. (0.0025 mole) of dicarboxylic acid II was added in several portions. After a few minutes, crystals started to separate. The reaction mixture remained at room temperature for 15 hr., was refluxed for 3 hr., and cooled in an ice bath to give 1.13 g. of crystals that were separated by filtration. The crystals were washed with ice-cold ethyl acetate and then ether. The residue was triturated with hot benzene to leave 647 mg. (57.8% yield) of dicyclohexylurea, m.p. (uncorr.) 228–230°C. The benzene solution was evaporated to dryness and the residue was washed with methyl alcohol to yield 363 mg. of the dinitrophenyl ester V, m.p. (uncorr.) 290–292°C. The mother liquor from the original reaction mixture was concentrated to an oily crystalline paste that was washed with ether and then with hot methyl alcohol to give an additional 325 mg. of crude diester V (total yield 42%), m.p. (uncorr.) 291–292°C. after recrystallization from a 1:10 mixture of benzene and methyl alcohol.

ANAL. Calcd. for $C_{38}H_{26}N_2O_8Si$: C, 68.45%; H, 3.94%; N, 4.20%; Si, 4.21%. Found: C, 68.72%; H, 3.88%; N, 4.56%; Si, 4.48%.

Bis(*p*-chlorocarbonylphenyl)diphenylsilane (VI). A mixture of 6.36 g. (0.015 mole) of dicarboxylic acid II and 120 ml. of thionyl chloride was refluxed for 40 min. The resulting clear solution was concentrated to dryness and the residue recrystallized from ligroin (b.p. 90–120°C.) to produce 6.3 g. (91% yield) of VI, m.p. (uncorr.) 183–185°C.

ANAL. Calcd. for $C_{26}H_{18}Cl_2O_2Si$: C, 67.68%; H, 3.93%; Cl, 15.37%; Si, 6.09%. Found: C, 67.62%; H, 4.44%; Cl, 15.07%; Si, 5.97%.

A dianilide derivative of VI was prepared by adding a solution of 0.12 g. (0.26 mmole) of VI in 7 ml. of dry benzene to 0.28 g. (3 mmole) of aniline dissolved in 5 ml. of the same solvent. Crystals separated immediately. The reaction mixture was stirred at room temperature for 40 minutes and filtered. The residue was washed thoroughly with benzene, petroleum ether, and finally with water to remove aniline hydrochloride. After drying, 0.19 g. (93% yield) of bis(*p*-carboanilidophenyl)diphenylsilane, m.p. (uncorr.) 268–270°C. was recovered. The derivative was recrystallized from acetone, m.p. (uncorr.) 269–271°C. The infrared spectrum was consistent with the structure of the product.

ANAL. Calcd. for $C_{38}H_{30}N_2O_2Si$: C, 79.41%; H, 5.26%; N, 4.88%; Si, 4.89%. Found: C, 79.15%; H, 5.18%; N, 5.08%; Si, 4.91%.

Synthesis of Silicon-Containing Polymers

Polyamide From *m*-Phenylenediamine (VII). To an ice-cooled solution of 2.306 g. (0.005 mole) of VI in 75 ml. of methylene chloride was added 0.54 g. (0.005 mole) of *m*-phenylenediamine and 0.53 g. (0.005 mole) of sodium carbonate in 50 ml. of water. The reaction mixture was cooled in an ice bath and stirred for 30 min. The precipitate that formed was separated by filtration and washed with water, acetone, and methylene chloride, and then several times in sequence with water and acetone to produce 2.1 g. (84.6% yield) of white polymer VII having an inherent viscosity of 0.95 (0.2% solution). The polymer was purified by dissolving it in dimethylformamide, filtering the solution, and pouring the filtrate into a large volume of water. The resultant precipitate was filtered under suction, washed with acetone and petroleum ether, and dried under vacuum over boiling water for several hours.

ANAL. Calcd. for $(C_{32}H_{24}N_2O_2Si \cdot H_2O)_n$: C, 74.68%; H, 5.09%; N, 5.44%; Si, 5.45%. Found: C, 74.64%; H, 5.04%; N, 6.28%; Si, 5.59%.

A solution of 0.914 g. (1.97 mmole) of VI in 25 ml. of chloroform was added to a mixture of 0.214 g. (1.97 mmole) of *m*-phenylenediamine, 10 ml. of chloroform, and 0.533 ml. (3.94 mmole) of triethylamine. The mixture was stirred vigorously until a heavy precipitate formed. It was then allowed to warm to room temperature and stirring was continued for 1 hr. After filtration, the precipitate was washed and dried as before to give 0.73 g. of polymer VII (74% yield) with inherent viscosity of 0.69 (0.5% solution).

ANAL. Calcd. for $(C_{32}H_{24}N_2O_2Si \cdot H_2O)_n$: C, 74.68%; H, 5.09%; N, 5.44%; Si, 5.45%. Found: C, 74.61%; H, 4.96%; N, 6.11%; Si, 5.72%.

Equimolar quantities of VI and *m*-phenylenediamine were interacted in dimethylacetamide for 0.5 hr. at −20 to 0°C. under nitrogen. After warming to room temperature and stirring for several hours, the mixture was poured into water. The precipitate was separated by filtration, washed with water and acetone, and dried to produce a 72% yield of silicon-containing polyamide VII having an inherent viscosity of 0.22 (0.5% solution).

Polyamide From *p*-Phenylenediamine (VIII). The procedures for the reaction of VI and *p*-phenylenediamine in different solvents was essentially the same as that described above.

The reaction in methylene chloride gave 72% yield of polymer VIII with inherent viscosity of 1.86 (0.2% solution). The polymer was dissolved in dimethyl acetamide, the solution was filtered, and the filtrate was poured into a threefold volume of water. The precipitate was filtered and dried under vacuum over boiling water for 8 hr.

ANAL. Calcd. for $(C_{32}H_{24}N_2O_2Si)_n$: C, 77.39%; H, 4.87%; N, 5.63%; Si, 5.66%. Found: C, 76.74%; H, 5.02%; N, 5.65%; Si, 5.76%.

An 88.5% yield of polymer VIII having an inherent viscosity of 0.78 (0.5% solution) was obtained when the reaction of VI and *p*-phenylenediamine was carried out in chloroform.

ANAL. Calcd. for $(C_{32}H_{24}N_2O_2Si \cdot H_2O)_n$: C, 74.68%; H, 5.09%; N, 5.44%; Si, 5.45%. Found: C, 74.58%; H, 4.95%; N, 6.05%; Si, 5.98%.

A 40% yield of polymer VIII with inherent viscosity of 0.26 (0.5% solution) was produced from reaction in dimethylacetamide.

Polyamide From Benzidine (IX). A mixture of 0.184 g. (1 mmole) of benzidine and 0.921 g. (1 mmole) of IV was refluxed in 20 ml. of *N*,*N*-diethylaniline for 52 hr. under a dry nitrogen atmosphere. After cooling to room temperature, 60 ml. of benzene was added to the semisolid reaction mixture. The insoluble fraction was separated by filtration and washed with benzene, ethyl acetate, and acetone to leave 0.37 g. (64.6% yield) of tan, solid polymer IX having an inherent viscosity of 0.20 (0.2% solution).

ANAL. Calcd. for $(C_{38}H_{28}N_2O_2Si)_n$: C, 79.69%; H, 4.93%; N, 4.89%; Si, 4.90%. Found: C, 78.17%; H, 5.29%; N, 5.25%; Si, 4.91%; Cl (from chain ends), 0.89%.

The reaction of benzidine and V in *N*,*N*-diethylaniline for 11 hr. under similar conditions gave an 18.8% yield of polymer IX with inherent viscosity of 0.38 (0.2% solution).

Polybenzimidazole (X). In an atmosphere of nitrogen a mixture of 1.842 g. (0.002 mole) of IV and 0.428 g. (0.002 mole) of 3,3′-diaminobenzidine suspended in 50 ml. of *N*,*N*-dimethylaniline was stirred vigorously for 15 min. at room temperature, and then heated in a Wood's metal bath. At 130°C. a clear solution was obtained. After refluxing for $^1/_2$ hr. (b.p., 197°C.), a yellow precipitate began to form. Refluxing was continued for another 3 hr. and the precipitate was separated by filtration, washed successively with *N*,*N*-dimethylaniline, benzene, acetone, and ethyl acetate, and dried under vacuum to give 0.98 g. (86.5% yield) of light orange polymer X having an inherent viscosity of 0.57 (0.5% solution).

ANAL. Calcd. for $(C_{38}H_{26}N_4Si)_n$: C, 80.53%; H, 4.62%; N, 9.89%; Si, 4.96%. Found: C, 77.07%; H, 4.76%; N, 9.73%; Si, 4.87%; Cl (from chain ends), 1.54%.

The inherent viscosity of the above product was increased substantially by refluxing a 0.30 g. sample in mixture with 30 ml. of tetralin under a nitrogen atmosphere for 37 hr. After filtration, the insoluble fraction was washed with benzene, ethyl acetate, and petroleum ether to produce an orange polymer with inherent viscosity of 1.23 (0.2% solution). The infrared spectrum of the product was identical to that obtained from the lower molecular weight polymer X.

ANAL. Calcd. for $(C_{38}H_{26}N_4Si)_n$: C, 80.53%; H, 4.62%; N, 9.89%; Si, 4.96%. Found: C, 78.66%; H, 4.82%; N, 9.45%; Si, 4.81%; Cl (from chain ends), 0.14%.

When polymer X with inherent viscosity of 0.57 (0.5% solution) was heated for 4 hr. at 340–350°C./1 mm. Hg pressure a tan product was obtained.

ANAL. Calcd. for $(C_{38}H_{26}N_4Si)_n$: C, 80.53%; H, 4.62%; N, 9.89% Si, 4.96%. Found: C, 78.46%; H, 4.96%; N, 9.89%; Si, 6.01%; Cl (from chain ends), 0.15%.

After dissolving the tan product in dimethylacetamide, the solution was filtered to remove about 30% by weight of insoluble fraction. Acetone was added to the filtrate to precipitate polymer X with an inherent viscosity of 0.56 (0.25% solution).

Polyhydrazide (XI). To a stirred ice-cooled solution of 1.384 g. (3 mmole) of acid chloride VI in 75 ml. of methylene chloride was added 0.39 g. (3 mmole) of hydrazine sulfate dissolved in 120 ml. of 0.1*N* potassium hydroxide. The mixture in an ice bath was stirred for 1 hr. and then allowed to remain for 1 hr. at room temperature. The precipitate thus produced was separated by filtration and washed with acetone, methyl alcohol, and benzene, and several times in sequence with acetone and water to give 1.18 g. (93.6% yield) of polymer XI with inherent viscosity of 0.56 (0.5% solution).

ANAL. Calcd. for $(C_{26}H_{20}N_2O_2Si)_n$: C, 74.26%; H, 4.79%; N, 6.66%; Si, 6.68%. Found: C, 74.31%; H, 4.42%; N, 6.80%; Si, 6.67%.

Polyoxadiazole (XII). A 0.5 g. sample of silicone-containing polyhydrazide XI was very well pulverized and heated at 1 mm. pressure within 1 hr. to 170°C. and maintained at that temperature for 1 hr. The temperature was raised to 240°C. and kept there for 40 min. and then elevated to 285°C. and maintained there for 35 min. The resulting beige-colored cake was cooled to room temperature, pulverized, and heated under vacuum for 4 hr. at 285°C. The product was washed with acetone, dissolved in 25 ml. of chloroform, and poured into 250 ml. of petroleum ether. The white precipitate was worked up in the usual manner to give 0.31 g. (64.6% yield) of silicon-containing polymer XII having an inherent viscosity of 0.23 (0.25% solution).

ANAL. Calcd. for $(C_{26}H_{18}N_2OSi)_n$: C, 77.58%; H, 4.50%; N, 6.96%; Si, 6.98%. Found: C, 77.26%; H, 4.54%; N, 6.61%; Si, 7.53%.

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Thermal Stability of Silicon-Containing Amide Benzimidazole, Hydrazide, and Oxadiazole Polymers

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Synopsis

Studies were undertaken to ascertain the thermal stability of several types of silicon-containing polymers. Results of thermal analysis investigations indicate that all of the polymers are unusually heat-resistant when heated in air at elevated temperatures. Solution-cast films of the polymers on aluminum showed excellent flexibility and adhesion characteristics after being heated in air for 100 hr. at 300°C. and then for 3.5 hr. at 400°C. Visual examination of the films after the heating sequence indicated that the silicon-containing polyamides and polybenzimidazole had darkened slightly, while the polyoxadiazole appeared to be unaffected in this respect. Infrared spectroscopy studies showed that all of the polymers underwent only very minor structural changes during the prolonged heating process.

INTRODUCTION

A previous paper[1] covering the synthesis and heat resistance of model compounds indicated that fully aromatic silicon-containing benzimidazole polymers based on such structures might be thermally stable and have useful properties. On this basis, studies were undertaken that led to the development of novel silicon-containing amide, benzimidazole, hydrazide, and oxadiazole polymers.[2] These polymers were found to be soluble in several organic solvents. Solution-cast films of the macromolecules generally were flexible and exhibited good adhesion to metal and glass surfaces. Similar amide,[3] benzimidazole,[4] and oxadiazole[5] polymers which do not contain a silicon atom in the repeating structures are reported to be insoluble in organic solvents and, therefore, are not very useful for preparing heat stable coatings and films.

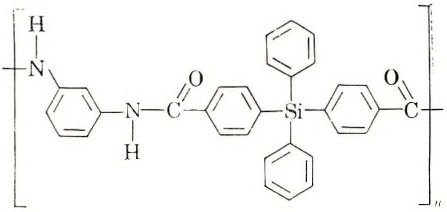
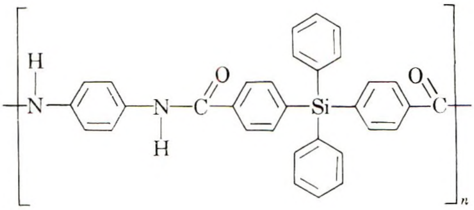
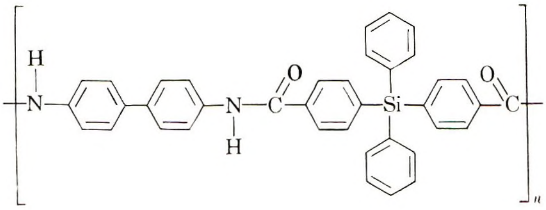
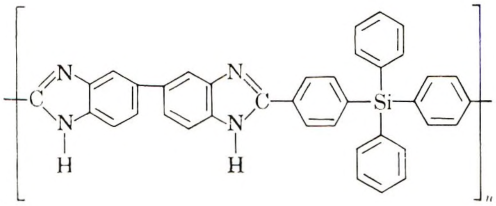
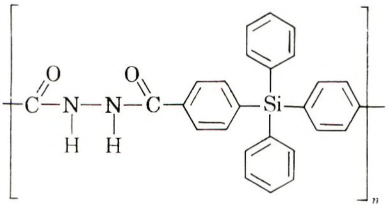
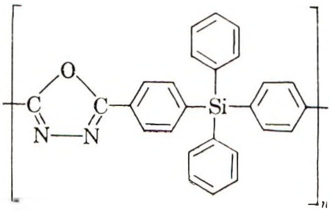
This paper presents the results of studies to determine the thermal resistance of the new silicon-containing polymers.

EXPERIMENTAL

Thermal Analysis

Thermogravimetric Analysis (TGA). The resistance of the polymers to thermal decomposition in air when heated at 3°C./min. was measured as described in a previous paper.[6]

TABLE I
Silicon-Containing Polymers

Designation	Recurring Structure
I	
II	
III	
IV	
V	
VI	

Differential Thermal Analysis (DTA). Approximately 3–5 mg. of polymer sample was sandwiched between alumina (Fisher Certified Reagent Grade, Catalogue No. A-591) in a manner similar to that reported in the literature.[7] The sample and another platinum container loaded with an equal volume of alumina were heated simultaneously in air at 5°C./min. in a Du Pont model 900 differential thermal analyzer equipped with a 1200°C. DTA cell. The furnace temperature and the temperature difference between the sample and the reference material were measured with a platinum–platinum + 13% rhodium differential thermocouple.

Isothermogravimetric Analysis (IGA). Weight changes of 35–60 mg. samples were recorded as described before[8] while being heated in air for several hours at 300 or 400°C. The sample was inserted into a furnace at room temperature and heated in about 1 hr. to the desired degree of heat.

Solution-cast films on aluminum and sodium chloride windows for infrared absorption analysis were heated at 300 or 400°C. in a Type 1400 Thermolyne electric furnace, Model F-A 1410M. Periodically, the samples were removed from the furnace and cooled to room temperature in a desiccator. The aluminum-coated specimens were visually inspected, and infrared spectra were obtained from the films on the sodium chloride crystals.

Infrared Spectrophotometry

Infrared absorption measurements over the 2.5–15.0 μ range were obtained from the solution-cast films on sodium chloride crystals. The spectra were recorded with a Perkin-Elmer model 337 grating spectrophotometer.

Materials

The recurring structures of the silicon-containing polymers that were examined in this study are presented in Table I.

RESULTS

Figures 1–3 present the TGA thermograms of the silicon-containing polymers. These data generally indicate that all of the polymers possess good resistance to decomposition when heated in air to about 400–450°C. Below this temperature range the heat stability of amide polymer I, high molecular weight benzimidazole IV, and oxadiazole VI appear to be about equal. Polymers II, III, and V seem to be somewhat less resistant. The weight losses up to about 450°C. may have been produced as a result of volatilization of occluded water or because of condensation reactions. All of the polymers appear to undergo radical thermal degradation at higher temperatures.

Figure 1 compares the thermograms from the silicon-containing polyamides. Results show that the polymer derived from *m*-phenylenediamine is somewhat more heat-resistant than the product prepared from the *para* isomer. The relative order of thermal stability of these polymers parallels the results obtained with aromatic amides without silicon atoms[3] and related model compounds.[1] Below 570°C., the polyamide synthesized from benzidine is slightly less heat stable than those derived from phenylene-

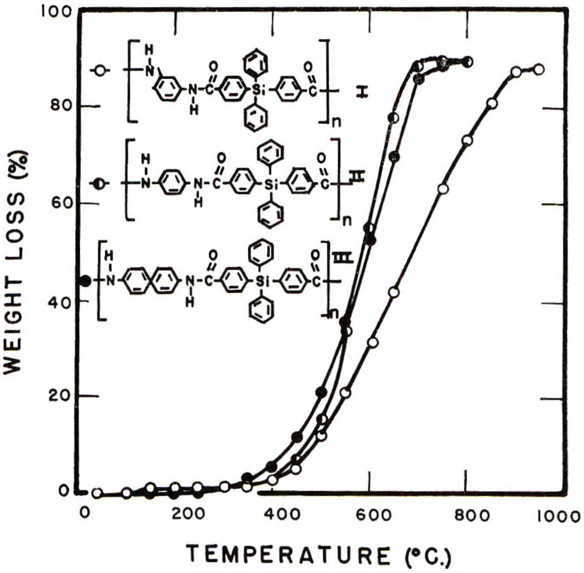


Fig. 1. TGA thermograms of amide polymers: (○) I; (◐) II; (●) III.

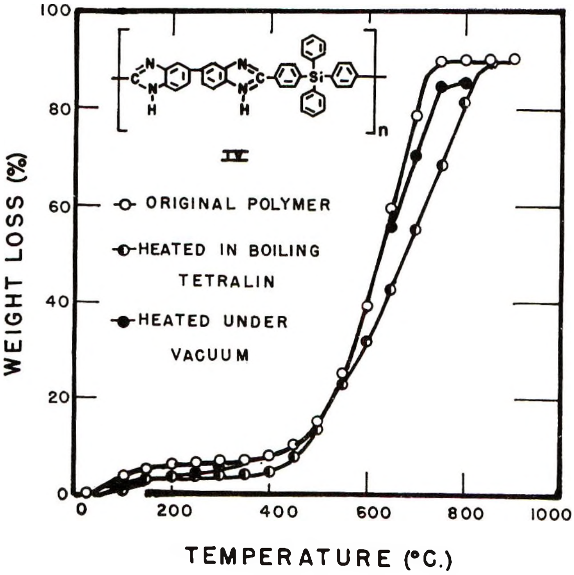


Fig. 2. TGA thermograms of benzimidazole polymer IV; (○) original polymer; (◐) heated in boiling tetralin; (●) heated under vacuum.

diamines. This is contrary to what would be expected from the general conclusions of studies of the relative heat resistance of aromatic acid amides.[3]

The thermograms from specimens of polybenzimidazole IV are shown in Figure 2. All of the samples were obtained originally from a polymerization reaction in boiling *N,N*-dimethylaniline, b.p. 194°C. A portion of the polymer was then treated further by boiling in tetralin, b.p. 207°C., for 37 hr. to increase its inherent viscosity from 0.57 to 1.23. Another sample of the original polymer was heated under vacuum for 4 hr. at 340–350°C. to produce an insoluble fraction (30% by weight) and a soluble portion having an inherent viscosity of 0.56. The thermogram was obtained from the polymer before it was separated into two parts by solvent fractionation.

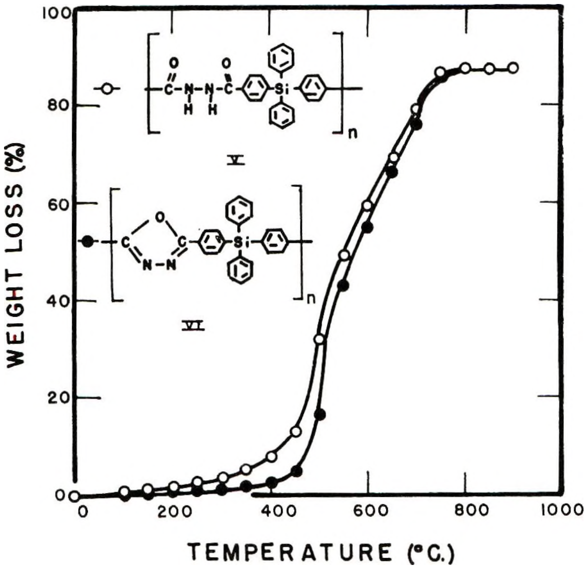


Fig. 3. TGA thermograms of hydrazide and oxadiazole polymers: (○) V; (●) VI.

The thermograms show that at temperatures up to about 400°C., the sample prepared by heating under vacuum at 340–350°C. generally lost less weight than the other polymer samples synthesized at lower temperatures. Results also indicate that the higher molecular weight polymer is somewhat more heat stable than the lower molecular weight specimens.

Figure 3 presents the TGA thermograms obtained for polyhydrazide V and polyoxadiazole VI. These data indicate that VI is slightly more heat-resistant than V. The oxadiazole polymer exhibited a weight loss of only 4.6% when heated to 450°C. The 0.6% weight loss observed up to 100°C. was probably due to volatilization of adsorbed water.[9] It is interesting to observe that the shapes of the thermograms at temperatures above 500°C. are very much alike. This can be explained by the fact that V is a precursor of VI.

The results of DTA studies are given in Figures 4–6. The absence of endotherms indicates that the polymers are not fusible below temperatures at which they are decomposed. The exothermic peaks and troughs correlate very well with the temperatures at which TGA data indicate the oc-

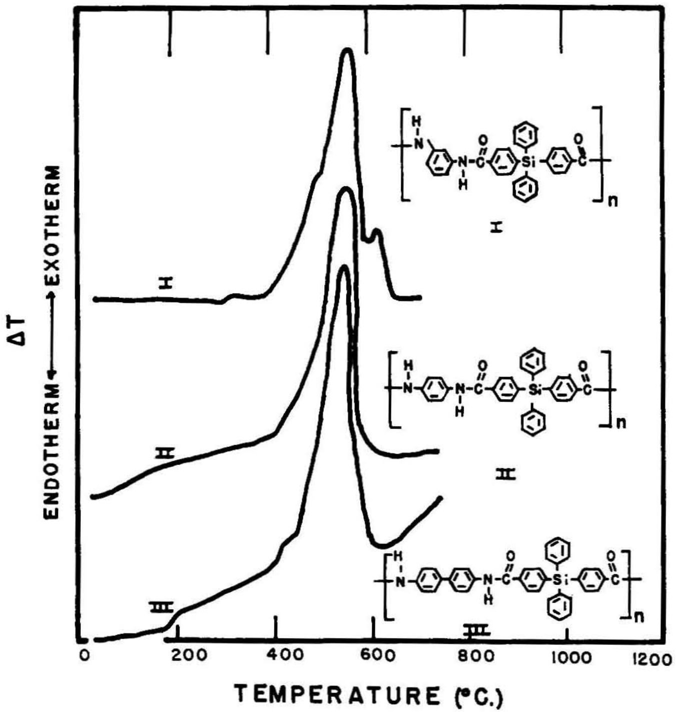


Fig. 4. DTA thermograms of amide polymers I, II, and III.

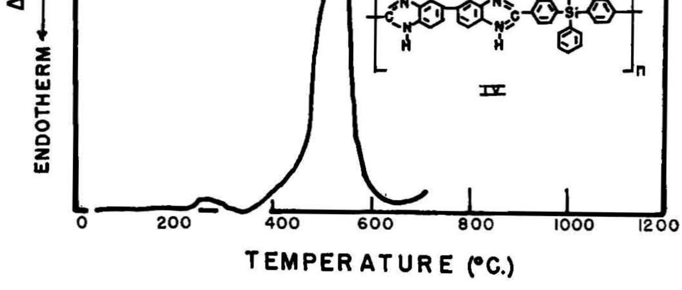


Fig. 5. DTA thermogram of benzimidazole polymer IV.

currence of maximum or minimum rates of weight loss. All of the thermograms contain a strong exotherm that reaches a peak in the region of 545–560°C. Since the diphenylsilarylene group is the only structure that is common to the different types of silicon-containing polymers, it seems reasonable to assume that this exothermic peak is connected with the thermooxidative decomposition of this unit. Brown and co-workers,[7] in a study of other silicon-containing products, reported that triphenyl-*p*-biphenylsilane exhibited a strong DTA exothermic peak in this temperature region.

The thermograms of the polyamides are compared in Figure 4. At temperatures below about 365°C. the thermograms of the polymers show weak exothermic changes that may be due to condensation reactions.

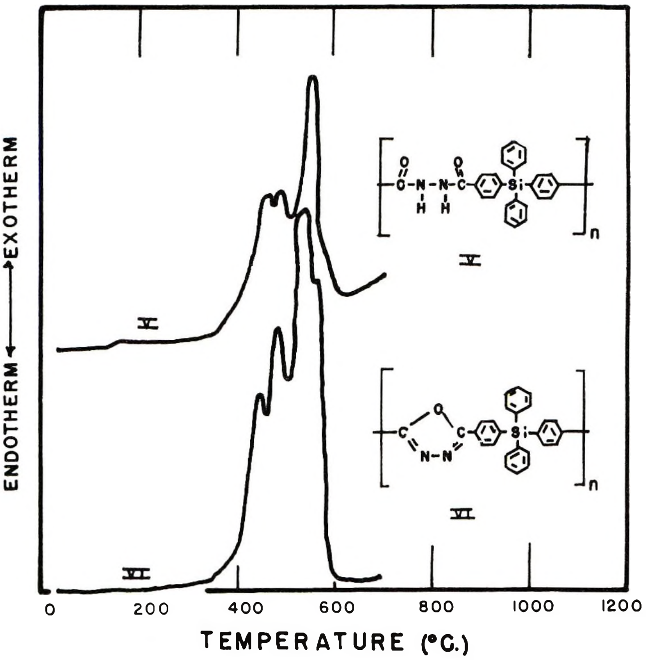


Fig. 6. DTA thermograms of hydrazide and oxadiazole polymers V and VI.

These data also indicate that the onset of the large exothermic change shown by the polyamide derived from benzidine occurred at a slightly higher temperature than that exhibited by the polymers prepared from the *meta* and *para* isomers of phenylenediamine. On this basis, it would seem that polyamide III is somewhat more heat-stable than polymers I and II. This agrees with previous studies,[3] which indicated that polyamides with biphenylene groups were more resistant to thermal decomposition than similar products with phenylene units. TGA data, however, showed that the weight loss from the benzidine-derived polyamide was slightly higher at most temperatures than that from polymers I and II. Additional information would be required to explain the difference in the relative behavior

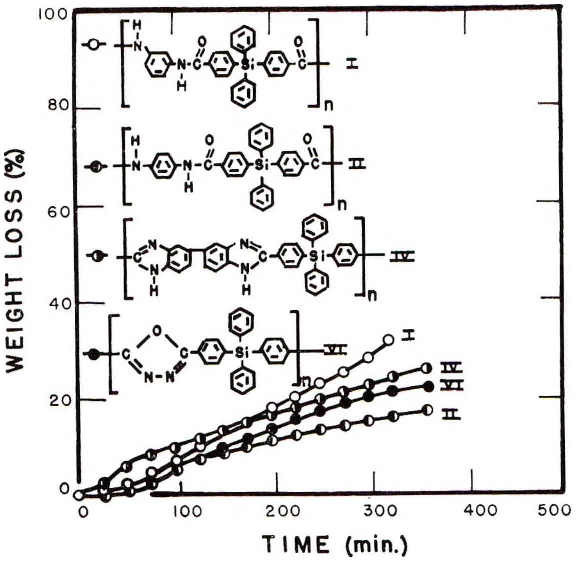


Fig. 7. Isothermograms of polymers at 400°C.; (○) I; (◐) II; (◑) IV; (●) VI.

of these products when examined under experimental conditions of TGA and DTA.

Figure 5 presents the DTA thermogram obtained from the benzimidazole polymer IV. As in the case of the polyamides, the relatively weak exotherm in the range of about 215–320°C. was probably the result of the condensation of chain ends. The stronger exothermic change beginning at about 320°C. was evidently due to the start of thermal oxidative decomposition of the polymer. This is consistent with results obtained from TGA studies which showed that weight losses started to accelerate in this temperature range.

Results of DTA studies of polyhydrazide V and polyoxadiazole VI are presented in Figure 6. The thermogram of polymer V shows a weak exotherm at about 175°C. which is absent in that from polyoxadiazole VI. It is presumed that this exotherm was produced because of a cyclodehydration reaction that resulted in the formation of oxadiazole rings.[5] The thermograms of V and VI then showed no change from the base line until about 350°C., when a series of exotherms began which peak at approximately 450, 500, and 550°C. Since it was previously assumed that the latter peak was associated with the diphenylsilarylene unit of the molecule, then it seems reasonable to consider that the other maxima were produced as a result of the degradation of oxadiazole rings. Studies of polyphenylene-1,3,4-oxadiazole indicated that at 460–560°C. the polymer degraded thermally mainly by nitrogen elimination and to a lesser extent by the formation of benzonitrile and phenyl isocyanate.[10]

After being exposed in air for 6 hr. at 300°C., the silicon-containing polyamides I, II, and III showed weight losses of only 2.0, 0.7, and 4.0%, respectively. The infrared spectra of films cast on sodium chloride crystals showed no changes after heating for an equivalent time period in a muffle furnace at 300°C. This suggests that the observed weight losses may have been due to the volatilization of adsorbed water or condensation products produced from the reaction of chain ends.

Except for the development of a very weak absorption band at 4.48 μ in the spectrum of polymer II, no changes were observed in the spectra of the polyamide films on sodium chloride after 50 hr. at 300°C. The spectra of polyamides I and III exhibited a similar weak vibration mode after 100 hours at this temperature. Films of the polyamides cast on aluminum and heated in air for 100 hr. at 300°C. exhibited excellent adhesion to the substrate when flexed manually, and were slightly darkened.

Polymers IV, V, and VI, when heated in air for about 6 hr. at 300°C., showed weight losses of 6.1, 5.4, and 0.7%, respectively. During the initial 2 hr. polybenzimidazole IV and polyhydrazide V very rapidly underwent weight losses of about 5.4 and 4.7%, respectively, and then the rate of weight loss declined appreciably. During this time period, polyoxadiazole VI showed no loss of weight. It is believed that within the first 2 hr. the weight loss shown by polymer IV was due to the volatilization of adsorbed water, trapped high-boiling solvent, and some endgroup reaction products.[4] Cyclodehydration of polyhydrazide V to form polymer VI would account for 4.3 of the 4.7% of weight loss observed during the initial 2 hr. Thereafter, the very small weight decreases shown by all of the polymers may have been due to additional condensation reactions. The infrared spectra of films on sodium chloride crystals that were heated for 6 hr. in air were identical to the spectra of the original polymers. The spectra of polymers IV, V, and VI exhibited no change until the materials were heated in air for 100 hr. at 300°C. when, as in the case of the polyamides, a small absorption mode appeared at 4.48 μ.

Figure 7 shows the weight decreases of polymers I, II, IV, and VI when heated in air for about 6 hr. at 400°C. These data indicate that the polymers lost more weight at 400°C. than at 300°C. This suggests that these products might have undergone some decomposition at the higher temperature. The infrared spectra of films on sodium chloride crystals that were heated for 100 hr. at 300°C. and then for 3.5 hr. at 400°C. showed a slight increase in the intensity of the 4.48 μ absorption mode. Otherwise, the spectra appeared to be identical to that obtained after heating the polymers for 100 hr. at 300°C. Films of the polymers cast on aluminum exhibited excellent flexibility and adhesion properties after being heated for 100 hr. at 300°C. and then for 3.5 hr. at 400°C. Polyoxadiazole VI showed no change of color after the heat treatment while polyamides I and II and polybenzimidazole IV appeared somewhat darker.

DISCUSSION

These thermoanalysis studies indicate that all of the silicon-containing polymers are remarkably stable when heated in air to about 400°C. After being exposed for 100 hr. in air at 300°C., infrared spectra of the residues showed that the structures of the polymers were essentially unchanged except for the appearance of a new, but very weak, absorption mode at 4.48 μ. This may be ascribed to the presence in the molecules of minute amounts of isocyanate (4.39–4.52 μ) or nitrile (4.46–4.50 μ) groups.[11]

From the literature,[12] it might be inferred that the 4.48 μ band appearing in the residues from the heated specimens of the polyamides and the polybenzimidazole was due to the formation of extremely small amounts of nitrile rather than isocyanate groups. Studies reported by Cotter and Knight[10] suggest that the very weak 4.48 μ band in the infrared spectra from the heated polyhydrazide and polyoxadiazole may be associated with the production of extremely small quantities of isocyanate and nitrile structures. It is not yet certain whether the formation of such linkages are the result of reactions of the terminal groups or recurring structures of the molecular chain.

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The opinions or assertions contained in this paper are the private ones of the authors and are not to be construed as official or reflecting the views of the Naval Service at large.

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Thermal Reactions of Polyacrylonitrile

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Synopsis

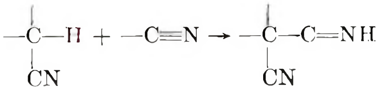
The exothermic process which occurs on heating polyacrylonitrile above 200°C. is studied with a differential scanning calorimeter and by following volatiles production. The process is associated with coloration of the polymer and the production of ammonia. It is not due to chain scission degradation, which occurs in this temperature range and also produces volatiles.

INTRODUCTION

Since the original study of Houtz,[1] the thermal reactions of polyacrylonitrile have been studied in detail[2–8] but there still remain considerable differences in reported details. The thermal reactions can be divided in two by temperature: a low-temperature reaction at 100–200°C., in which crosslinking and coloration proceed with the evolution of little or no volatiles; a high-temperature reaction at above 240°C., in which decomposition occurs with the evolution of volatiles and the production of a thermally stable residue, the extent of volatilization and stabilization of the residue increasing with temperature.

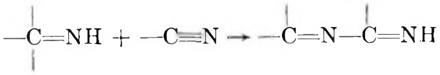
The low-temperature coloration has been interpreted as a polymerization of the cyanide groups. This mechanism was substantiated by initiation studies and infrared analysis of the colored residues from homopolymers and copolymers of acrylonitrile and methacrylonitrile[6,7] as shown in eqs. (1) and (2):

Initiation:



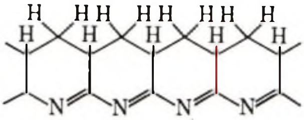
$$-\underset{\mathrm{CN}}{\overset{|}{\mathrm{C}}}-\mathrm{H} + -\mathrm{C}\equiv\mathrm{N} \rightarrow -\underset{\mathrm{CN}}{\overset{|}{\mathrm{C}}}-\mathrm{C}=\mathrm{NH} \qquad (1)$$

Propagation:



$$-\underset{|}{\overset{|}{\mathrm{C}}}=\mathrm{NH} + -\mathrm{C}\equiv\mathrm{N} \rightarrow -\overset{|}{\mathrm{C}}=\mathrm{N}-\overset{|}{\mathrm{C}}=\mathrm{NH} \qquad (2)$$

In general, the colored product is considered to consist of condensed tetrahydronaphthyridene rings, i.e.,



Such a structure is, however, idealized, as there is evidence of considerable irregularities in the propagation reaction, i.e., crosslinking.

The higher temperature decomposition reaction is generally attributed to stabilization of the colored product by the formation of condensed aromatic naphthyridene rings. The decomposition products reported, however, seem to vary with reaction conditions. Burlant and Parsons[2] found that ammonia was the major product at low temperatures, while Madorsky and Straus[5] and later Monahan[8] obtained little or no ammonia but isolated hydrogen cyanide, acrylonitrile, acetonitrile and other chain fragments (or their addition products).

Kennedy and Fontana[9] reported that polyacrylonitrile exhibited an exothermic process in the temperature range 250–325°C. More recently Thompson[10] has shown that this effect is molecular weight-dependent and accompanied with a substantial weight loss. This paper describes a study of the exothermic process in polyacrylonitrile and its copolymers with a differential scanning calorimeter, and considers it in terms of the coloration and decomposition reactions.

EXPERIMENTAL

The polymers and copolymers used were prepared as described previously when their coloration characteristics were compared.[6,7]

A differential scanning calorimeter, Perkin-Elmer-DSC I B, was used both isothermally and at a constant heating rate of 8°C./min. with 2–10 mg. samples encased under nitrogen in thin-walled aluminum pans.

RESULTS

Initial Degradation Studies

Polymer samples were treated in a dynamic molecular still under vacuum, at about 5°C./min., and the instantaneous pressure of volatiles developed on distillation from sample to a liquid nitrogen trap was measured on a Pirani gage.[6,7] The pressure–temperature profile is shown in Figure 1. Trace impurities adsorbed on the polymer were evolved just above the glass transition temperature otherwise no volatiles were detected until above 230°C. An initial maximum rate of evolution of volatiles was reached about 260°C., after which the rate rapidly dropped but later progressively increased again with temperature. The initial maximum rate of evolution of volatiles corresponded with that described in detail by Kennedy and Fontana.[9] Volatiles were not detected between 130 and 220°C., the temperature range in which coloration of the polymer proceeds at measureable rates.[6,7]

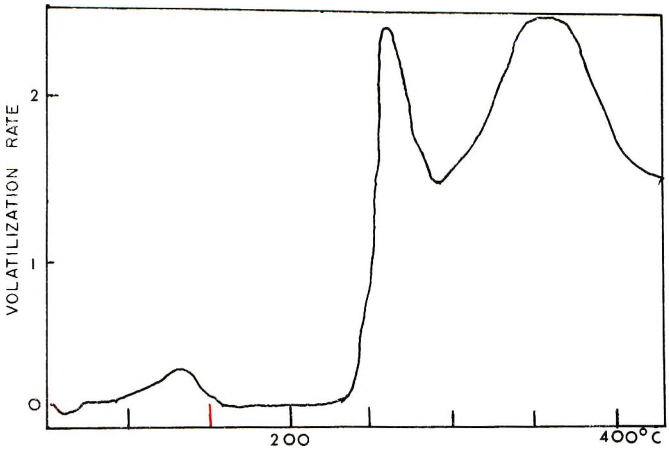


Fig. 1. TVA curve for polyacrylonitrile; heating rate 5°C./min.

The volatiles produced on degrading polymer up to 400°C. were condensed in a liquid nitrogen trap, or on the cooler walls of the pyrolysis vessel, and analyzed for convenience as four fractions: (I) a gaseous product which by infrared analysis contained ammonia and hydrogen cyanide; (II) a volatile, colorless liquid, molecular weight 80 ± 5, containing amine (3350 cm.$^{-1}$) saturated (2230 cm.$^{-1}$) and unsaturated cyanide (2180 cm.$^{-1}$) and double bonds (1640, 1625, and 960 cm.$^{-1}$) absorption bands in its infrared spectrum and having a nitrogen content of 26.2%; (III) a less volatile red liquid, molecular weight 160 ± 5, with an infrared spectrum similar to (II); and (IV) a black solid residue, completely insoluble in all solvents, containing no cyanide group but very strong amino (3350 cm.$^{-1}$), unsaturated bonds (1650–1550 cm.$^{-1}$), and aromatic ring (1360, 1280, 1250, 1150, 1070, 800, 790, 750, 680 cm.$^{-1}$) absorption bands in its infrared spectrum.

Liquids II and III corresponded with the volatile components listed by Madorsky and Straus:[5] acrylonitrile, vinyl acetonitrile, acetonitrile and other chain fragments (or their addition products). Liquid III analyzed by chemical composition, molecular weight, and infrared spectrum corresponded to acrylonitrile trimers.

ANAL. Calcd. for trimers: C, 67.5%; H, 6.25%; N, 26.25%; mol. wt. 159. Found: C, 67.3%; H, 6.3%; N, 26.2%; mol. wt. 160 ± 5.

Calorimetry

Polymer samples were analyzed on the DSC at a standard scanning rate of 8°C./min. and an exothermic process observed above 240°C. with a maximum in rate of heat evolution at 295°C. ($T_{\max}$, see Figure 2). This value was independent of sample size and reproducible to 2°C. The process was associated with the evolution of 5–6 kcal./mole. A less evident endothermic process which increased progressively with temperature accompanied the exothermic process and heat treating the sample above 290°C. for several minutes was sufficient to remove the exotherm leaving only the endotherm. Samples once heat-treated to remove the exotherm could not be further induced by heating or cooling cycles to reproduce it again. It is unlikely that the exotherm is associated with a phase transition.

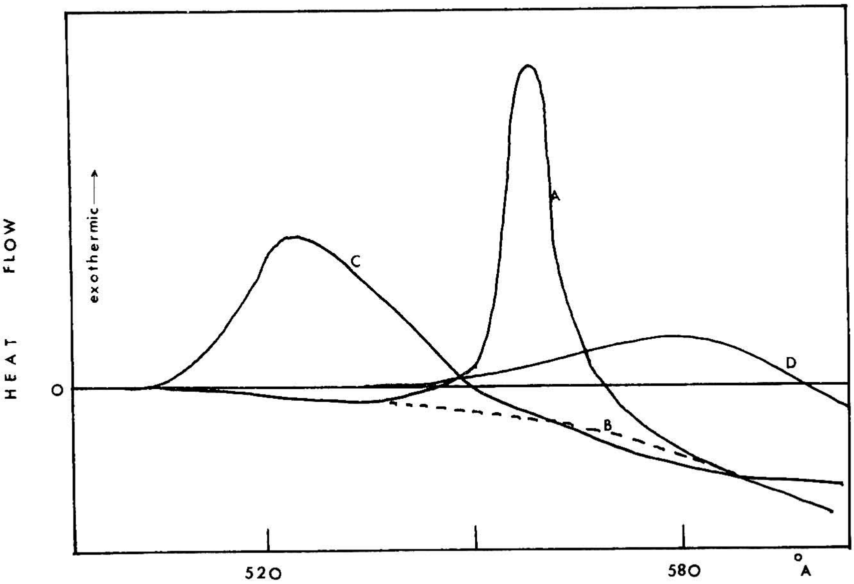


Fig. 2. DSC curves, heating rate 8°C./min.: (*A*) polyacrylonitrile; (*B*) heat-treated polyacrylonitrile; (*C*) 50% methacrylonitrile copolymer; (*D*) $7^1/_2$% methyl methacrylate copolymer.

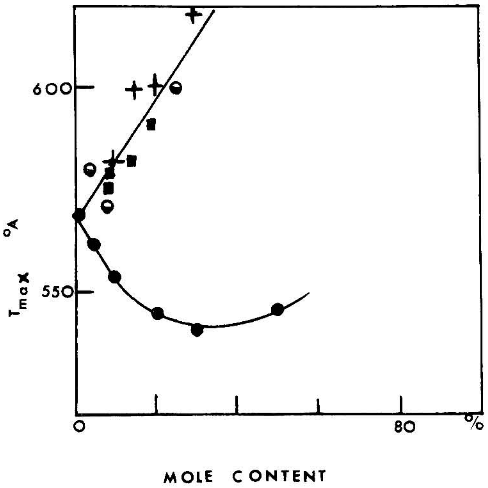


Fig. 3. T_{max} values of copolymers: (+) methyl vinyl ketone; (O) styrene; (■) methyl methacrylate; (●) methacrylonitrile.

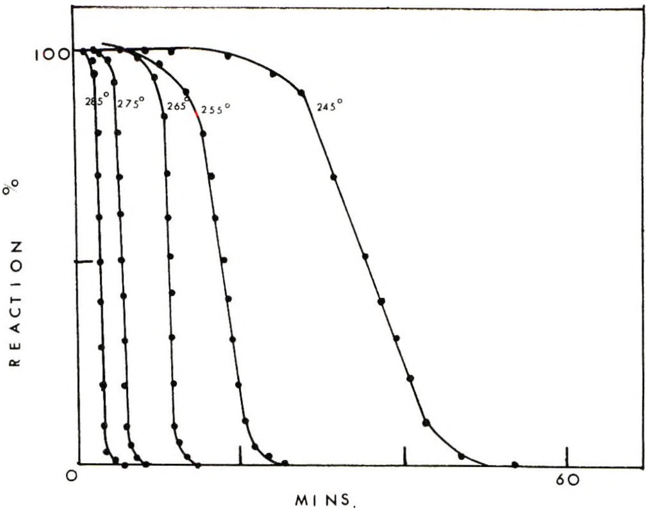


Fig. 4. Integrated Isothermal DSC curves.

In order to consider the nature of the endotherm further, copolymers of styrene, methyl methacrylate, and methyl vinyl ketone, rich in acrylonitrile, were also studied and found to exhibit an exotherm, the T_{max} value of which increased progressively (Fig. 3), but the intensity of which decreased with composition. Finally at 60–70% acrylonitrile content, the process was too diffuse to measure and considerably masked by the endothermic process. Methacrylonitrile copolymers, on the other hand, showed a progressive decrease in T_{max} value with increasing methacrylonitrile content. Polymethacrylonitrile and copolymers of less than 40% acrylonitrile, however, did not show an exotherm although the residues of the heat treatment were highly colored.

The T_{max} values observed, although reproducible, have little absolute significance, being determined by heating rate; the process could also be studied isothermally in the temperature range 230–270°C. These isotherms are shown integrated in Figure 4. The process is obviously autocatalytic with a pronounced induction period which is temperature-dependent and also independent of sample size.

The temperature range studied was limited by the sensitivity of the calorimeter, 1 mcal./sec.; since the process obviously proceeded at lower temperatures. Heat-treating the polymer sample at 200°C. for 30 hr. was sufficient to remove completely the exotherm at higher temperatures, while treatment for shorter periods reduced the induction period and the intensity of the exotherm.

During the exothermic process considerable decomposition of the sample occurred, with loss of weight, production of a condensate and coloration of the residue. However, most of the weight loss and production of condensate was associated with the endothermic process as they continued beyond the initial exothermic process. In the temperature range 230–270°C., the

TABLE I
Degradation Characteristics: Calorimetry

Temp., °C.	Induction period, min.	Wt. loss, %	Activation energy, kcal./mole
245	26	1.2	
255	13.5	3.0	30
265	10.5	7.0	
275	4.5	6.0	
285	2.5	—	

exothermic process was associated with a weight loss (extrapolated) of about 2–5% (Table I).

Volatile Evolution

The exothermic process occurred in the same temperature region in which volatile production was observed, and the characteristics of the evolution were studied in detail for comparison. For this purpose polymer samples were heat treated in thin-walled Pyrex tubes and the volatiles measured manometrically.[11] The rate characteristics of the evolution of volatiles were similar to those of the exothermic process (Fig. 5). Both processes occurred at similar rates, were autocatalytic, had similar apparent induction periods (measured by extrapolating the maximum rate to zero conversion), and their maximum rates exhibited the same temperature dependence, i.e., 30 kcal./mole (Table II).

TABLE II
Degradation Characteristics: Volatile Production

Temp., °C.	Induction period, min.	Volatiles, mole-%	Activation energy, kcal./mole
234	65	—	30
241	46	4.5	
247	24	7.0	
251	15	—	
283	3.0	10.0	

Volatiles and signs of decomposition were also detected by prolonged heating at 200°C. (after 30 hr.). The volatile production was accompanied with progressive coloration of the polymer residue, disappearance of the —CN absorption band, and appearance of N—H and unsaturated bond absorption bands in the infrared spectrum of the product.

The gaseous volatiles were expanded, then condensed with liquid nitrogen into a collector trap and analyzed by mass spectrometry as almost 90% ammonia with hydrogen, hydrogen cyanide, a compound of mass 54 (HCN dimer?), and traces of acrylonitrile and other residues. The volatile com-

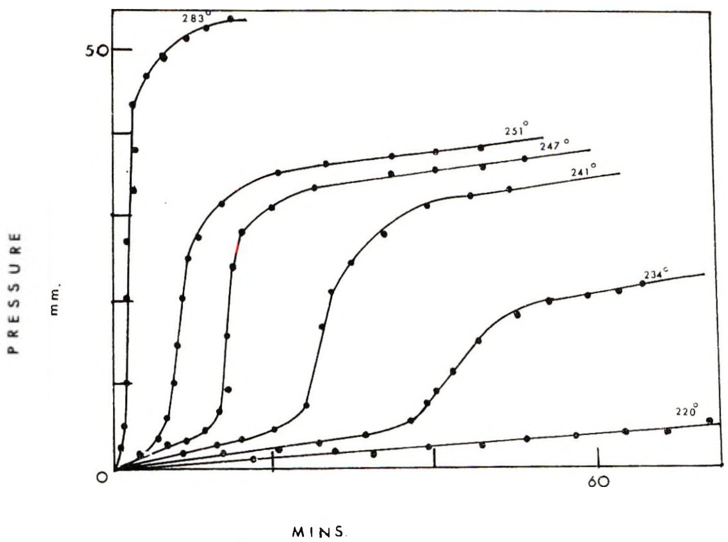


Fig. 5. Pressure–time curves of polyacrylonitrile.

position was found to be effectively constant with reaction extent except at the initial and final stages of the reaction (Table III). The method of analysis underestimated the amounts of hydrogen and ammonia present, since hydrogen was noncondensible in liquid nitrogen, and ammonia would be adsorbed to some extent in the mass spectrometer.[12] From the volume fraction of noncondensibles in the total volatile product the hydrogen content cannot be in error by more than 50%. However, at low reaction extents the absence of ammonia may also be attributable to adsorption. The volatile product of the reaction is clearly ammonia with some hydrogen cyanide, and the total yield of product increased progressively with temperature, i.e., 4–7 mole-% in the temperature range 230–290°C.

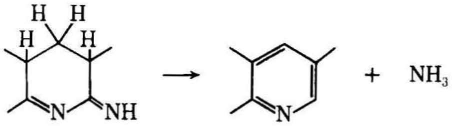
TABLE III
Degradation Characteristics: Volatile Analysis for Degradation at 230°C.

Collecting time, min.	Mole ratio				
	H_2	HCN	NH_3	$(HCN)_2$	Acrylonitrile
0–30	1.0	0.8	0.0	0.1	0.1
0–60	1.0	1.9	15.5	0.5	1.0
60–90	1.0	5.0	73.2	1.0	1.0
90–180	1.0	5.5	84.5	7.0	1.6
180–720	1.0	1.5	15.8	7.2	1.5

The evolution of ammonia from the coloring product has similar characteristics to that of the exothermic process. It is accompanied with decomposition and production of chain fragments which has been associated with the endothermic process.

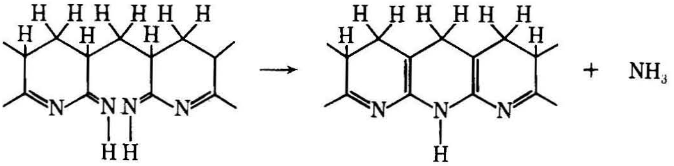
DISCUSSION

The increase in $T_{\max}$ value with copolymer composition shows that the exothermic process cannot be explained in terms of a recrystallization process, although the isotherms are similar in characteristics to an Avrami process.[13] It must accordingly be attributed to an autocatalytic reaction, and a study of the volatile suggests that the process is associated with the elimination of ammonia and hydrogen cyanide. Both processes are associated with the coloration reaction, being reduced by the insertion of inert comonomer units, i.e., styrene and methyl methacrylate, while methacrylonitrile units which accelerate the color reaction and maintain the length of conjugated sequences[6] facilitate both processes. The process is also associated with acrylonitrile units, as methacrylonitrile polymers and copolymers, although coloring, do not exhibit an exotherm. These points can be reconciled if the ammonia production is exothermic and is produced either in aromatization of the propagating color unit [eq. (3)]:



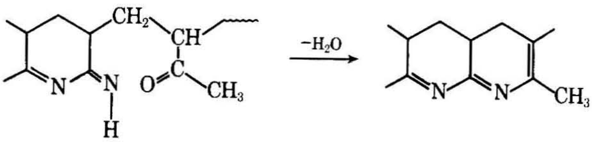
(3)

or the chance interaction of two propagating units [eq. (4)]:



(4)

This mechanism involves the tertiary hydrogen atom of acrylonitrile units and would be prevented by the methyl group of methacrylonitrile units. It is also associated with the color-producing reaction. Methyl vinyl ketone units also facilitate the coloration reaction of polyacrylonitrile[7] by maintaining the conjugated sequences [eq. (5)]:



(5)

In doing so, however, it reduces the imine group concentration and so the ammonia-producing reaction. The elimination of water from poly(methyl vinyl ketone), uncatalyzed and catalyzed with amine groups, was not found to be exothermic.

The elimination of ammonia by either of the above mechanisms depends on the prior production of a color producing structure and as such would be expected to exhibit the observed induction period. Prior treatment at

200°C. encouraged this formation and reduced the induction periods of the exotherms at higher temperatures.

The exotherms were accompanied with endotherms, particularly at the higher temperatures, and both were associated with the evolution of volatile chain fragments. The ammonia content of these volatiles exhibited similar characteristics to that of the exothermic process, while the endothermic process, which can be measured separately, is associated with the evolution of hydrogen, hydrogen cyanide, monomer, and other chain fragments. Some ammonia may also be evolved in this process. TVA and DSC show that the endothermic process is more obvious at temperatures in excess of 300°C.

It would appear that at least three distinct thermal processes compete with one another in the thermal degradation of polyacrylonitrile: coloration, by cyanide group polymerization; ammonia evolution from the coloring structures; and chain scission and decomposition. The variation in reported details of the decomposition may thus reflect differences in the effective competition of these reactions.

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Quantitative Study on Hydrogen Bonding between Urethane Compound and Ethers by Infrared Spectroscopy

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Synopsis

A quantitative infrared spectroscopic study of a model urethane-type compound was carried out in order to obtain basic data on hydrogen bonding in polyurethanes. First, the absolute intensity of free N—H groups of *N*-phenylurethane, which was adopted as the model urethane, was determined by Wilson-Wells' method to be 3.59×10^3 l./mole-cm.^{2}. The free N—H of this urethane absorbed at 3447 cm.$^{-1}$, and hydrogen-bonded N—H absorbed near 3300 cm.$^{-1}$. Then, the extents of hydrogen bonding of the urethane at various concentrations were determined, and the hydrogen bonding between the urethane and ethers was studied by using the above-mentioned absolute intensity. For comparison, diphenylamine was also used as proton donor. Di-*n*-butyl ether and poly(oxyethylene glycol) were examined and proved to be able to act as proton acceptors. The frequency shifts of N—H stretching vibration of diphenylamine and *N*-phenylurethane caused by hydrogen bonding with di-*n*-butyl ether were 96 cm.$^{-1}$ and 150 cm.$^{-1}$, respectively. The equilibrium constants were 4.8×10^{-1} l./mole for the former system 4.6×10^{-1} l./mole for the latter.

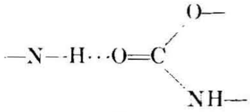
INTRODUCTION

It can be expected that interchain hydrogen bonding affects physical properties of urethane elastomers. In order to understand the structure–property relationships of this type of elastomer, it is necessary to determine the extent of hydrogen bonding.

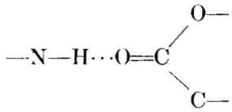
Weisfeld et al.[1] proposed a practical method of estimating the contribution of hydrogen bonding to the moduli of urethane elastomers. They resolved the observed moduli into secondary ones due to secondary bonding and primary ones due to chemical crosslinking by the method of trial and error on the assumption that the temperature dependence of the former obeys the Arrehenius equation and that of the latter obeys ideal rubber elasticity. Although their method is unique and valuable, there remains some uncertainty since they assumed ideal rubber elasticity, which is not always realized in urethane elastomers.[2,3]

For the investigation of hydrogen bonding, an infrared technique is probably most suitable. However, only a few studies concerning hydrogen bonding in polyurethanes have been published in the literature.[4–7]

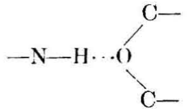
The aim of the present work is to obtain basic data on hydrogen bonding in urethane elastomers. In these polymers the proton donor is primarily the N—H of urethane units. The proton acceptor, however, may vary, for polyester-based urethane and polyether-based urethane. The former have more C=O groups than the latter because of the presence of repeating ester units. In addition, there is some possibility that the —O— of repeating ether units plays a role of proton acceptor. Therefore, it should be noted that three types of hydrogen-bonding will be possible in polyurethanes as shown in structures I–III.



I



II



III

The relative proportion of each of these types is dependent on the proton-accepting ability and relative amount of each acceptor. Some kind of spatial effect (configurational limitation or fitness) will also affect hydrogen bonding. In order to avoid this complication, hydrogen bonding of some model compounds and that between urethane and ethers were studied quantitatively by using infrared technique.

Since urethane compounds have both N—H and C=O groups in the structure, there is the capacity for self-association. Although in highly diluted solutions the N—H of the urethane unit may become free, it was desired to study a more simple system for the investigation of hydrogen bonding between N—H and —O—. For this purpose secondary aliphatic amines (diethylamine, and di-*n*-propylamine, diisopropylamine, di-*n*-butylamine, and diisobutylamine) were examined. These compounds, however, showed somewhat peculiar spectra in the N—H stretching region, that is, an unexplainable band, although weak, existed in the lower frequency side of free N—H and bonded (N—H···N) bands. The position of this absorption is not coincident with that of corresponding primary amines. This small band may be assigned to $^{\delta}$+N—H absorption or the hydrogen bond between N—H and $^{\delta}$−CH_2—CH_3. In addition to these observations two facts make it difficult to study infrared spectra quantitatively. First, secondary aliphatic amines easily absorb carbon dioxide to form the carbonic acid salt. Second, the absorption coefficient of N—H is small. As a result of preliminary studies, diphenylamine, a secondary aromatic amine, was adopted as a model N—H compound; it has single absorption in N—H stretching region and large absorption coefficient.

The results will be valuable for the clarification of the relation between structure and physical properties of polyurethanes.

EXPERIMENTAL

Model Compounds

N-Phenylurethane (PhU) and diphenylamine (DPA) were obtained commercially and purified by recrystallization from absolute ethanol solution (m.p. 52–53°C., 54°C.).

As proton acceptors di-*n*-butyl ether (DBE) and poly(oxyethylene glycol) 6000 (PEG 6000) were used. The former has a structure similar to that of the repeating unit of PEG. Both ethers were obtained commercially. The former was purified by fractional distillation, and the latter was used after dehydration by passing dry nitrogen gas into the melted state at 100–110°C. PEG of high molecular weight can not be used because it is insoluble in carbon tetrachloride.

Solvent for Infrared Measurement

Commercial carbon tetrachloride (analytical grade) was dehydrated with potassium hydroxide and phosphorus pentoxide and then fractionally distilled. The solvent was proved to be free from common impurities such as carbon disulfide by chemical tests.

Infrared Measurement

The infrared spectrometer employed was a Perkin-Elmer Model 337, double-beam, single-path, grating-type recording instrument. A normal slit program and slow scanning speed were used for all measurements. Since the extent of hydrogen bonding varies with concentration, spectral measurements were carried out on solutions of various concentrations. For relatively concentrated solutions, an ordinary sealed liquid cell was used, and for the dilute solutions special glass cells, 3–50 mm. in length, with a demountable NaCl plate, were used. Use of such a long path cell permits measurements of absorptions of free N—H group up to extremely dilute solutions of model compounds. All measurements were made at room temperature (23 ± 2°C.).

The procedure is as follows. First, the absorption of the pure solvent is recorded. The absorption of the solution in the same cell is then recorded on the same chart. In the 3 μ region of the chart the spectrum of ammonia gas is recorded for the purpose of calibration.[8] Other regions can be calibrated against the spectrum of indene.[8]

The coordinate of the recorded transmittance curve is measured accurately with a comparator and transformed into absorption curve by calculating the optical density.

RESULTS

Integrated Absorption Coefficients of Free N—H Group

***N*-Phenylurethane.** Two bands were obtained in the region of the stretching vibration of N—H groups; one of these is assigned to molecules associated by intermolecular hydrogen bonding, and the other to free molecules. When the solution is extremely dilute, only one band remains, indicating that there is no association. Thus it is possible to determine the absorption coefficient of N—H groups in free molecules by means of the following methods; (*a*) the peak-height method,[9] (*b*) Ramsay's method,[10] (*c*) Sandorfy-Cabana's method,[11] and (*d*) Wilson-Wells' method.[12]

As is well known, the peak-height method is the simplest method. It does not require transformation of the transmittance curve into an absorption curve, and therefore this has been adopted in many infrared studies. However, the values obtained in this method by using different spectrometers do not always agree with one another. Even with the same spectrometer the variation of slit width causes the variation of absorption coefficient. To avoid this uncertainty, the use of absolute intensity is recommended; this is possible by use of methods of (*b*), (*c*), and (*d*).

Of the integrated absorption methods, Ramsay's method is most convenient. However, this method requires the assumption of a Lorentzian form of absorption curve and the knowledge of spectral slit width. This assumption was not realized in the absorption of this urethane, as shown in Figure 1, where absorption is shown by a normalized form. The asymmetry factor, which is the ratio of the width of the higher and lower frequency sides of the absorption peak, was measured at different heights of the normalized absorption curve and is also shown in Figure 1. These ratios were used for the separation of free N—H absorption from hydrogen-bonded absorption overlapping the former. It is seen that the deviation from Lorentzian form is appreciable in the lower frequency side of the peak. Sandorfy-Cabana's method, which is a development of Ramsay's method and requires a full knowledge of the shape of absorption curve, gives a good approximation for unsymmetric absorptions. However, the result calculated from this method was not coincident with that from Wilson-Wells' method, which is most direct and reliable. In addition, the last method is of great advantage to the estimation of the free N—H absorption in polyurethane. In this case it was difficult to estimate accurately the shape of free N—H absorption because of the overlap with hydrogen-bonded absorption to a large extent. For these reasons the integrated intensity was determined by means of Wilson-Wells' method. The integrated absorption coefficient was obtained according to eq. (1):

$$S = \int_{\text{band}} \ln (T_0/T) d\nu = Bcl \qquad (1)$$

where S is the area of absorption (in cm.$^{-1}$), T_0 is the transmittance of the solvent, T that of solution, ν the frequency, B the apparent integrated

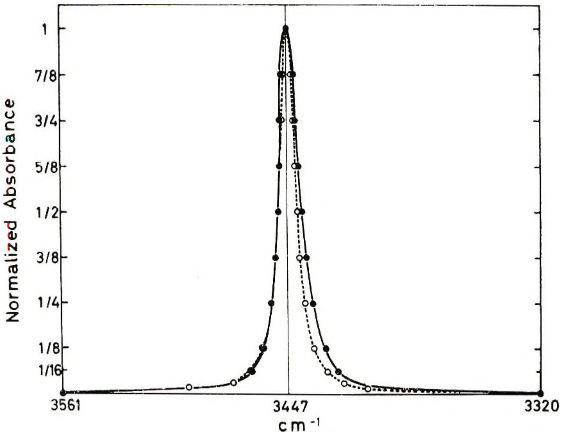


Fig. 1. Normalized absorption curve of free N—H of *N*-phenylurethane: (——●) observed curve; (- -○) Lorentzian curve. $R_{7/8} = 1.16$; $R_{3/4} = 1.18$; $R_{5/8} = 1.46$; $R_{1/2} = 1.54$; $R_{3/8} = 1.62$; $R_{1/4} = 1.59$; $R_{1/8} = 1.56$; $R_{1/16} = 1.35$; $R_{0/1} = 1.11$. $R_{n/m}$ = asymmetry factor = width on right of band maximum/width on left of band maximum; n/m = intensity ratio to band maximum.

molar absorption coefficient (in l./mole-cm.^{2}), c the concentration of solution (in mole/l.), and l the cell length or the optical path (in cm.). The area S can be estimated by a planimeter or by weighing a piece of tracing paper cut carefully in the shape of absorption curve. The extrapolation of B to $cl = 0$ gives the true integrated molar absorption coefficient or absolute intensity A. In Table I are shown the values of B' ($B' = B/2.303$) of PhU with those of c, l, and S' ($S' = S/2.303$). Extrapolation was carried out by the least-square method. The value of A, which is represented by practical unit recommended by IUPAC and is defined by

TABLE I
Absolute Integrated Intensity of Free N—H in *N*-Phenylurethane

$c \times 10^3$, mole/l.	l, cm.	$cl \times 10^3$, mole-cm./l.	S', cm.$^{-1}$	$B' \times 10^{-3}$, l./mole-cm.^{2}
8.00	0.960	7.68	25.54	3.33
5.00	0.960	4.80	16.19	3.37
1.00	0.960	0.960	3.63	3.78
2.00	0.960	1.92	6.67	3.47
2.50	0.960	2.40	8.72	3.63
3.00	0.960	2.88	10.05	3.49
4.00	0.960	3.84	13.60	3.54
2.50	0.530	1.33	4.56	3.43
3.00	0.530	1.59	5.28	3.32
4.00	0.530	2.12	7.73	3.65
5.00	0.530	2.65	8.89	3.35
6.00	0.530	3.18	10.70	3.36
			Extrapolated value	3.59

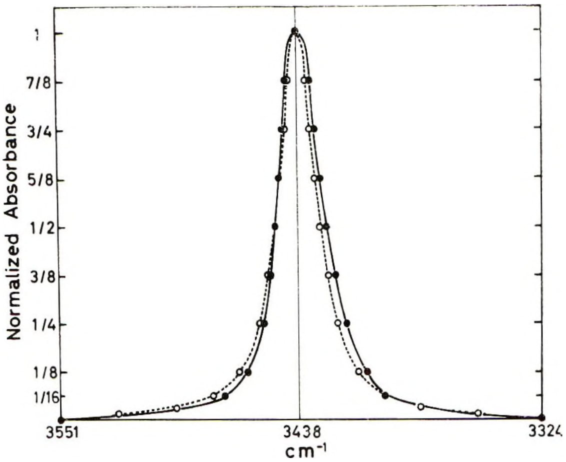


Fig. 2. Normalized absorption curve of free N—H of diphenylamine: (——●) observed curve; (- -○) Lorentzian curve. $R_{7/8} = 1.06$; $R_{3/4} = 1.17$; $R_{5/8} = 1.23$; $R_{1/2} = 1.33$; $R_{3/8} = 1.42$; $R_{1/4} = 1.42$; $R_{1/8} = 1.37$; $R_{1/16} = 1.17$; $R_{0/1} = 1.01$.

eq. (2), is 3.59×10^3 l./mole-cm.^{2}, in good agreement with the reported value[13] of 3.4×10^3 l./mole-cm.^{2} (calculated from the original value of 3.9×10^{-7} cm.^{2}/molecule-sec.,

$$A = \int_{\text{band}} \epsilon_\nu d\nu \tag{2}$$

where

$$\epsilon_\nu = (1/cl) \log (I_0/I)_\nu$$

where I_0 is the optical density of solvent and I that of solution.

Diphenylamine. In dilute solutions the N—H of DPA shows a single absorption, indicating that there is no association of the N—H···N type. The free N—H absorbs at 3438 cm.$^{-1}$. The free N—H absorption was not observed to be completely symmetric, as illustrated in Figure 2, where absorption is shown by the normalized curve. It is also seen that the Lorentzian form is not realized in this case. Accordingly, the absolute intensity is not obtained by the simple Ramsay's method but can be calculated from Wilson-Wells' method as pointed out previously. By extrapolating the value of B to $cl = 0$, the absolute intensity A can be obtained. The value of A determined by the method of least squares and represented by practical units is 2.01×10^3 l./mole-cm.^{2}, which coincides with the reported value[13] of 1.94×10^3 l./mole-cm.^{2} (original value is 22.2×10^{-8} (cm.^{2}/molecule-sec.).

Shift of Absorption Peak in PhU

Absorption peaks of N—H stretching vibrations shift to lower frequency on formation of hydrogen bonds. In Figure 3 are shown the N—H

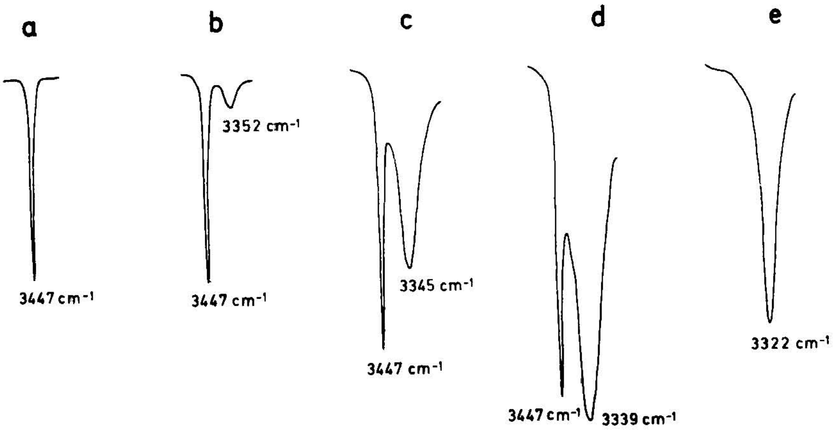


Fig. 3. N—H stretching vibrations of *N*-phenylurethane: (*a*) $c = 0.002$ mole/l., $l = 0.96$ cm.; (*b*) $c = 0.1$ mole/l., $l = 0.0212$ cm.; (*c*) $c = 0.6$ mole/l., $l = 0.0095$ cm.; (*d*) $c = 1.2$ mole/l., $l = 0.0095$ cm.; (*e*) KBr disk.

stretching vibrations of PhU in different states. There is no association in highly dilute solution. The free N—H peak is at 3447 cm.$^{-1}$. In concentrated solutions a new peak appears at a lower frequency, which is assigned to associated molecules. This hydrogen-bond peak shifts to lower frequency with increasing concentration of the solution. The peak for free C=O is at 1747 cm.$^{-1}$, and a shift similar to that of the N—H peak is observed. In KBr disks only one band was obtained, which is attributable to the absorption of a hydrogen-bonded system of only one species. These observations suggest that there are a number of degrees of association among PhU molecules in solution, that is dimeric, trimeric, and polymeric association as in the case of amides and alcohols.[14] In the crystalline state only polymeric association is possible.

Frequencies of the hydrogen-bonded C=O peak in CCl_4 solution were not obtained with sufficient accuracy because the absorption coefficient of the acceptor is not changed significantly by hydrogen bonding compared with that of the donor.

Determination of the Extent of Hydrogen Bonding in PhU

By using the integrated absorption coefficient the extent of free N—H groups can be determined. The absorption curve which consisted of two bands (free N—H and hydrogen-bonded N—H) is resolved into each absorption band by assuming an appropriate base line. Then, the area of the free N—H absorption is measured by the method described above. The concentration of free N—H groups is calculated by eq. (1) with the reasonable assumption that B is practically identical with A. It is thus possible to determine the proportion of free N—H group by eq. (3)

$$\text{Free N—H, \%} = (c_{\text{free}}/c_0) \times 100 = 100\, S'/c_0 A l \qquad (3)$$

TABLE II
Percentage Hydrogen Bonding of *N*-Phenylurethane

c_0, mole/l.	$l \times 10^2$, cm.	S', cm.$^{-1}$	c_{free} mole/l.	Free, %	Bonding %
0.100	2.12	6.92	0.0909	90.9	9.1
0.500	2.12	20.6	0.271	54.2	45.8
0.800	0.950	11.1	0.325	40.6	59.4
1.000	0.950	12.3	0.361	36.1	63.9
1.200	0.950	13.4	0.393	32.8	67.2

where c_0 is the total concentration of N—H groups (in mole/l.) and c_{free} is that of free N—H. The results are shown in Table II.

Equilibrium Constant of PhU Association

The equilibrium between free and associated molecules in a solution of PhU is complex, since there are a number of degrees of association. In fact, the equilibrium constants calculated by eq. (4), which is based on the stoichiometry of the formation of dimer, did not give a constant value when the concentration was varied.

$$K = [\text{dimer}]/[\text{monomer}] = [\text{N—H}_{\text{bonded}}]/([\text{N—H}_{\text{free}}] - [\text{N—H}_{\text{bonded}}])^2 \quad (4)$$

Also, eq. (5), which is based on the assumption that N—H and C=O groups behave independently, did not give a constant value.

$$K = [\text{N—H}\cdots\text{O=C}]/[\text{N—H}][\text{C=O}] \quad (5)$$

Hydrogen Bonding between DPA and DBE

Solutions of DPA and DBE of different concentrations were prepared. The concentration of amine is limited to that range where self-association of amine does not occur. Then, absorption curve is obtained by the

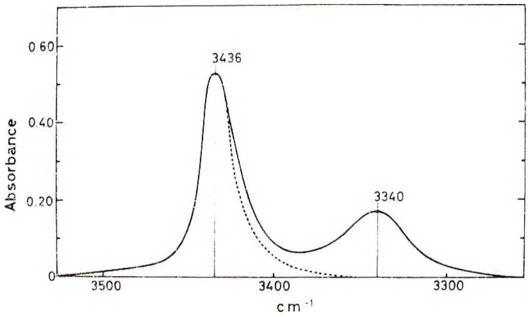


Fig. 4. Hydrogen bonding between diphenylamine and di-*n*-butyl ether (——) observed curve; (- -) resolved free N—H curve. Concentration of DPA = 0.03 mole/l., concentration of DBE = 0.5 mole/l.; l = 0.349 cm.

TABLE III

Hydrogen Bonding between Diphenylamine and Di-*n*-butyl Ether

c_{A0}, mole/l.	c_{E0}, mole/l.	c_{E0}/c_{A0}	l, cm.	S', cm.$^{-1}$	$c_{Af} \times 10^3$, mole/l.	$c_{Ab} \times 10^3$, mole/l.	c_{Ef}, mole/l.	Hydrogen bonding, %	K
0.0100	0.200	20	0.960	18.552	9.614	0.386	0.1996	3.9	0.201
0.0100	0.200	20	0.960	18.159	9.411	0.589	0.1994	5.9	0.314
0.0100	0.300	30	0.960	17.308	8.970	1.030	0.2990	10.3	0.384
0.0100	0.400	40	0.960	15.108	7.830	2.170	0.3978	21.7	0.697
0.0100	0.600	60	0.349	5.905	8.418	1.582	0.5984	15.8	0.314
0.0200	0.100	5	0.960	36.404	18.866	1.134	0.0989	5.7	0.608
0.0200	0.100	5	0.960	35.630	18.465	1.535	0.0985	7.7	0.844
0.0200	0.400	20	0.960	33.043	17.124	2.876	0.3971	14.4	0.423
0.0200	0.600	30	0.349	10.684	15.230	4.770	0.5952	23.9	0.526
0.0200	1.000	50	0.349	10.102	14.401	5.599	0.9944	28.0	0.391
0.0200	2.000	100	0.102	2.712	13.229	6.771	1.9932	33.7	0.257
0.0200	3.000	150	0.102	2.762	13.473	6.527	2.9935	32.6	0.162
0.0300	0.500	16.7	0.349	16.168	23.048	6.952	0.4930	23.2	0.612
0.0300	3.000	100	0.102	3.856	18.810	11.190	2.9888	37.3	0.199
0.0400	0.500	12.5	0.349	20.151	28.726	11.274	0.4887	28.2	0.803
0.0500	0.500	10	0.349	24.347	34.707	15.293	0.4847	30.6	0.909
								Mean	0.478

method similar to that described before, as illustrated in Figure 4. The I_0 line is obtained by measurements on another CCl_4 solution of ether with the corresponding concentration prepared separately.

Figure 4 shows that a new broad absorption appeared in the lower frequency side of free N—H absorption, suggesting the occurrence of hydrogen bonding between amine and ether. In this case free N—H appeared at 3436 cm.$^{-1}$ and bonded N—H at 3340 cm.$^{-1}$. The difference, $\Delta\nu$, is 96 cm.$^{-1}$.

The overlapped N—H absorption curve may be resolved into the two species. By assuming that the broad tail of bonded absorption does not overlap with the free N—H absorption peak to a large extent, the asymmetry factor shown in Figure 2 can be used to resolve the free N—H absorption curve. Thus the integrated absorption of free N—H may be obtained by measuring the area of this absorption as described before, which gives the proportion of free N—H species. The per cent hydrogen bonding and apparent equilibrium constants were calculated by eqs. (6) and (7), and the results are tabulated in Table III.

$$\text{H bonding, }\% = (c_{\text{Ab}}/c_{\text{Ao}}) \times 100 \tag{6}$$

$$K = c_{\text{Ab}}/c_{\text{Af}}\, c_{\text{Ef}} \tag{7}$$

$$c_{\text{Af}} = S'/Al \tag{8}$$

$$c_{\text{Ab}} = c_{\text{A0}} - c_{\text{Af}} \tag{9}$$

$$c_{\text{Ef}} = c_{\text{E0}} - c_{\text{Ab}} \tag{10}$$

where c_{A0} is the concentration of amine, c_{E0} that of ether, c_{Af} that of unassociated amine, c_{Ef} that of unassociated ether, and c_{Ab} that of associated amine (all in mole/l.); S' is the area of absorption (in cm.$^{-1}$) ($S' = S/2.303$), A is the absolute intensity of DPA (2.01×10^3 l./mole-cm.^{2}), l is the cell path (in cm.), and K is the equilibrium constant.

Hydrogen Bonding between PhU and DBE

Hydrogen bonding between PhU and DBE was studied in a similar way. The coexistence of DBE in a solution of PhU at a concentration sufficiently low to be unassociated leads to the appearance of the new broad band in the lower frequency side of free N—H absorption. A typical absorption curve is shown in Figure 5. The new band cannot be assigned to hydrogen bonding among PhU molecules because the shift and the shape are different from those observed in the latter case. As described previously, hydrogen bonding among PhU molecules gives a shift of 90–110 cm.$^{-1}$, but in this case it is 150 cm.$^{-1}$. The per cent hydrogen bonding and apparent equilibrium constants were calculated by eqs. (11) and (12), and the results are tabulated in Table IV.

$$\text{H bonding, }\% = (c_{\text{Ub}}/c_{\text{U0}}) \times 100 \tag{11}$$

$$K = c_{\text{Ub}}/c_{\text{Uf}}\, c_{\text{Ef}} \tag{12}$$

TABLE IV

Hydrogen Bonding between *N*-Phenylurethane and Di-*n*-butyl Ether

$c_{U0} \times 10^3$, mole/l.	c_{E0}, mole/l.	c_{E0}/c_{U0}	l, cm.	S', cm.$^{-1}$	$c_{Uf} \times 10^3$, mole/l.	$c_{Ub} \times 10^3$, mole/l.	c_{Ef}, mole/l.	Hydrogen bonding, %	K
2.00	0.500	250	0.790	4.703	1.658	0.342	0.4997	17.1	0.413
2.50	0.500	200	0.790	5.955	2.100	0.400	0.4996	16.0	0.381
3.00	0.500	167	0.790	6.940	2.447	0.553	0.4994	18.4	0.453
4.00	0.500	125	0.790	7.711	2.719	1.281	0.4987	32.0	0.945
4.00	1.000	250	0.350	3.649	2.904	1.096	0.9989	27.4	0.378
4.00	1.500	375	0.350	3.731	2.969	1.031	1.4990	25.8	0.232
5.00	0.500	100	0.960	15.278	4.433	0.567	0.4994	11.3	0.256
5.00	0.500	100	0.790	11.477	4.047	0.953	0.4990	19.1	0.472
5.00	1.000	200	0.350	3.502	2.787	2.213	0.9978	44.5	0.796
5.00	1.000	200	0.960	14.484	4.203	0.797	0.9992	15.9	0.190
5.00	1.500	300	0.350	4.194	3.338	1.662	1.4983	33.2	0.332
6.00	0.500	83	0.790	13.297	4.688	1.312	0.4987	21.9	0.561
6.00	1.000	167	0.350	5.452	4.339	1.661	0.9983	27.7	0.383
6.00	1.500	250	0.350	3.961	3.152	2.848	1.4972	47.5	0.604
8.00	0.500	63	0.960	22.547	6.542	1.458	0.4985	18.2	0.447
								Mean	0.456

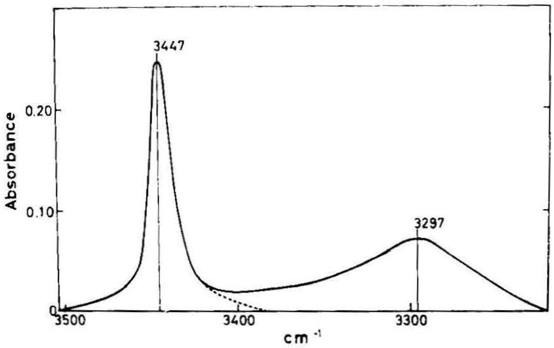


Fig. 5. Hydrogen bonding between *N*-phenylurethane and di-*n*-butyl ether: (——) observed curve; (- -) resolved free N—H curve. Concentration of PhU = 0.006 mole/l., concentration of DBE = 1.0 mole/l.; l = 0.349 cm.

where

$$c_{\mathrm{Uf}} = S'/Al \tag{13}$$

$$c_{\mathrm{Ub}} = c_{\mathrm{U0}} - c_{\mathrm{Uf}} \tag{14}$$

$$c_{\mathrm{Ef}} = c_{\mathrm{E0}} - c_{\mathrm{Ub}} \tag{15}$$

Here c_{U0} is the concentration of urethane, c_{Ub} that of associated urethane; A is the absolute intensity of PhU (3.59×10^3 l./mole-cm.[2]), and other symbols have same meaning as above.

Hydrogen Bonding between DPA and PEG 6000

Because of the poor solubility of PEG in CCl_4, a quantitative study of hydrogen bonding was difficult. PEG 6000 was dissolved slightly in CCl_4 (ca. 0.5%). Slight warming was sufficed to bring it into solution. After the spectrum of this solution was recorded, a small amount of DPA was added and the spectrum was recorded. The spectrum is shown in Figure 6. In this measurement the concentration of N—H is 0.01 mole/l., which is sufficiently small to keep N—H unassociated.

It is seen that a new band appeared at 3351 cm.$^{-1}$. This is not assigned to hydrogen bonding of the N—H···N type, which is ascertained to appear at about 3385 cm.$^{-1}$. This observation shows that the —O— units in PEG can act as proton acceptors for hydrogen bonding.

Hydrogen Bonding between PhU and PEG 6000

Hydrogen bonding between PhU and PEG 6000 was studied by a method similar to that described above. In this case the measurements were carried out at various concentration of PhU. The spectra of N—H and C═O stretching vibration undergo considerable change with the increase of concentration. The spectra are shown in Figure 7. It is seen that a new broad band appears, which is evidence of the formation of hydrogen bonding between N—H and repeating ether unit. For comparison, this figure shows also spectra of PhU at corresponding concentrations. From the relative intensity of the two carbonyl absorptions, one is free and the other is a hydrogen-bonded species the relative proportion of each species can be deduced. Thus the possibility of hydrogen bonding of

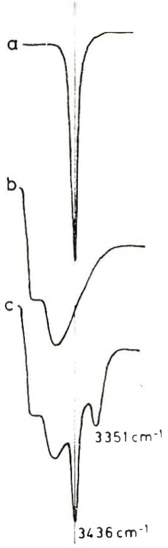


Fig. 6. Hydrogen bonding between N—H group of diphenylamine and poly(oxyethylene glycol) 6000 in CCl_4: (*a*) DPA, c = 0.01 mole/l.; (*b*) PEG 6000, c = 0.5 wt.-%; (*c*) DPA (c = 0.01 mole/l.) + PEG 6000 (c = 0.5 wt.-%).

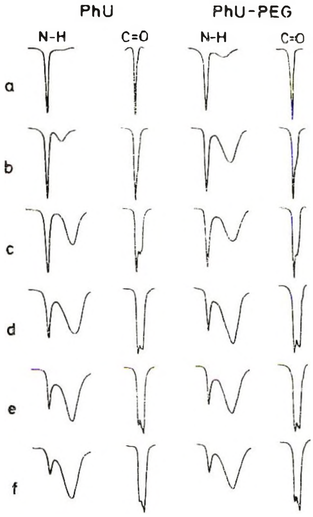


Fig. 7. Hydrogen bonding between *N*-phenylurethane and poly(oxyethylene glycol) 6000: (*a*) c = 0.01 mole/l., l = 0.0975 cm.; (*b*) c = 0.10 mole/l., l = 0.0025 cm.; (*c*) c = 0.50 mole/l., l = 0.0012 cm.; (*d*) c = 1.00 mole/l., l = 0.0012 cm.; (*e*) c = 1.20 mole/l., l = 0.0012 cm.; (*f*) c = 1.50 mole/l., l = 0.0012 cm.

the repeating ether unit may be verified by comparing the two series of spectra in Figure 7. The bonded carbonyl absorptions in the series containing ether are considerably weaker as compared with those of corresponding urethane concentrations in another series. This is due to the participation of the repeating ether unit in hydrogen bonding.

DISCUSSION

As pointed out previously, the apparent absorption coefficient varies with the concentration and the cell length. Therefore, for the accurate determination of the concentration of absorbing groups the use of the apparent absorption coefficient for the given concentration and cell length is reasonable.

The cell thickness is known, but the concentration of the free N—H group is not known in the present state. The best way of estimating the concentration may be as follows. From several experiments the true optical density of the free N—H absorption, which may be determined by extrapolation of the apparent optical density to $l = 0$, is obtained. Then, the absolute integrated molar absorption coefficient may be used to calculate the concentration. This method is reasonable in principle. However, it is anticipated that the extrapolation will introduce a large error because of the weak absorption measured by using small cell path. Therefore we accepted the preceding method and used the absolute intensity in place of the apparent absorption coefficients. Since the difference between the absolute intensity and the apparent integrated absorption coefficient is small where the concentration of the groups in question is small, it can be expected that the calculation will not cause serious error practically.

Although the extent of hydrogen bonding was determined in this way, the equilibrium constants of each degree of association were not determined because of the possibility of polymeric associations. Therefore it is impossible to discuss thermodynamic properties of the hydrogen-bonding system at present. However, there remains some possibility for obtaining a reliable estimate of the equilibrium constant for dimer formation in the dilute state.

It was shown above that the N—H of DPA and PhU can form hydrogen bonds with —O— of DBE. This result is coincident with that obtained by Harting and Brandt,[15] who studied the association between DPA and tetrahydrofuran. The values of $\Delta\nu$, which is the shift of bonded N—H absorption from free one, are large compared with those of hydrogen bonding between N—H and C=O. This observation leads us to the conclusion that there may be strong hydrogen bonding between N—H and —O—.

Nevertheless, the calculated equilibrium constants are relatively small, showing that only a small portion of the N—H groups participate in hydrogen bonding. In the system of N—H and —O— of PEG, a situation similar to that of DBE is realized. As a result, it is natural to conclude that the hydrogen bonding between N—H and —O— is weak compared with ordinary hydrogen bonding of the N—H · · · O═C type.

It should be noted that the appearance of the new band in the lower frequency side of free N—H absorption is evidence for the formation of hydrogen bonds but is not evidence for the formation of associated molecules. It seems convenient to differentiate between the two situations. However, the two situations are equivalent in the context of the existence of intermolecular force. The principal difference is in the order of the bonding energy.

The hydrogen bonding in the system of PhU and ether is rather complicated because there are two types of acceptors, i.e., —O— and C═O. Experimental results showed that even in extremely dilute solutions, the N—H of urethane can form hydrogen bonds when a proton acceptor of —O— type is present in sufficiently high concentration. However, as the concentration of urethane is increased, the association of urethane molecule by means of the strong hydrogen-bonding ability of C═O becomes possible. This situation was seen in Figure 7 and explained in the Results. When urethane is present in high concentrations only N—H · · · O═C hydrogen bonding will be possible, even in the presence of a large amount of ether type acceptor. In the concentrated state, only the polymeric association of urethane groups will be possible.

From these observations it can be suggested that in polyether-based urethane systems a rather complicated equilibrium of hydrogen bonding among N—H and C═O of urethane unit and —O— of the repeating ether unit exists. When the concentration of N—H in polyether-based urethane is small, most of the N—H of urethane will form hydrogen bonds with ether units of polyether chains. Such a situation is realized when the polyurethane is prepared from polyethers of considerably high molecular weight. In these cases, secondary interchain bonding of relatively small bonding energy will be scattered in the bulk of polymer. When the concentration is high (in the case of polyurethane based on relatively low molecular weight polyethers), secondary bonding of the polymeric N—H · · · O═C type will be localized. Thus, there is a possibility that the configuration of network chains of polyether-based urethane rubbers will undergo a change as the concentration of urethane group is varied.

In the system of polyester-based urethane polymers, a relatively strong acceptor of the C═O type originating from the repeating ester units is predominant. In this case there is a possibility that N—H associates with the C═O of ester units to give secondary bonding which is not localized in the bulk of polymer even if the concentration of urethane units becomes high. The possibility of a situation similar to that of polyether-based urethane types still remains, however. The situation actually realized in polyurethane depends on the relative hydrogen-bonding capacity for the two types of C═O, that is, urethane type and ester type. The proton-accepting ability of the former may be greater than that of the latter owing to the resonance effect of an amide-type structure. Further investigations should be based on thermodynamical consideration.

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Effects of Methyl Sidegroup on the Extent of Hydrogen Bonding and Modulus of Polyurethane Elastomers

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Synopsis

The effects of methyl sidegroup on the properties of polyurethane elastomers, mainly hydrogen bonding and elastic properties, were studied. Polyurethanes of almost equal crosslinking density and urethane group concentration, but with different side methyl groups, were prepared by a prepolymer method. The extent of hydrogen bonding was determined by an infrared technique. The density and Young's modulus are decreased by the introduction of methyl sidegroup, swelling ratio and T_g are increased, but the extent of hydrogen bonding is not affected.

INTRODUCTION

In the preceding paper[1] the authors reported a method of quantitative determination of hydrogen bonding of urethane compounds. As mentioned in the discussion of the preceding paper, the molar absorption coefficient of the N—H stretching vibration of a model urethane compound can be used to determine the extent of hydrogen bonding in polymers of polyurethane types.

The importance of the role of interchain hydrogen bonding in the physical properties of polymers is well known. In fact, a number of phenomena have been explained successfully by the concept of hydrogen bonding, as shown by studies on crystal structure, high cohesive energy density, melting point, and so on.

It is interesting to consider the relation between structure and physical properties of polymers of polyamide, polyurethane, and polyurea types. These polymers are analogous to one another in structure and have N—H groups which can form hydrogen bonds with the carbonyl groups in them. The physical properties of these polar polymers are somewhat complicated compared with those of nonpolar polymers, because there is a possibility of various coexisting intermolecular forces.

Thus, the concept of hydrogen bonding has been used to explain the relation between structure and physical properties. For example, the fact that the even-odd polyamides have lower melting points than the even-

even ones has been explained by the unsuitability of configuration in the former for the formation of interchain hydrogen bonding. This explanation has been accepted for a long time because the picture of an extended chain of even–odd type illustrated the unsuitability for interchain hydrogen bonding which leads to a lower cohesive energy density and the melting point. This, however, is not true. As clarified by Terenzi,[2] most N—H groups of both types participate in hydrogen bonding. This finding is not surprising if we consider a three-dimensional crystal lattice in which the polyamide chains are packed to satisfy all possible sites for interchain hydrogen bonds.

This simple fact has been misunderstood for a long time. We seem to have depended too much upon hydrogen bonding in the explanation of property-structure relationships. Now, it seems the time to reconsider the effect of interchain hydrogen bonding for the further understanding of the physical properties of polymers.

In this paper we report on the correlation of extent of hydrogen bonding and the modulus of polyurethanes with methyl sidegroups of various concentration. It can be reasonably deduced that the introduction of short side chains leads to the decrease of modulus because of the interruption of interchain hydrogen bonding. The actual observation of the decrease in modulus of polyurethane with increasing of the content of methyl sidegroup is thus explained safely. The true situation, however, is not so simple, as discussed below.

EXPERIMENTAL

Preparation of Polyurethane

Polyurethanes were prepared from a mixture of poly(ethylene adipate) (PEA) and poly(propylene adipate) (PPA) and tolylene diisocyanate (TDI) by prepolymer technique. The crosslinking agent was trimethylolpropane (TMP).

PEA was supplied by the courtesy of Japan Oil Seal Company. PPA was prepared by polycondensation of propylene glycol with adipic acid to the same chain length. The number-average molecular weights were determined by acetylating the hydroxyl endgroups;[3] $\bar{M}_n$ values of PEA and PPA were 2110 and 2250, respectively. TDI (2,4- and 2,6-isomers in 80:20 ratio) was supplied by the courtesy of Takeda Chemical Company and purified by fractional distillation. The purity was checked by the amine-equivalent method.[4] TMP was obtained commercially and purified by fractional distillation.

The details of the preparation of polyurethane are as follows. The blended polyester, which was previously dried by passing nitrogen gas through the melted material, was weighed into a three-necked separable flask equipped with a nitrogen inlet and outlet connected to drying tube, thermometer, and vacuum stirrer.

The flask was heated to 80°C. in an oil bath, and was then evacuated to degas the polyester. Double the molar equivalent of diisocyanate was weighed accurately into the flask. The reaction mixture was stirred vigorously. Small portions of the reaction mixture were taken at appropriate time intervals and the content of residual isocyanate groups titrated by amine-equivalent method[4] in order to check the extent of the reaction.

When the reaction was completed, a molar equivalent of curing agent was added and the mixture vigorously agitated. After the agent was thoroughly dispersed, the flask was evacuated to eliminate the bubbles. Because of the short gelation time of the reaction mixture, prompt operation was required, otherwise the mixture would turn into a solid containing many small bubbles.

The resultant viscous liquid was then poured onto trays and molds coated with silicone varnishes. Next the reaction mixture was heated to 80°C. for 30 hr. in the air bath to complete the crosslinking reaction.

The three-dimensional polyurethanes obtained were rubbery at room temperature except for that from pure PEA, which has a tendency to harden by the formation of crystallites.

The content of methyl groups can be controlled by selecting the mixing ratio of the two polyesters, that is, PEA and PPA. When the molar ratio of OH of polyester to NCO of diisocyanate is kept constant, prepolymer of same chain length will be obtained. The stoichiometrical use of TMP will make polyurethanes with almost equal crosslinking density and urethane group concentration.

The extent of the crosslinking reaction was traced in thin films by analyzing characteristic infrared bands of the isocyanate group at 2300 cm.$^{-1}$[5] and by measuring the modulus of the polymer at 60°C. Since the resulting polymers had no residual isocyanate groups, showed a constant modulus over 20 hr., and were scarcely soluble in benzene, it is assumed that the network is almost perfect. Likewise, it may be said that the polyurethanes were synthesized quantitatively in accordance with the estimated value, so far as stoichiometrical considerations were concerned. Thus, careful syntheses make possible formation of polyurethanes of known structures with respect to the degree of crosslinking and concentrations of urethane and methyl groups.

Gel Fraction and Swelling Measurement

Gel fraction and swelling properties were measured. A small piece of polyurethane was immersed in benzene. The specimen was weighed at appropriate time intervals after absorbing varying amounts of swelling solvent. After the sol fraction was dissolved in solvent and swelling equilibrium was attained, the weight of the specimen becomes constant. The gel fraction and swelling ratio were then calculated by eqs. (1)–(3):

$$g = W_b/W \tag{1}$$

$$Q = \frac{(W_a - W_b)/\rho_s}{W_b/\rho_p} \tag{2}$$

$$q = 1 + Q \tag{3}$$

where g denotes gel fraction, Q is the volume ratio of solvent in the swollen state to gel in the unswollen state, q is the swelling ratio; W is the weight of specimen, W_a is the weight of swollen specimen, and W_b is that of gel; ρ_s and ρ_p are density of solvent and polymer, respectively.

Modulus of Polymer

A strip 1.74 mm. × 2.0–3.0 mm. × 38.0 mm. cut from the polyurethane sheet was used for these measurements. The thickness of the specimen was measured by a thickness gage. Then the stress–strain relationship was measured by a Shimadzu Autograph (an Instron-type automatic tensile tester with constant temperature bath). All measurements were carried out at constant temperature (20–100°C.) and a constant extension speed of 5 mm./min. The strain rate was 0.125 min.^{-1}. From the recorded load–elongation curve the stress–strain relationship was calculated. The plot of log σ versus log γ, where σ is stress and γ the strain, should be a straight line having a slope of unity for the completely elastic materials. For the viscoelastic materials, however, this is not expected because the flow was included in the deformation mechanism. Therefore it was recommended to calculate the modulus after this slope is confirmed to be unity.[6] In our case the plots of log σ versus log γ for various polyurethanes show a straight line of slope approximately unity, pointing out that these polymers behave almost completely elastically at this temperature. At low or high extension ratios ($1.1 > \alpha$, $\alpha > 2.5$), the plots deviate from the straight line. The measurement error in the former and the crystallization or high stretching of network chains in the latter may be the sources of these deviations.

Determination of the Extent of Hydrogen Bonding

The extent of hydrogen bonding was determined by the infrared technique with the use of a Perkin-Elmer Model 337, grating-type, double-beam single-path automatic-recording infrared spectrometer. A normal slit program and slow scanning speed were adopted. Thin films of polyurethanes were obtained by using a freezing microtome with a special holding stage which can fix the block of polymer under cooling by Dry Ice. At an appropriate temperature (near the glass transition temperature) the thin film can be cut. The films obtained were dried over phosphorus pentoxide for at least 24 hr., and the infrared spectra were then recorded. As mentioned in the preceding paper,[1] two bands were obtained in the N—H stretching region. One is assigned to free N—H species and the other to hydrogen-bonded species. The coordination of the recorded transmittance curve are measured by a comparator and the calculated optical densities are replotted on an appropriate scale against frequencies. By assuming a reasonable I_0 line the absorption curve is resolved into free N—H and hydrogen-bonded absorption. The area of the former is then measured by weighing the piece of tracing paper which was cut in the same shape. Integrated absorption is obtained by dividing the weight of this area with that of unit area. The concentration of free N—H groups is then calculated by eq. (4):

$$c_{\text{free}} = S/Al \tag{4}$$

where c_{free} is the concentration of free N—H groups, S the integrated absorption of free N—H, A the true integrated molar absorption coefficient (absolute intensity) of free N—H, and l the thickness of the film. The per cent hydrogen bonding is then calculated from eq. (5):

$$\text{H bonding, \%} = 100(c_{\text{total}} - c_{\text{free}})/c_{\text{total}} \tag{5}$$

where per cent hydrogen bonding refers to the proportion of hydrogen-bonded species, c_{total} is the stoichiometrical total concentration of N—H groups, and c_{free} the concentration of free N—H group. 2,4-Tolylene diethyl urethane was used as model diurethane. The true integrated molar absorption coefficient of the free N—H of this diurethane was measured according to the Wilson-Wells' method as described in the previous paper.[1]

Glass Transition Temperature T_g

The glass transition temperature T_g was determined from the length-temperature curve.[7] At T_g this curve has an abrupt change in slope which is due to the fact that above T_g the coefficient of expansion is greater than the value below T_g.

RESULTS AND DISCUSSION

The properties of obtained polyurethanes are tabulated in Table I. From the data of gel fraction, which is nearly unity, it can be said that the

TABLE I
Properties of Polyurethanes

PPA, %	Density, g./cm.^{3}	Gel fraction in benzene, %	Swelling ratio in benzene	T_g, °C.
0	1.243	99.2	2.096	−25.8
10	1.226	100	2.220	−24.7
20	1.234	100	2.299	−24.2
30	1.226	97.8	2.442	−23.5
40	1.211	97.6	2.683	−22.6
50	1.220	96.9	2.761	−21.5
60	1.223	96.7	2.898	−19.9
70	1.210	99.6	2.893	−19.3
80	1.193	98.5	3.040	−18.5
90	1.195	99.8	3.158	−17.6
100	1.178	98.2	3.220	−17.2

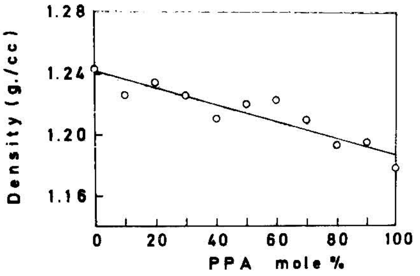

Fig. 1. Effect of methyl group on density.

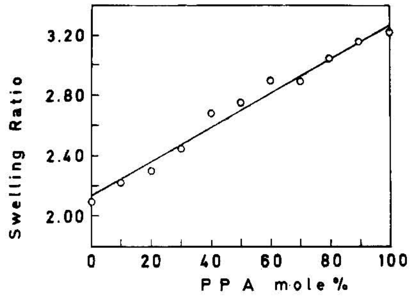

Fig. 2. Effect of methyl group on swelling ratio in benzene.

crosslinking reaction is almost perfect. In the preparation of these polyurethanes an equal number of network chains should be obtained by the reaction of equal molar ratios of reactants. However, the volume occupied by the resultant networks differs, depending on the content of PPA. This is observed in the decrease of density with the increase of the content of PPA, as shown in Figure 1. Apparently the introduction of a methyl sidegroup seems to interfere with the packing of molecular chains. This deduction is verified by the increase of swelling ratio with the increase of PPA content, as shown in Figure 2. Thus the elastically effective elements in the unit volume, (ν_e/V), calculated from eq. (6),[8] differ in number with the change of the content of methyl sidegroup:

$$\nu_e/V = (2\nu_0/V)(K - 1)(1 - 2M) \tag{6}$$

where

$$K = \frac{\text{NCO}}{\text{OH}} = \frac{\text{moles of diisocyanate}}{\text{moles of polymer glycol}} \tag{7}$$

$$M = \frac{\text{moles of curing agent}}{\text{moles of NCO in prepolymer}} \tag{8}$$

Here ν_e is moles of elastically effective chain element, ν_0 is moles of polymer glycol, and V is the total volume of the system.

In Table II are shown $(\nu_e/V)_{\text{calc}}$ and the concentration of urethane groups, which decreases continuously with the increase of methyl sidegroups.

TABLE II
Structure of Polyurethanes

PPA, %	[CH_3], mole/l.	[Urethane], mole/l.	$(\nu_e/V)_{calc}$, mole/l.
0	0	1.92	0.320
10	0.61	1.91	0.318
20	1.22	1.92	0.320
30	1.80	1.89	0.315
40	2.36	1.86	0.310
50	2.96	1.86	0.310
60	3.54	1.86	0.310
70	4.06	1.83	0.305
80	4.55	1.79	0.298
90	5.11	1.79	0.298
100	5.56	1.79	0.298

TABLE IIIA
Effect of Methyl Group on Young's Modulus at 20°C.

PPA, %	E_{obs}, kg./cm.^{2}	E_{calc}, kg./cm.^{2}	$E_{calc}g$, kg./cm.^{2}	$E_{obs}/E_{calc}g$
0	25.6	23.9	23.7	1.08
10	24.7	23.7	23.7	1.04
20	23.9	23.9	23.9	1.00
30	21.4	23.5	23.0	0.930
40	17.6	23.1	22.5	0.782
50	19.9	23.1	22.4	0.888
60	17.3	23.1	22.3	0.776
70	21.2	22.7	22.6	0.938
80	19.5	22.2	21.9	0.890
90	19.0	22.2	22.2	0.856
100	15.7	22.2	21.8	0.720

TABLE IIIB
Effect of Methyl Group on Young's Modulus at 40°C.

PPA, %	E_{obs}, kg./cm.^{2}	E_{calc}, kg./cm.^{2}	$E_{calc}g$, kg./cm.^{2}	$E_{obs}/E_{calc}g$
0	29.5	25.5	25.3	1.17
10	25.7	25.3	25.3	1.02
20	24.3	25.5	25.5	0.953
30	20.4	25.1	24.5	0.833
40	19.5	24.7	24.1	0.809
50	19.9	24.7	23.9	0.833
60	16.7	24.7	23.9	0.699
70	19.1	24.3	24.2	0.789
80	19.1	23.7	23.3	0.820
90	19.6	23.7	23.7	0.827
100	14.8	23.7	23.3	0.635

TABLE IIIC
Effect of Methyl Group on Young's Modulus at 60°C.

PPA, %	E_{obs}, kg./cm.^{2}	E_{calc}, kg./cm.^{2}	$E_{\text{calc}g}$, kg./cm.^{2}	$E_{\text{obs}}/E_{\text{calc}g}$
0	30.2	27.1	26.9	1.12
10	28.7	26.9	26.9	1.07
20	26.0	27.1	27.1	0.959
30	20.5	26.7	26.1	0.785
40	20.2	26.3	25.7	0.786
50	21.8	26.3	25.5	0.855
60	18.3	26.3	25.4	0.720
70	20.7	25.8	25.7	0.805
80	15.3	25.2	24.8	0.617
90	20.9	25.2	25.1	0.833
100	14.8	25.2	24.7	0.599

TABLE IIID
Effect of Methyl Group on Young's Modulus at 80°C.

PPA, %	E_{obs}, kg./cm.^{2}	E_{calc}, kg./cm.^{2}	$E_{\text{calc}g}$, kg./cm.^{2}	$E_{\text{obs}}/E_{\text{calc}g}$
0	34.6	28.7	28.5	1.21
10	29.9	28.6	28.6	1.05
20	27.0	28.7	28.7	0.941
30	23.4	28.3	27.7	0.845
40	23.2	27.8	27.1	0.856
50	22.6	27.8	26.9	0.840
60	19.9	27.8	26.9	0.740
70	21.4	27.4	27.3	0.784
80	21.7	26.8	26.4	0.822
90	21.4	26.8	26.7	0.801
100	16.8	26.8	26.3	0.639

TABLE IIIE
Effect of Methyl Group on Young's Modulus at 100°C.

PPA, %	E_{obs}, kg./cm.^{2}	E_{calc}, kg./cm.^{2}	$E_{\text{calc}g}$, kg./cm.^{2}	$E_{\text{obs}}/E_{\text{calc}g}$
0	36.3	30.4	30.2	1.20
10	32.2	30.2	30.2	1.07
20	28.5	30.4	30.4	0.938
30	24.0	29.9	29.2	0.822
40	23.1	29.4	28.7	0.805
50	24.4	29.4	28.5	0.856
60	20.6	29.4	28.4	0.725
70	22.8	28.9	28.8	0.792
80	23.5	28.3	27.9	0.842
90	22.5	28.3	28.2	0.798
100	18.0	28.3	27.8	0.647

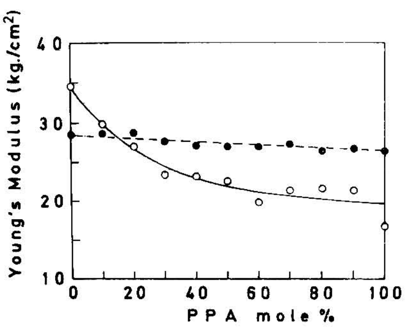

Fig. 3. Effect of methyl group on Young's modulus at 80°C.: (○) E_{obs}; (●) $E_{calc}g$.

The decrease of (ν_e/V) leads to a decrease in modulus according to the theory of rubber elasticity. As a matter of fact, the moduli for simple elongation, E_{obs}, which are tabulated in Table III and shown in Figure 3, decrease with the decrease of $(\nu_e/V)_{calc}$ according to this expectation. The expected moduli, $E_{calc}g$, as calculated from eq. (9):

$$E_{calc}g = 3RT(\nu_e/V)_{calc}g \tag{9}$$

are also given in Table III and Figure 3, where g is gel fraction of the polymer.

The ratio, $E_{obs}/E_{calc}g$, is constant if the methyl side groups have no effect upon elastic modulus. Thus, this ratio will be expected to be a criterion of the effect of the methyl sidegroup. As is seen in Table III and Figure 4, the ratio decreases with increasing methyl sidegroup content. Thus it may be safely concluded that the introduction of methyl groups leads to the decrease of modulus. This conclusion seems to be plausible if we consider the disruption of intermolecular hydrogen bonding by the existence of methyl sidegroup.

The absolute intensity of 2,4-tolylene diethyl diurethane calculated from the data in Table IV was 3.87×10^3 l./mole-cm.^{2}. The error in the estimation of the extent of hydrogen bonding caused by the use of absolute intensity has already been discussed in the previous paper.[1]

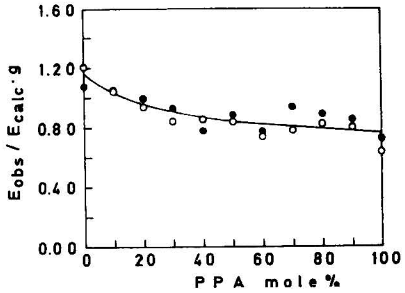

Fig. 4. Effect of methyl group on $E_{obs}/E_{calc}g$: (○) at 80°C.; (●) at 20°C.

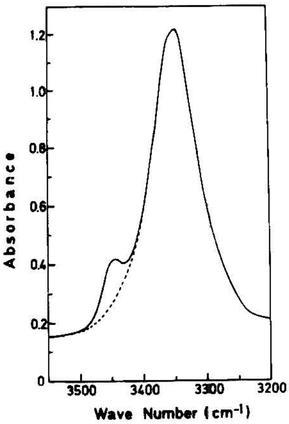

Fig. 5. Infrared spectrum of polyurethane in the ν_{N-H} region, PPA = 10 mole-%: (——) observed ν_{N-H} absorption curve; (- -) resolved free ν_{N-H} absorption curve.

In Figure 5 is shown an infrared spectrum typical of the polyurethanes. The extent of hydrogen bonding calculated from eqs. (4) and (5) is shown in Table V and Figure 6. If we remember the rather complicated method of determination of this value, it can be concluded that the methyl sidegroups do not interrupt intermolecular hydrogen bonding in this case, as the value of about 85% hydrogen bonding is quite high.

From the above observation, it may be deduced that the decrease in modulus caused by the introduction of methyl sidegroup is due to the change of the nature of chain itself. This of course originates from the change of free energy of chain which is decided by the potential energy of rotation of bonds and the excluded volume effect. Although the precise estimation of these factors is almost impossible, it is quite conceivable that the introduction of methyl sidegroups makes the energy difference between *trans* and *gauche* position in the sequence of carbon atom in main chain

TABLE IV
Calculation of The Absolute Intensity of 2,4-Tolylene Diethyl Diurethane[a]

c, mole/l.$^{-1}$ × 10^3	*l*, cm.	*cl*, mole-cm./l. × 10^3	*S*, cm.$^{-1}$	*B*, l./mole-cm.^{2} × 10^{-3}
1.00	2.91	2.91	11.19	3.85
1.00	3.99	3.99	15.78	3.95
1.00	4.92	4.92	19.29	3.92
2.00	0.96	1.92	7.35	3.83
2.00	2.10	4.20	15.41	3.67
2.00	2.91	5.82	22.01	3.78
2.00	3.99	7.98	30.27	3.79
			Extrapolated value	3.87

[a] *c* = concentration of diurethane, *l* = cell length, *S* = the area of the free N—H absorption, *B* = the apparent intensity.

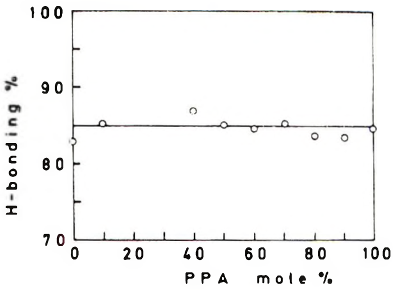

Fig. 6. Effect of methyl group on the extent of hydrogen bonding.

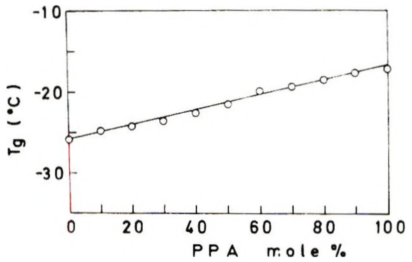

Fig. 7. Effect of methyl group on T_g.

smaller than that in chains without methyl groups. This will make the root-mean-square end-to-end distance of the chain smaller and the slope of distribution function of chain displacement less steep. The resulting smaller entropy change in the stretching process of chain leads to a smaller modulus.

TABLE V

Extent of Hydrogen Bonding of Polyurethanes[a]

PPA, %	$l \times 10^3$, cm.	$Al \times 10^{-1}$, l./mole-cm.[a]	S, cm.$^{-1}$	c_{free}, mole/l.	c_{total}, mole/l.	Free N—H, %	Bonded N—H, %
0	5.6	2.17	7.13	0.329	1.92	17.1	82.9
10	5.7	2.21	6.22	0.281	1.91	14.7	85.3
40	8.0	3.10	7.51	0.242	1.86	13.0	87.0
50	9.5	3.68	10.2	0.277	1.86	14.9	85.1
60	8.3	3.21	9.20	0.287	1.86	15.4	84.6
70	12.1	4.68	12.6	0.269	1.83	14.7	85.3
80	13.3	5.15	15.1	0.293	1.79	16.4	83.6
90	9.3	3.60	10.7	0.297	1.79	16.6	83.4
100	16.3	6.31	17.4	0.276	1.79	15.4	84.6

[a] l = film thickness A = the absolute intensity of model diurethane = 3.87×10^3 l./mole-cm.^{2}; c_{free}, c_{total} denote the concentrations of the free N—H group and total N—H group, respectively.

The variation of the glass transition temperature which is shown in Table I and Figure 7 is also interesting and is closely related to the above discussion. It is seen that T_g was elevated by the introduction of methyl sidegroup. Apparently introduction of methyl groups restricts bond rotation. A similar elevation of T_g is seen in other polymer systems; for example, polypropylene has a higher T_g than polyethylene. One can visualize these situations by considering the rotation of polymeric chains. By this consideration one can imagine also the tendency of leveling the rotational potential curve due to the existence of methyl sidegroup.

The conclusion that what decides primarily the elastic property is not interchain hydrogen bonding but the rotational isomerism of the chain itself may not be so surprising. However, now it should be suggested that the effect of hydrogen bonding must not be overestimated in the consideration of property–structure relationships of polymers.

Finally, the observation that the extent of hydrogen bonding is not affected by methyl sidegroups must be noticed. It seems that the equilibrium of hydrogen-bond formation is governed primarily by the concentration of urethane group. This is an interesting problem which should be investigated in the future. Although a large value of hydrogen bonding (85%) suggests the thermodynamically stable structure of hydrogen bonds, in a mechanical process this secondary bond is weak and may be ruptured by stress. The fairly good agreement of calculated modulus obtained on the basis of the theory of rubber elasticity with observed modulus clearly shows above consideration.

The authors wish to thank T. Oji and T. Amano for their assistance in the experimental work.

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Polymerization of α-Amino Acid *N*-Carboxy Anhydrides. III. Mechanism of Polymerization of L- and DL-Alanine NCA in Acetonitrile*

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Synopsis

The polymerization of L- and DL-alanine NCA initiated with *n*-butylamine was carried out in acetonitrile which is a nonsolvent for polypeptide. The initiation reaction was completed within 60 min.; there was about 10% of conversion of monomer. The number-average degree of polymerization of the polymer obtained increased with the reaction period, and it was found to agree with value of W/I, where W is the weight of the monomer consumed by the polymerization and I is the weight of the initiator used. The initiation reaction of the polymerization was concluded as an attack of *n*-butylamine on the C_5 carbonyl carbon of NCA. The initiation, was followed by a propagation reaction, in which there was attack by an amino endgroup of the polymer on the C_5 carbonyl carbon of NCA. The rate of polymerization was observed by measuring the CO_2 evolved, and the activation energy was estimated as follows: 6.66 kcal./mole above 30°C. and 1.83 kcal./mole below 30°C. for L-alanine NCA; 15.43 kcal./mole above 30°C., 2.77 kcal./mole below 30°C. for DL-alanine NCA. The activation entropy was about −43 cal./mole-°K. above 30°C. and −59 cal./mole-°K. below 30°C. for L-alanine NCA; it was about −14 cal./mole-°K. above 30°C. and −56 cal./mole-°K. below 30°C. for DL-alanine NCA. From the polymerization parameters, x-ray diffraction diagrams, infrared spectra, and solubility in water of the polymer, the poly-DL-alanine obtained here at a low temperature was assumed to have a block copolymer structure rather than being a random copolymer of D- and L-alanine.

INTRODUCTION

The polymerization of α-amino acid *N*-carboxy anhydride initiated with primary amine has been studied extensively.[1–8] The initiation reaction of NCA with primary amine has been considered to occur by nucleophile attack of the amine on the C_5 carbonyl carbon of NCA [eq. (1)]. Thereafter, the propagation reaction proceeds by the addition of a terminal amine group to the C_5 carbonyl of NCA.[1–8] In some solvents, the initiation of NCA with primary amine has been reported to be caused by proton abstraction from the nitrogen of the NCA,[9] just as in tertiary amine initiation.[9–13]

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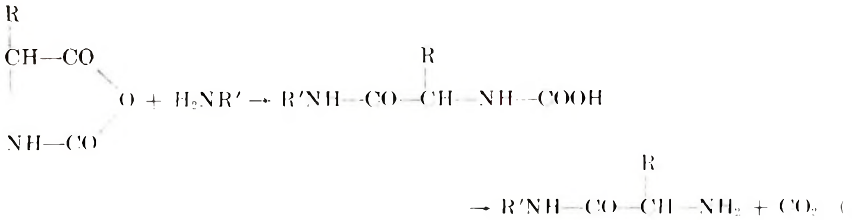
* For the preceding papers in this series, see Iwakura, Uno, and Oya.[1,2]



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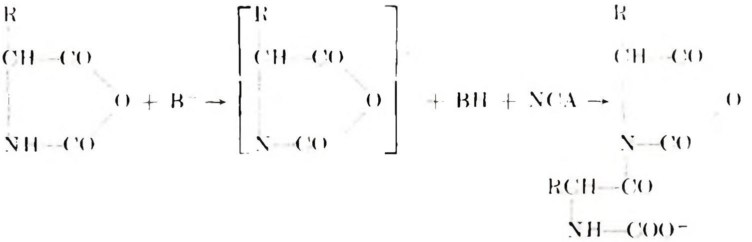

(2)

Almost all studies on polypeptides to date have been carried out with γ-benzyl L-glutamate NCA in nitrobenzene, tetrahydrofuran, dioxane, and dimethylformamide in which the polypeptides formed are soluble.

No kinetic study has been carried out on polymerization of DL- and L-alanine NCA in acetonitrile which is not a solvent for polyalanine. In previous papers, we reported that the molecular weight of polyalanine produced by polymerization of NCA in acetonitrile was much higher than that obtained in nitrobenzene in which the polymer produced was highly swollen.[14, 15] The present study describes details of polymerization of DL- and L-alanine NCA initiated with *n*-butylamine in acetonitrile.

RESULTS AND DISCUSSION

The results of polymerization of DL-alanine NCA initiated with *n*-butylamine in acetonitrile are shown in Table I. The polymerization system became turbid within a few minutes after starting the polymerization, and polymer precipitated. After about 60 min. conversion of the monomer was about 10%; the polymer formed was isolated easily by filtration, and no more polymer precipitated from the filtrate in spite of the presence of a large amount of NCA in it. The isolated polymer was extracted with hot absolute acetonitrile. On pouring the extract into a NCA solution, no polymerization occurred. Isolated polymer showed no activity for further polymerization after drying, but the undried polymer without drying continued to polymerize further when it was added to a solution of NCA; the degree of polymerization of the polymer produced here was larger than that of the polymer used initially. This suggests that there was no initiator (free *n*-butylamine) in the solution 60 min. after starting the polymerization. Consequently the polymerization of NCA after this time would be considered to proceed only through a propagation of the polymer end produced. The results of an endgroup analysis for the poly-DL-alanine are also shown in Table I. The number of carboxyl endgroups in the polymer was negligibly small. The number-average degree of polymerization obtained from amine endgroup analysis agreed with that obtained by osmotic pressure and the value of the molar ratio W/I, where W represents the monomer consumed by polymerization and I is the initiator used.

On the polymerization of DL-alanine NCA in acetonitrile initiated with *n*-butylamine, the molecular weight of the polymer increased with polymerization time. Therefore, in polymerization of DL-alanine NCA in acetonitrile there seemed to be no termination by a cyclization reaction.[8]

In the polymerization of γ-benzyl L-glutamate NCA with the primary amine indioxane, it has been reported that 70% of initiator was involved in attack on the C_5 carbonyl carbon of NCA, but the remaining 30% was involved in abstraction of the proton from the nitrogen of NCA.[9] Polymerization in tetrahydrofuran has been known to give similar result.[12] In these cases, the molecular weight of the polypeptide obtained was much larger than the value of W/I. On the other hand, in the polymerization in dimethylformamide the degree of polymerization of polypeptide almost agreed with the value of W/I. However the polymerization of alanine NCA with *n*-butylamine in acetonitrile would be concluded to proceed by attack by the initiator on the C_5 carbonyl carbon of NCA. These results indicate that the mechanism of initiation depends on the solvent used.

Similar results were obtained for the polymerization of L-alanine NCA initiated by *n*-butylamine, as shown in Table II. When a small amount of *n*-butylamine was used as initiator, a high molecular weight poly-L-alanine, having an intrinsic viscosity in dichloroacetic acid as high as >5, was produced.

In the polymerization of NCA in acetonitrile, the polymer formed precipitated as described above, and further polymerization occurred between solid polymer and liquid monomer. The rate of polymerization in a heterogeneous system may not be discussed in the same way as the polymerization in a homogeneous system; however, as the degree of polymerization of polypeptide obtained here agreed well with W/I, the kinetics of polymerization will give some information regarding the mechanism.

The rate of polymerization of L- and DL-alanine NCA initiated with *n*-butylamine was measured in acetonitrile and nitrobenzene. The results are summarized in Tables I and II. The weight of the polymer formed and CO_2 evolved were used to evaluate the rate. The two methods gave fairly good agreement with each other. It is known that the rate of polymerization of NCA initiated by a primary amine can be represented as follows:

$$R_p = -d[M]/dt = k[M][I] \tag{3}$$

where $[M]$ and $[I]$ denote the molar concentrations of anhydride and initiator. The plots of log $[M_0]/[M_t]$ versus polymerization time are shown in Figures 1–3, where $[M_0]$ and $[M_t]$ are the concentrations of anhydride initially and at polymerization time t, respectively. The plots for the polymerization of DL-alanine NCA in nitrobenzene showed nearly straight lines. The polymerization of L-alanine NCA in nitrobenzene showed an accelera-

TABLE I
Polymerization in Acetonitrile of DL-Alanine NCA

Temp., °C.	Polymerization time, min.	Conversion, %		$\ln \eta_{rel}/c = [\eta]$ in DCA	P			COOH, mole-%
		By CO_2	By weight		NH_2 end-groups[a]	Osmometric[b]	Calcd.[c]	
8	60	6.4	4.2	0.060	9	9	12	0.16
	90	10.4	10.3	0.098	13	20	20	0.16
	120	13.9	11.9	0.116	20	24	23	0.16
	180	19.9	19.9	0.134	28	29	40	0.16
	300	27.0	27.2	0.192		47	54	0.16
20	65	8.7	8.6	0.086	12	19	16	0.17
	100	13.5	14.6	0.137	22	29	29	
	170	23.3	24.0	0.220	38	57	49	
	240	31.4	29.0	0.280		78	58	
30	52	8.6	8.9	0.086	12	18	17	
	79	16.0	17.0	0.115	20	23	34	
	130	22.0	24.0	0.189	27	46	48	
	170	24.8	25.3	0.230	39	61	51	
	210	27.0	29.6	0.241		65	59	
	240	28.3	30.0	0.275		76	60	
	1710	61.2	67.9	0.475		128	135	

35	67	18.7	21.8	0.146	32	43
	127	29.0	34.9	0.288	83	70
	150	33.2	36.0	0.310	92	72
40	30	9.9	7.7	0.136	29	14
	43	13.0	13.0	0.163	36	26
	60	21.0	25.7	0.212	53	51
	85	27.0	32.0	0.223	59	64
	113	40.0	38.0	0.227	60	76
	130	45.0	39.0	0.237	63	78
	400	59.8	56.0	0.327	99	112
30[d]	74	10.2	20.0	0.187	19	20
	302	32.6	35.0	0.250	68	65
	837	53.6	50.0	0.295	85	107
	1424	81.7	83.0	0.305	90	163

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[a] Average degree of polymerization by analysis for amino endgroup. The degree of polymerization by amino endgroup deviated from that obtained by osmotic pressure in the range of high molecular weight because of inaccuracy of endgroup analysis.

[b] Average degree of polymerization by osmotic pressure.

[c] Average degree of polymerization calculated from W/I.

[d] Polymerization in nitrobenzene.

TABLE II
Polymerization in Acetonitrile of L-Alanine NCA

Temp., °C.	Polymerization time, min.	Conversion, %		$\ln \eta_{rel}/c = [\eta]$ in DCA
		By CO_2	By weight	
8	87	16.3	16.8	0.537
	147	23.1	20.8	0.659
	190	29.7	29.7	0.761
	210	31.1	33.4	0.787
20	67	21.0	18.2	0.655
	100	27.0	26.6	0.687
	180	36.0	34.9	0.897
	205	39.7	39.7	0.945
	240	42.2	42.2	1.145
30	40	14.3	11.7	0.580
	70	19.1	20.5	0.660
	105	32.0	30.5	0.690
	212	41.2	42.0	1.363
	240	47.0	48.0	1.482
	1440	95.0	98.0	2.300
35	30	15.3	19.4	0.539
	50	24.0	25.0	0.836
	150	44.0	44.4	1.482
	240	52.0	45.7	1.490
30[a]	30	4.6	25.7	1.58
	190	27.0	90.4	1.95

[a] Polymerization in nitrobenzene.

tion of the rate in a very early stage. In nitrobenzene, as the polymer was in the form of a highly swollen gel, the polymerization behavior may agree with results reported[4] for γ-benzyl L-glutamate NCA. The plots for polymerization of DL-alanine NCA in acetonitrile showed straight lines except at 8°C. On the contrary, polymerization of L-alanine NCA in acetonitrile gave a two-step rate curve in every case. The straight lines in Figure 2 and 3 show that the kinetics of the polymerization of L- and DL-alanine NCA in acetonitrile obey the eq. (3) in spite of their heterogeneous polymerization reaction. About 60 min. after the starting of the polymerization, the rate was considered to express only the rate of propagation as described above. If the initiation reaction is faster than the propagation reaction, a decrease in the rate of polymerization of L-alanine NCA (Fig. 3) might occur when the initiation reaction was completed. However, in the polymerization of DL-alanine NCA in acetonitrile, there was no appearance of a decrease in rate except at 8°C. Therefore the above consideration could not be acceptable. The conformation of the various polyalanines obtained in acetonitrile was the α form.[14] Therefore the decrease in rate of polymerization of L-alanine NCA could not be caused by a conformational change during the polymerization.

Logarithmic plots of the rate constant versus reciprocal absolute temperature T are shown in Figure 4. These plots were connected with two straight

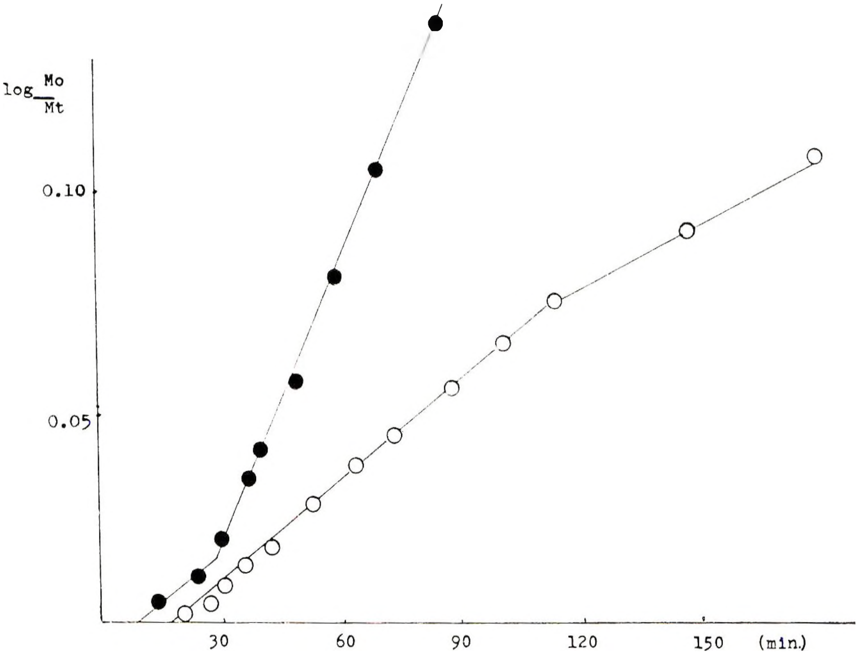

Fig 1. Polymerization rate of DL- and L-alanine NCA in nitrobenzene at 30°C.: (○) DL-alanine NCA; (●) L-alanine NCA.

lines in both cases. The difference of slope above 30°C., and below 30°C. was quite marked for poly-DL-alanine. Kinetic parameters calculated from these results are shown in Table III. Activation energies below 30°C. were smaller than those obtained above 30°C. Therefore, at a low temperature, polymer end and monomer could take a rather preferable state with respect to further polymerization. The difference between activation energies above 30°C. was much larger than that of L-alanine NCA, and the value for DL-alanine NCA approached that of L-alanine NCA below 30°C. This result might indicate about the same relation between polymer end and monomer in polymerization of both DL- and L-alanine NCA.

The difference of activation entropies between above 30°C. and below 30°C. was small for L-alanine NCA, but it was very large for DL-alanine

TABLE III
Activation Energies and Entropies of L- and DL-Alanine NCA

	Polymerization temp., °C.	ΔE, kcal./mole	ΔS, cal./mole
L-Alanine NCA	30–40	6.66	−43.33 to −43.37
	8–30	1.83	−59.13 to −59.27
DL-Alanine NCA	30–40	15.43	−14.07 to −14.17
	8–30	2.77	−56.32 to −56.41

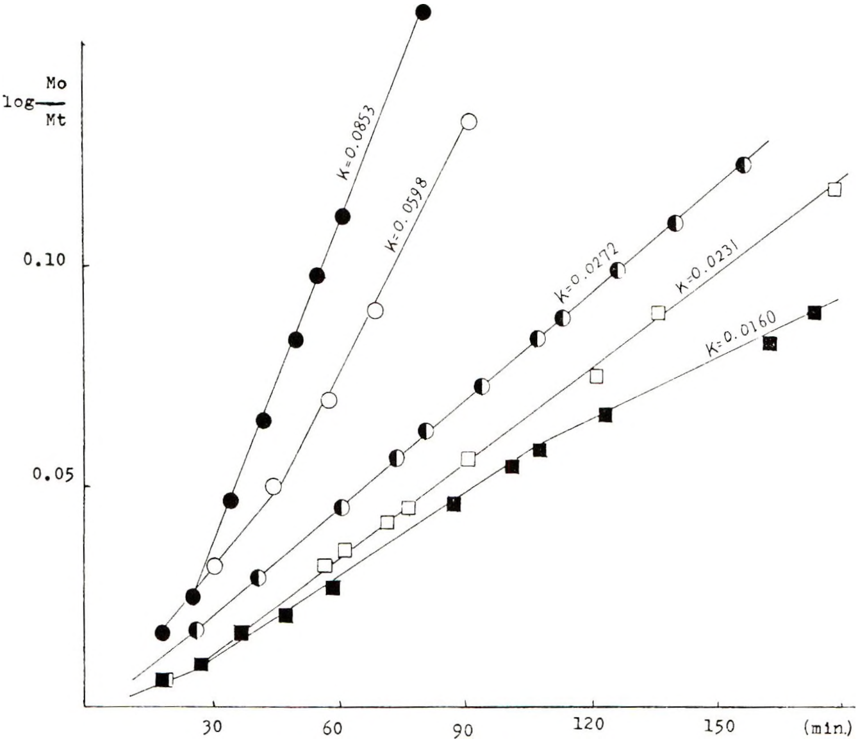

Fig 2. Polymerization rate of DL-alanine NCA in acetonitrile: (■) 8°C.; (□) 20°C.; (◐) 30°C.; (○) 35°C.; (●) 40°C.

NCA. However, the absolute values of activation entropies on polymerization of DL- and L-alanine NCA were very similar at low temperature. These data may be interpreted as showing the influence of an assembly of polymer chains, i.e., the polymer chains of L-alanine make a closely packed arrangement of regular conformation which is little influenced by temperature variation, while for polymerization of DL-alanine NCA, the situation is quite different. At a high temperature, the polymer chains of DL-alanine can not be arranged so closely, and the activation entropy has a small negative value; at a low temperature, the affinity between polymer chains formed becomes large and permits a closely packed arrangement. From the same value of activation entropy in both L- and DL-alanine NCA at low temperature, it might be imagined that not only the conformation but also the sequence of units in the DL-alanine polymer chain are similar with that of L-alanine. Such a consideration on reaction parameters could also lead to an interpretation of the polymerization behavior described above. After 60 min., the average degree of polymerization was about 20, and at this time the affinity between polymer chains would be evident. Therefore, with L-alanine NCA the rate of polymerization becomes slower because of the packed arrangement. On the contrary, for DL-alanine above 30°C., the affinity of polymer chains is not so strong, and a slowing down of the

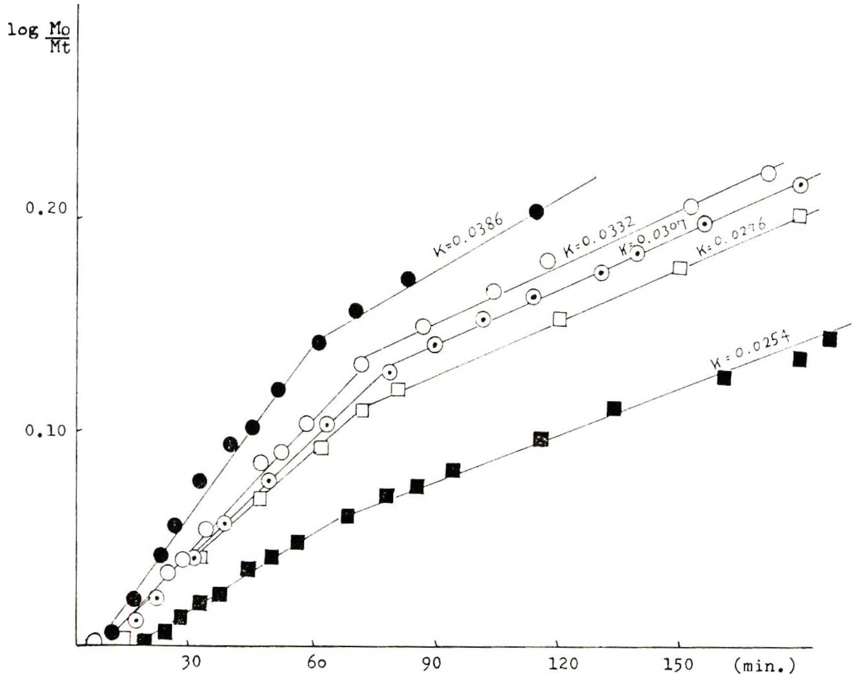

Fig 3. Polymerization rate of L-alanine NCA in acetonitrile: (■) 8°C.; (□) 20°C.; (⊙)25°C.; (○) 30°C.; (●) 35°C. $[M_0]$ = initial monomer concentration = 0.213 mole/l. (20 cc.); $[M_t]$ = monomer concentration at t min.; [I] Initiator concentration 0.001085 mole/l. (0.5 mole-% on monomer) n-butylamine.

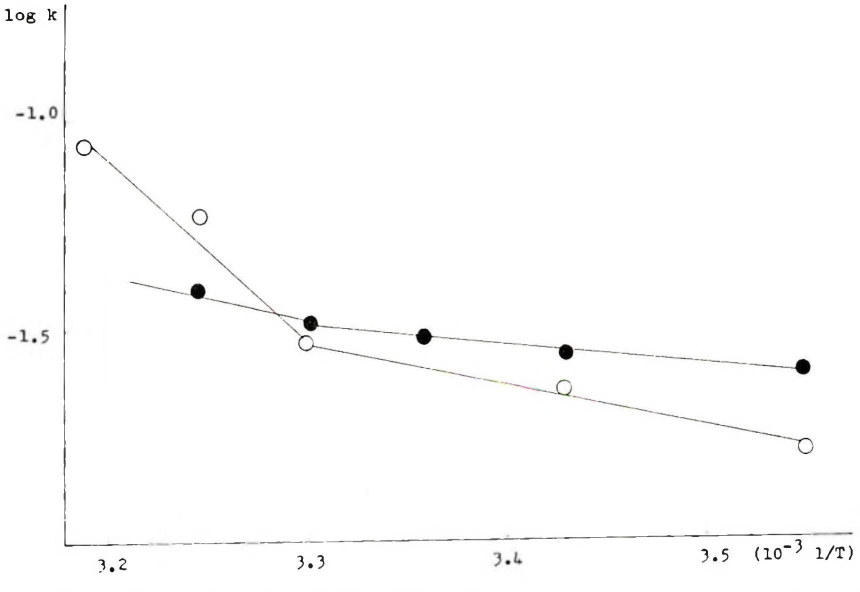

Fig 4. Dependence of logarithmic plot of the rate constants propagation k on reciprocal absolute temperature: (○) DL-alanine NCA; (●) L-alanine NCA.

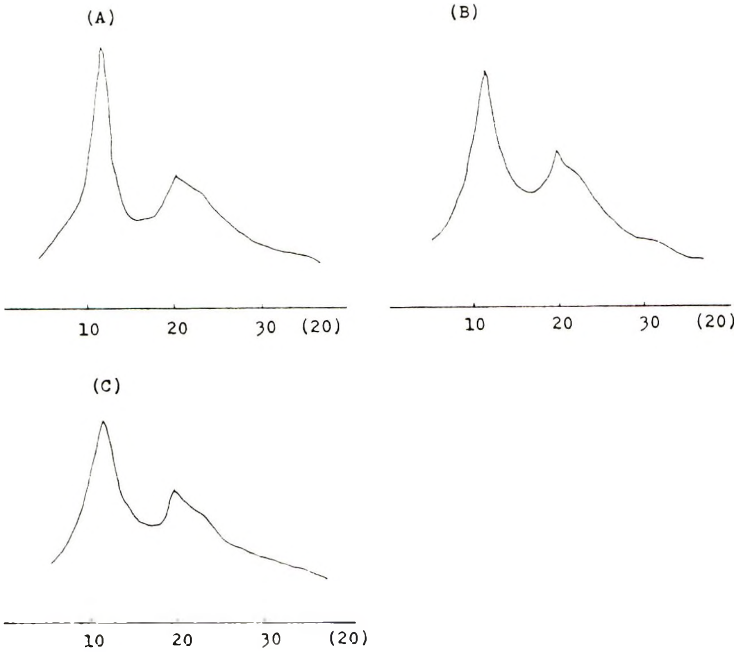

Fig. 5. X-ray diffraction diagram of polyalanines in acetonitrile: (*A*) poly-L-alanine obtained at 30°C.; (*B*) poly-DL-alanine obtained at 0°C.; (*C*) poly-DL-alanine obtained at 30°C.

rate cannot be observed. At a low temperature, however, the affinity comes much larger and then slowing down of the rate can be observed.

The x-ray diffraction diagram of poly-L- and -DL-alanines obtained in acetonitrile under various conditions are shown in Figure 5. The diffraction peaks in these patterns were the same in every case. The crystallinity of the poly-L-alanine was highest, and next was poly-DL-alanine obtained at 0°C., and last was poly-DL-alanine obtained at 30°C.

The solubility in water of poly-DL-alanine obtained in acetonitrile at various temperatures is shown in Table IV. The proportion of water-insoluble material in the polymer increased as with decreasing polymerization temperature.

TABLE IV
Solubility of Poly-DL-alanine in Water

No.	Polymerization solvent	Polymerization temp., °C.	ln η_{rel}/c	Insoluble in water, %
1	Acetonitrile	8	0.391	59
2	"	20	0.280	32
3	"	30	0.475	24
4	"	35	0.434	22
5	Nitrobenzene	30	0.305	5

Infrared spectra of these polymers are shown in Figure 6. The absorption at 1305 cm.$^{-1}$, which has been considered to be characteristic of the crystalline α-helix,[16] increased with decreasing solubility in water.

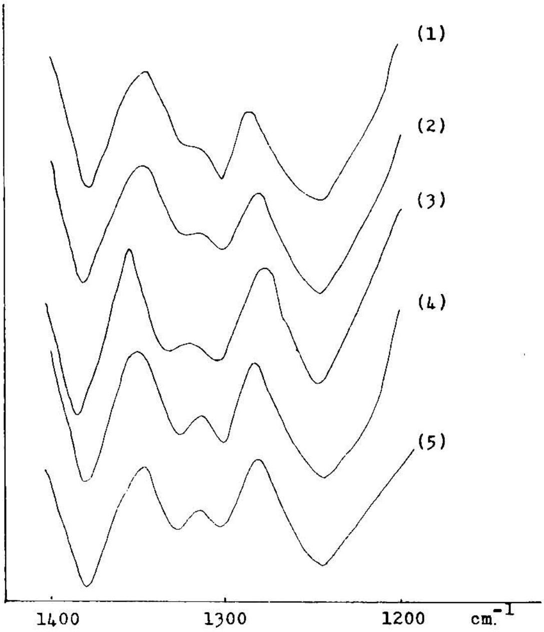

Fig. 6. Infrared spectra of poly-DL-alanine shown in Table IV.

From the consideration of the polymerization parameters, the result of x-ray diffraction diagrams, solubility data, and infrared spectra, the structure of poly-DL-alanine may be assumed to be a block-type copolymer rather than a random copolymer of D- and L-alanine, especially for the polymer obtained at low temperature.

EXPERIMENTAL

N-Carboxy DL-Alanine Anhydride and *N*-Carboxy L-Alanine Anhydride

DL-Alanine NCA and L-alanine NCA were prepared in high purity and good yield (chlorine content <0.02%) as reported previously.[15]

Rate of Polymerization

The rate of polymerization was followed by measuring the amount of CO_2 evolved by the method of Katchalski and Shalitin.[17,18] Carbon dioxide-free nitrogen was bubbled through the reaction mixture to transfer the CO_2 into a solution of benzylamine in a mixture of ethanol and dioxane. The CO_2 absorbed was titrated with 0.1*N* sodium methoxide, thymol blue being used as an indicator.

The rate was also followed by measuring the weight of the polymer formed. Isolation of the polymer was carried out by the method reported previously.[15]

The rate constant was estimated by the equation:[2]

$$k = \frac{\ln([M_0]/[M_{t_2}]) - \ln([M_0]/[M_{t_1}])}{(t_2 - t_1)\,[I]}$$

where $[M_0]$ is the initial concentration of NCA, $[M_{t_1}]$ and $[M_{t_2}]$ are concentrations of the NCA remaining at times t_1 and t_2, respectively, and $[I]$ is the molar concentration of initiator.

Solubility in Water

The solubility of the polymer in water was determined as follows. An 8–15 mg. portion of the polymer was put into 10 ml. of water and shaken for 24 hr. at room temperature. The insoluble polymer was separated on a glass filter and washed with water and ether. The residue was dried *in vacuo* at room temperature and weighed. The insoluble portion of the polymer was determined as follows:

$$\text{Per cent insoluble} = \frac{\text{weight of residue}}{\text{weight of initial polymer}} \times 100$$

Endgroup Analysis

Endgroup analysis was determined by the method of Michael.[19]

Molecular Weight by Osmotic Pressure

The molecular weight of the poly-DL-alanine was determined by the use of a high-speed osmometer in 2,2,2-trifluoroethanol of one by Drs. L. Mandelkern, R. Glick, and A. Takahashi at The Florida State University. The viscosity of the polymer was measured in dichloroacetic acid.[15] Data obtained were as follows: $\eta_{sp}/c = 0.18, 0.46, 0.53$, and 1.06 for average molecular weights of 2900, 8200, 9200, and 24,000, respectively. From these data the equation,

$$[\eta] = 5.1 \times 10^{-4} \times M^{0.73}$$

was obtained. The values in Table I were estimated by this equation.

Authors are pleased to thank Prof. Mandelkern, Dr. Glick, and Dr. Takahashi for extremely useful data on the molecular weight of poly-DL-alanine.

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Studies in Some New Initiator Systems for Vinyl Polymerization. II. Ammonia–Halogen System as the Redox Initiator

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Synopsis

The ammonia–halogen redox system has proved a promising initiator for polymerizing a number of vinyl monomers in aqueous media. Chlorine and bromine are most efficient, whereas iodine fails to initiate polymerization, probably due to its inhibitive tendency. Endgroups are halogen and amine and total about 0.5 per chain. On the basis of results of endgroup analysis, a mechanism of initiation through halogen and amine radicals, mainly through hydrogen atoms, is suggested. Consistent with the proposed mechanism the endgroup profile changes significantly with changes in pH.

INTRODUCTION

Earlier[1] we reported from this laboratory some preliminary observations on molecular halogens and amino compounds as redox initiators. The present paper reports our results on aqueous ammonia–halogen initiating systems with particular reference to endgroups and the mechanism of initiation involved.

EXPERIMENTAL

Materials

Purified methyl methacrylate (MMA), ethyl acrylate (EA) and other vinyl monomers were used. Chlorine was generated by the reduction of HCl (analytical reagent grade) with potassium permanganate and purified by passing through distilled water. Bromine and other reagents used were of analytical grade.

Polymerization Procedure

Aqueous polymerization of purified monomers was carried out at ambient temperature (≈ 30°C.) under nitrogen atmosphere in conical Pyrex flasks in the dark. The polymers obtained in a coarse precipitated form were filtered, washed several times with distilled water, dried in an air-oven at 45°C. and then purified through the usual procedures.[2] To carry out polymerization at the acid pH's hydrochloric acid (analytical reagent grade) was used.

Determination of Molecular Weight

The molecular weight of the resulting polymers was calculated viscometrically with the help of eqs. (1) and (2) for poly(methyl methacrylate)[3] and poly(ethyl acrylate), respectively, in benzene at 35 ± 0.1°C.

$$\bar{M}_n = 2.81 \times 10^5[\eta]^{1.32} \tag{1}$$

$$[\eta] = 6.06 \times 10^{-3}(\mathrm{DP})^{0.67} \tag{2}$$

Endgroup Analysis

The purified polymers were subjected to appropriate dye tests for halogen,[5] amine,[6,7] and hydroxyl[8] endgroups. Since both the amine and halogen endgroups respond to the same dye reagent, disulfine blue, the excess absorbance of the developed color due to the quaternized polymer over that due to the original polymer would calculate its halogen endgroup content, when both amine and halogen are present as endgroup in the same polymer. During quaternization some amine endgroup is liable to be lost (about 7–10%). This is allowed for by running a control experiment with the polymer in benzene.

RESULTS AND DISCUSSION

Monomer Selectivity

An interesting feature of the ammonia–halogen initiating system is its monomer selectivity, shown in Table I.

The long induction period and low yield in the case of styrene are presumably due to the very limited solubility of the monomer in water. The failure of this initiating system to polymerize acrylonitrile, acrylic acid, and vinyl acetate may arise from the more facile addition of chlorine to these monosubstituted monomers as contrasted with monomers of the type $CH_2{=}CXY$. The same suggestion was made by Bacon[9] and others[10,11] to account for the failure of bisulfite compounds to polymerize such monosubstituted monomers.

Endgroup Analysis

Results of endgroup analysis of poly(methyl methacrylate) and poly(ethyla crylate) obtained by aqueous initiation with the ammonia-halogen system are presented in Table II.

During preliminary investigations[1] we failed to detect the amino endgroup, probably because the incorporation was very low. However, under more favorable experimental conditions and more exhaustive experimentation, 0.23–0.32 amino endgroup per chain of poly(methyl methacrylate) has been found (Table II). The chlorine endgroup has been

TABLE I
Aqueous Polymerization of Vinyl Monomers with Ammonia–Chlorine Initiating System[a]

Monomer	[Monomer], mole/l.	Induction period, min.	Yield in 3 hr. (approx.), %	Intrinsic viscosity
Methyl methacrylate	0.094	Nil	80	1.10
Ethyl methacrylate	0.102	Nil	82	1.15
Methylacrylate	0.201	20	50	0.82
Ethyl acrylate	0.231	Nil	75	0.98
Methacrylic acid	0.238	30	60	0.56
Acrylic acid	0.412	—	No initiation	—
Acrylonitrile	0.220	—	No initiation	—
Acrylamide	0.563	60	20	0.65
Styrene	1 cc./100 cc. water	240	10	1.72
Vinyl acetate	0.134	—	No initiation	—

[a] $[Cl] = 1.30 \times 10^{-3}M$; $[NH_3] = 7.302 \times 10^{-1}M$; 30°C., N_2 atmosphere.

TABLE II
Results of Endgroup Analysis of Polymers Obtained by Aqueous Initiation with Ammonia–Halogen Systems[a]

Halogen	[Halogen], mole/l. $\times 10^3$	[Ammonia], mole/l. $\times 10^2$	$[\eta]$	Endgroups per chain: Amine	Endgroups per chain: Halogen	Endgroups per chain: Total
	Monomer: 0.094*M* methyl methacrylate					
Cl	0.937	5.55	1.57	0.23	0.21	0.44
	1.874	5.55	1.24	0.25	0.28	0.53
	4.686	5.55	0.87	0.24	0.31	0.55
	9.370	5.55	0.64	0.28	0.38	0.66
	1.874	11.10	1.11	0.28	0.26	0.54
	1.874	16.65	0.98	0.32	0.30	0.62
Br	3.31	5.21	0.60	0.24	0.41	0.65
	6.62	5.21	0.48	0.29	0.45	0.74
	13.34	5.21	0.41	0.31	0.44	0.75
	31.30	5.21	0.29	0.32	0.51	0.83
	Monomer: 0.231*M* ethyl acrylate					
Cl	1.302	73.02	0.98	0.05	0.37	0.42
	2.604	73.02	0.73	0.08	0.48	0.56
	3.906	73.02	0.51	0.17	0.51	0.68
	6.510	73.02	0.42	0.24	0.55	0.79
	1.302	146.04	0.40	0.16	0.40	0.56

[a] 30°C., N_2 atmosphere.

found incorporated to the extent of 0.21–0.38 per chain. It is remarkable that response for hydroxyl endgroup was always negative, though in most aqueous polymerization some OH endgroup is generally present. The average total endgroup content per chain was, in all cases, in the vicinity of 0.5. In the case of poly(ethyl acrylate) initiated by an ammonia–chlorine system the increase of amino and halogen endgroup content with increase of halogen concentration is well marked from 0.05 to 0.24 and 0.37 to 0.55 per chain, respectively (Table II).

With bromine–ammonia initiator the yield of poly(methyl methacrylate) ($\approx 40\%$) and the intrinsic viscosity of the polymer are rather low, but the endgroup results are effectively the same as with the ammonia–chlorine system, with the difference that halogen incorporation is somewhat higher, about 0.4–0.5 per chain. The total endgroup content per chain is also somewhat greater than 0.5.

Iodine in combination with ammonia failed to initiate the polymerization of vinyl monomers even in presence of ultraviolet light, probably due to its strong inhibitive tendency.

Effect of Change of pH

In the systems of Table II the pH of the medium was found to lie between 9 and 11; under these conditions polymerization started with practically no induction period. On decreasing the pH of the media by addition of HCl, the induction period increased, while the rate, yield, and intrinsic viscosity decreased as happens in many other cases.[9,12,13] Increase of acidity of the media increases the halogen and amino endgroup content as illustrated in Table III for ethyl acrylate.

TABLE III
Effect of pH on the Endgroup Content of Poly(ethyl Acrylate) Obtained by Initiation with Ammonia–Chlorine System in Aqueous Media[a]

		Endgroup per chain		
pH	$[\eta]$	Amine	Halogen	Total
10.12	0.73	0.08	0.41	0.49
6.00	0.61	0.10	0.45	0.55
3.85	0.59	0.25	0.52	0.77

[a] $[NH_3] = 7.302 \times 10^{-1}M$; $[Cl] = 2.604 \times 10^{-3}M$; $[EA] = 0.231M$; 30°C., N_2 atmosphere.

Mechanism

Any proposed mechanism has to account for the following experimental results: (*1*) absence of hydroxyl endgroups; (*2*) incorporation of amino and halogen endgroups; (*3*) total endgroup content about 0.5 per polymer chain; (*4*) increase of halogen and amine incorporation with decrease of pH.

It appears that the polymerization reaction proceeds through the intermediacy of free radicals, since the reaction is completely inhibited by hydro-

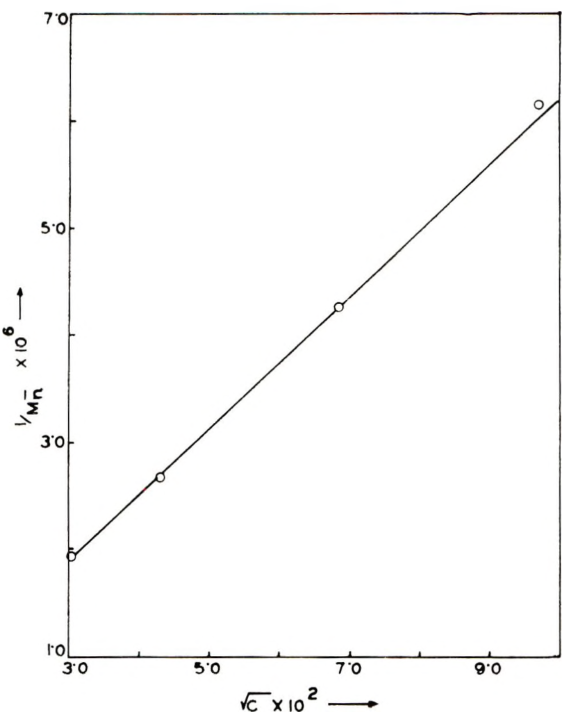
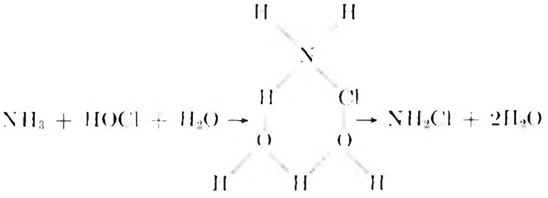


Fig. 1. Reciprocal of number-average molecular weight vs. square root of chlorine concentration (in mole/l.) [MMA] = 0.094 mole/l.; [NH$_3$] = 0.0555 mole/l.

quinone and that the plot of $1/\bar{M}_n$ against the square root of initiator (chlorine) concentration shows a linear relationship (Fig. 1). Well and Morris[14] studied the kinetics of the formation of monochloramines from aqueous chlorine and ammonia in the region of pH 12. From the observed bimolecular nature of the reaction,

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O \qquad (1)$$

they postulated the formation of a cyclic activated complex:



(2)

Although this intermediate structure can account for the formation of both amino and halogen radicals, it fails to explain the very low value of the total endgroups, about 0.5 per polymer chain as obtained in our experiments.

Alternatively, based on the findings of Bhome and Krause,[15] the initiation reaction may be thought of as proceeding through the intermediate formation of an unstable quaternary compound of ammonia as shown in eqs. (3)–(5).

$$X_2 + H_2O \rightleftharpoons HX + HOX \tag{3}$$

$$NH_3 + X_2 \rightarrow [X\overset{+}{N}H_3]X^- \tag{4}$$

$$NH_3 + HOX \rightarrow [H\overset{+}{N}H_3]OX^- \tag{5}$$

These molecular complexes have only transitory existence and decompose immediately, as suggested by Walling and Indictor.[16]

$$[X\overset{+}{N}H_3]X^- \rightarrow \cdot\overset{+}{N}H_3 + X\cdot + X^- \tag{6}$$

$$[H\overset{+}{N}H_3]OX^- \rightarrow \cdot\overset{+}{N}H_3 + H\cdot + OX^- \tag{7}$$

Since these reactions will be operative simultaneously, all the three types of radicals, $\cdot\overset{+}{N}H_3$, $X\cdot$, and $H\cdot$ will be generated at the same time. At higher concentration of X_2, (4) and consequently reaction (6) become predominant, and halogen atom initiation increases at the cost of initiation by hydrogen atom. As a result an increase in the halogen content in the polymer results. On the other hand, as the concentration of X_2 decreases, reaction (5) and accordingly reaction (7) become predominant; initiation by hydrogen atom increases at the cost of halogen atom initiation, and there results a reduction in the halogen content in the polymer. Again, when halogen incorporation increases, hydrogen initiation is suppressed. Consequently increase in halogen incorporation is accompanied with an increase in amine incorporation. As initiation by H atoms is more efficient than by $\cdot\overset{+}{N}H_3$ or $X\cdot$ radicals, there is more preponderance of polymers without endgroup. This accounts for the low value (about 0.5) of the total endgroup per chain as obtained in our experiments.

Lowering of pH shifts the equilibrium of eq. (3) towards the left, thus favoring reactions (4) and (6). Consequently, the probability of hydrogen atom initiation decreases, and somewhat greater incorporation of halogen endgroup accompanied with an increase in amine incorporation results.

With ammonia–bromine initiator the rate, $[\eta]$, and yield are much lower, which may possibly arise from the fact that some substitution and addition as well as termination by bromine radical may be taking place.

Hydroxyl radicals, if generated in the medium, are absent in the polymer endgroup, probably due to the well-known scavenging action of ammonia and amines on oxidizing radicals.

Sincerest thanks are due to Dr. M. K. Saha for his valuable suggestions during the start of the work.

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Mode of Termination in the Copolymerization of Vinyl Acetate–Isobutyl Methacrylate and Methyl Methacrylate–Methyl Acrylate at 60°C.

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Synopsis

The mode of termination in the vinyl acetate–isobutyl methacrylate (VA–IBMA) and methyl methacrylate–methyl acrylate (MMA–MA) copolymerization systems has been investigated at 60°C. by using the dye-interaction technique for functional endgroup estimation. The results show that pairs of poly(vinyl acetate) radicals interact almost exclusively through a disproportionation mechanism. In the homopolymerization of methyl methacrylate and methyl acrylate, about 1.16 and 1.22 carboxyl-containing endgroups per polymer molecule have been estimated, which shows the predominance of disproportionation over combination in these termination reactions. In poly(isobutyl methacrylate) about 1.55 tagged initiator fragments per chain indicate that 29% of the total radicals terminate through the disproportionation mechanism. Cross termination in the (VA–IBMA) copolymerization system occurs almost entirely through combination for monomer feeds richer in isobutyl methacrylate content while for the MMA–MA system, combination is more important at intermediate monomer feed ratios. These results have been discussed in the light of different explanations for the reaction mechanism.

INTRODUCTION

Pairs of polymer radicals can interact either by a combination [eq. (1)] or by a disproportionation [eq. (2)] mechanism:

$$2\ \mathrm{RCH_2CXY^*} \rightarrow \mathrm{RCH_2CXYCXYCH_2R} \tag{1}$$

$$2\ \mathrm{RCH_2CXY^*} \rightarrow \mathrm{RCH{=}CXY} + \mathrm{RCH_2CHXY} \tag{2}$$

where R represents a long polymer chain. Polymers prepared with initiators having a functional group contain one functional endgroup per molecule for the disproportionation reaction and two endgroups per molecule for combination reaction. And, in the absence of other complicating side reactions, the number of functional endgroups per molecule gives a quantitative indication of the relative importance of the two types of termination reactions in the polymerization process.

The mode of termination in the homopolymerization of a number of vinyl monomers has been determined by using different physical and chemical methods, but, with the exception of the styrene–methyl methacrylate system,[1] no other copolymerization system has ever been studied to elucidate the mechanism of the cross-termination reaction. In copolymerization systems, a knowledge of the mode of termination is essential for the correct evaluation of the rate of initiation for proper kinetic analysis. Unless the mechanism is understood, this quantity is subject to an uncertainty of a factor of two. With this end in view, the present investigations on the mode of termination in the copolymerizations of vinyl acetate with isobutyl methacrylate and of methyl methacrylate with methyl acrylate have been carried out at 60°C.

EXPERIMENTAL

Materials

Methyl methacrylate and isobutyl methacrylate (I.C.I. Ltd.) and methyl acrylate (I.C.I. Ltd.) were purified by washing with 5% and 2% caustic soda solutions, respectively, until free from inhibitors, subsequently washed with distilled water, dried over fused calcium chloride, and finally purified by vacuum fractional distillation. Vinyl acetate (Eastman Kodak Co.) was purified as described by Palit and Das.[2]

4,4′-azobis(4-cyanopentanoic acid) was prepared by the method described by Haines and Waters[3] and purified by recrystallization from warm water. The equivalent weight of the purified product was 141 (theory = 140.1).

Recrystallized Calcozine Rhodamine 6GX conc. (C.I. No. 45160) was supplied as a gift sample by I.C.I. Ltd. and used without further purification. AR benzene (B.D.H.) and dimethylformamide (E. Merck) were used after a simple distillation.

Procedures

Osmometry. Osmotic pressure measurements were performed in Pinner-Stabin type osmometers in methyl ethyl ketone solution at 35.75 ± 0.01°C. by a static elevation method with the use of 600 grade ultracella filter membranes.

The number-average molecular weight of the polymers was calculated from osmotic pressure data by using the equation

$$(\pi/c)^{1/2} = (\pi/c)_0^{1/2}[1 + (\Gamma_2/2)c]$$

where c is expressed in grams per liter.

Polymerization Experiments. Reaction mixtures containing different feed ratios of monomers were charged in Pyrex sealing tubes, freed from dissolved oxygen by alternate freezing and thawing, and finally sealed under vacuum. The rate of polymerization was varied by using different concentrations of 4,4′-azobis(4-cyanopentanoic acid) and the reaction was carried out at 60 ± 0.05°C. up to about 5% conversion. The polymer obtained was isolated by double precipitation with methanol or petroleum ether and dried *in vacuo* at 50°C. The majority of the experiments were performed in duplicate runs. Since the solubility of the initiator in the monomers is very small, dimethylformamide was used as a solvent to the extent of 10% and 33.3% of the total volume in the VA–IBMA and MMA–MA copolymerization systems, respectively.

Dye-Interaction Experiment. Prior to the dye-interaction experiment, the polymers were subjected to rigorous purification by precipitating the polymer twice from a benzene–dimethylformamide mixture (about 10:1 by volume) and subsequently twice from benzene solution alone with methyl alcohol or petroleum ether as the precipitant.

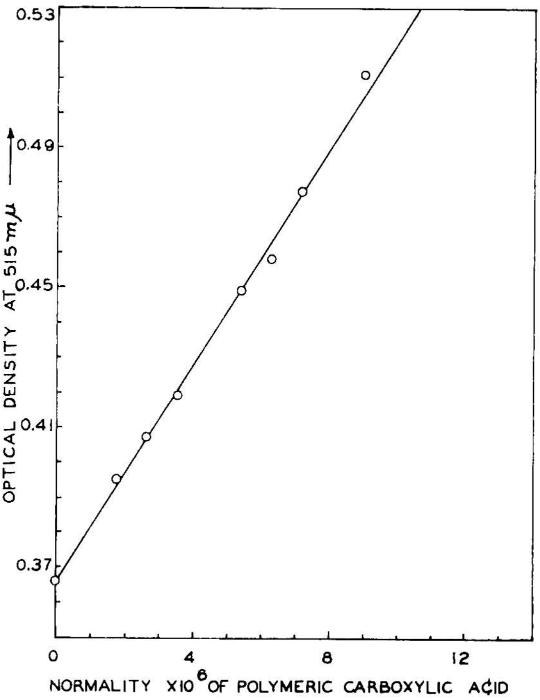

Fig. 1. Calibration curve for the estimation of carboxyl-containing endgroups in polymers.

Since 4,4′-azobis(4-cyanopentanoic acid) was used as the thermal sensitizer, polymers prepared are expected to have $COOH(CH_2)_2—C(CH_3)CN$ as an endgroup. The amount of carboxyl groups in the polymer can be easily estimated by the interaction of the polymer solution with the dye reagent, Rhodamine 6G. Details of the theory and the experimental method of the dye-interaction technique have been described elsewhere.[4,5] The color developed by treatment of polymer solution with dye reagent has been measured spectrophotometrically and the amount of carboxyl endgroups calculated by comparison of the optical density with a calibration curve (Fig. 1) for poly(methyl methacrylate) having a known amount of carboxyl endgroups.[6] The low molecular weight polymer used for calibration was prepared by using 4,4′-azobis(4-cyanopentanoic acid) as the initiator and ferric chloride as the chain terminator. The amount of carboxyl groups in the polymer was estimated by repeated titrations in an acetone–water mixture.

Method of Calculation

Calculation of Number of Carboxyl-Containing Endgroups per Molecule. The number of carboxyl-containing endgroups per molecule n has been calculated by using the relation

$$n = xM/c$$

where x is the equivalent carboxyl group concentration (in moles per liter), c is the concentration of polymer solution in benzene (in grams per liter), and M is the molecular weight of polymer.

Calculation of Fraction of Disproportionation and Combination. It is easy to show[1] that the fractions of radicals undergoing disproportionation and combination are, respectively, $(2 - n)/n$ and $2(n - 1)/n$.

Of all the interradical reactions in a copolymerization system of monomers M_1 and M_2, the fraction occurring by M_1^*–M_1^* interaction is $k_{t_{11}}[M_1^*]^2/R_i$, the fraction by M_2^*–M_2^* interaction is $k_{t_{22}}[M_2^*]^2/R_i$ and that by M_1^*–M_2^* interaction is $k_{t_{12}}[M_1^*][M_2^*]/R_i$. From a knowledge of the fractions of disproportionation for total interradical reactions (from copolymerization studies) and for M_1^*–M_1^* and M_2^*–M_2^* interactions (from homopolymerization studies), the fraction of disproportionation for M_1^*–M_2^* interaction can be calculated provided the reactivity ratios and propagation and termination rate constants for the monomers are known. Details of the method of calculation have been described by Bevington et al.[1]

In the copolymerization system of isobutyl methacrylate (M_1) and vinyl acetate (M_2) at 60°C., the following values have been chosen for the different rate constants and reactivity ratios: $k_{p_{11}} = 589$ l./mole-sec.,[7] $k_{p_{22}} = 3600$ l./mole-sec.,[7] $k_{t_{11}} = 7.84 \times 10^6$ l./mole-sec., $k_{t_{22}} = 2.1 \times 10^8$ ./mole-sec.,[7] $r_1 = 29.8$, $r_2 = 0.025$.[8] The corresponding values for the copolymerization system of methyl methacrylate (M_1) and methyl acrylate (M_2) at 60°C. are $k_{p_{11}} = 589$ l./mole-sec.,[7] $k_{p_{22}} = 2090$ l./mole-sec.,[9] $k_{t_{11}} = 1.87 \times 10^7$ l./mole-sec.,[10] $k_{t_{22}} = 4.7 \times 10^6$ l./mole-sec.,[9] $r_1 = 1.8$, $r_2 = 0.35$.[11]

The propagation rate constant in the polymerization of alkyl methacrylates is known to be independent of the size of the alkyl group,[12] and the same value of k_p has been used for both the methacrylates.

RESULTS AND DISCUSSION

Tables I–III show the results of the investigations on the copolymerization of isobutyl methacrylate and vinyl acetate at 60°C. while Tables IV–VI show those for the copolymerization of methyl methacrylate and methyl acrylate at 60°C.

TABLE I
Copolymerization of Isobutyl Methacrylate (IBMA) and Vinyl Acetate (VA) at 60°C.

Sample	Mole fraction of IBMA in feed	Initiator concn., g./l.	$R_p \times 10^5$, mole/l.-sec.	Osmotic molecular weight $\times 10^{-5}$	Concn. polymer solution in dye-interaction test, g./l.	O.D. at 515 mμ	No. carboxyl-containing endgroups per molecule
1	1	1.0	21.36	4.66	1.02	0.418	1.55
2	1	1.5	26.34	3.71	1.00	0.434	1.63
3	1	0.5	14.72	6.62	2.00	0.434	1.46
4	0.635	1.0	13.40	4.12	1.912	0.487	1.70
5	0.448	1.0	9.94	3.58	1.800	0.498	1.71
6	0.293	1.0	7.22	2.71	1.330	0.503	1.81
7	0.162	1.0	4.13	2.05	1.192	0.531	1.84
8	0	0.2	44.11	1.26	0.960	0.478	0.96
9	0	0.1	31.37	1.83	1.0	0.441	0.90

TABLE II
Copolymerization of Isobutyl Methacrylate (M_1) and Vinyl Acetate (M_2) at 60°C.

			Fraction of interradical reactions		
Sample	$[M_1^*] \times 10^8$, mole/l.	$[M_2^*] \times 10^{12}$, mole/l.	M_1^*–M_1^* ($= f_1$)	M_2^*–M_2^* ($= f_2$)	M_1^*–M_2^* ($= 1 - f_1 - f_2$)
4	5.24	4.12	0.276	≈0	0.724
5	4.79	8.08	0.270	≈0	0.730
6	4.52	14.96	0.240	≈0	0.760
7	3.68	26.05	0.210	≈0	0.790

TABLE III
Copolymerization of Isobutyl Methacrylate (M_1) and Vinyl Acetate (M_2) at 60°C.

Sample	Average no. carboxyl-containing endgroups per molecule	Fraction of disproportionation for total interradical reactions	Fraction of disproportionation calculated for M_1^*–M_2^* reaction
1, 2, 3	1.55	0.290	—
4	1.70	0.180	0.137
5	1.71	0.170	0.126
6	1.81	0.105	0.047
7	1.84	0.087	0.033
8, 9	0.93	≈1	—

In homopolymerization or copolymerization experiments with different monomers, the initiator concentrations have been kept in such a range that primary radical termination or thermal polymerization is negligible.

Dimethylformamide has a low chain transfer coefficient (about 2×10^{-5}) with poly(methyl methacrylate) radicals; but, unfortunately, the magnitude of the coefficient with other polymer radicals is not known accurately. We have, therefore, neglected the effect of the solvent in the calculation of functional endgroups per polymer chain.

Molecular weight measurement by osmometry and functional endgroup estimation by the dye-interaction technique were performed on the same polymer sample so that the loss of low molecular weight polymer in the purification process should not affect the number of initiator fragments per polymer molecule.

Homotermination

In the polymerization of isobutyl methacrylate at 60°C., about 1.55 carboxyl-containing endgroups are found per polymer molecule. This shows that in the termination of poly(isobutyl methacrylate) radicals, both combination and disproportionation mechanisms are operative, and about 29% of the total reaction occurs through disproportionation.

TABLE IV
Copolymerization of Methyl Methacrylate (MMA) and Methyl Acrylate at 60°C.

Sample	Mole fraction of MMA in feed	Initiator concn., g./l.	$R_p \times 10^5$, mole/l.-sec.	Osmotic molecular weight $\times 10^{-5}$	Concn. of polymer solution in dye-interaction test, g./l.	O.D. at 515 mμ	No. carboxyl-containing endgroups per molecule
1	1	2.0	23.03	2.47	0.5	0.401	1.14
2	1	1.5	19.76	3.06	0.5	0.395	1.16
3	1	0.5	11.13	5.62	1.0	0.398	1.18
4	0.718	1.5	21.13	2.96	1.0	0.438	1.40
5	0.459	1.5	23.92	2.85	1.0	0.447	1.50
6	0.221	0.5	18.43	3.17	1.0	0.431	1.33
7	0	0.2	34.12	8.14	2.0	0.415	1.30
8	0	0.5	55.82	4.35	1.0	0.409	1.22
9	0	0.1	22.35	13.44	2.0	0.392	1.14

TABLE V
Copolymerization of Methyl Methacrylate (M_1) and Methyl Acrylate (M_2) at 60°C.

			Fraction of interradical reactions		
Sample	$[M_1^*] \times 10^8$, mole/l.	$[M_2^*] \times 10^9$, mole/l.	$M_1^*-M_1^*$ ($= f_1$)	$M_2^*-M_2^*$ ($= f_2$)	$M_1^*-M_2^*$ ($= 1 - f_1 - f_2$)
4	5.250	1.130	0.53	≈0	0.47
5	5.067	3.268	0.40	≈0	0.60
6	2.737	5.314	0.20	0.002	0.80

TABLE VI
Copolymerization of Methyl Methacrylate (M_1) and Methyl Acrylate (M_2) at 60°C.

Sample	No. average carboxyl-containing endgroups per molecule	Fraction of disproportionation for total interradical reactions	Fraction of disproportionation calculated for $M_1^*-M_2^*$ interaction
1, 2, 3	1.16	0.72	—
4	1.40	0.43	0.103
5	1.50	0.33	0.070
6	1.33	0.50	0.443
7, 8, 9	1.22	0.64	—

The results for vinyl acetate polymerization indicate about one initiator fragment per polymer chain and suggest the exclusive occurrence of the disproportionation mechanism. Within experimental error, this result agrees well with the results of radiochemical studies on vinyl acetate polymerization at 60°C. by Funt and Pasika.[13] Previous investigations of this system by Burnett et al.[14] indicated an unusual variation in the number of fragments from 1.6 to 6.0 per molecule in the temperature range of +27°C. to −38°C. An increase in the number of initiator fragments in poly(vinyl acetate) with decrease in temperature has been mentioned by Funt and Pasika[13] also.

In the present study, about 1.16 and 1.22 carboxyl-containing endgroups per poly(methyl methacrylate) and poly(methyl acrylate) chains, respectively, have been estimated to be present. The result with poly(methyl methacrylate) is in good agreement with the previous tracer technique studies on this system.[1,15,16] There is no other reported investigation on the mode of termination in methyl acrylate polymerization to compare with our results.

The availability of hydrogen atoms at both the penultimate carbon atom in the chain and at the α-methyl group together with the steric effects due to methyl and ester groups on the α-carbon may explain the importance of the disproportionation reaction in the interaction of poly(methyl methacrylate) radicals. However, such an explanation fails to account for the lesser importance of disproportionation in the case of isobutyl methacrylate which has the same number of available hydrogen atoms but a greater steric effect due to the bulkier isobutyl ester group.

Although the number of available hydrogen atoms at the α-carbon atom of vinyl acetate or methyl acrylate is less than that for alkyl methacrylates, the polymer radicals of vinyl acetate and methyl acrylate are very much more reactive than the methacrylate radicals. This increased reactivity of the radicals may account for the predominance of disproportionation in the case of the two monomers.

Cross-termination

Results show that the cross-termination reaction is very much favored in the copolymerization of vinyl acetate and isobutyl methacrylate at 60°C., and about 72–80% of the total inter-radical reactions occur by a cross-termination mechanism. The contribution of terminations by interaction of poly(vinyl acetate) radicals is, however, negligible. From Table III it is evident that cross termination in the copolymerization of isobutyl methacrylate and vinyl acetate occurs almost entirely by the combination mechanism in case of monomer feeds richer in vinyl acetate content. At the lowest vinyl acetate content studied, only about 14% of the cross termination is through disproportionation.

It has been argued by Ayrey et al.[17] that polar effect is important in interradical interactions and that the electronegative polystyrene radical and the electropositive polymethyl methacrylate radical are mutually attracting so that the combination type of cross termination is very much favored in the copolymerization of this system. However, such an interpretation fails to account for the results obtained in the copolymerization of isobutyl methacrylate and vinyl acetate.

In the copolymerization of methyl methacrylate and methyl acrylate, the importance of the cross-termination reaction increases with the concentration of methyl acrylate in the feed; combination is relatively favored in cross termination at intermediate monomer feed ratios.

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Aminimides. V. Preparation and Polymerization Studies of Trimethylamine-4-Vinylbenzimide

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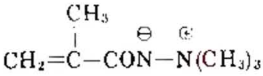
Synopsis

Trimethylamine-4-vinylbenzimide (TAVBI) has been homo- and copolymerized with styrene, methyl methacrylate, and hydroxypropyl methacrylate by free-radical initiators to soluble, low molecular weight polymers containing pendant aminimide groups along the backbone of the polymer molecules. The reactivity ratios in the copolymerization of TAVBI (M_1) with styrene (M_2) were determined: $r_1 = 0.63 \pm 0.07$, $r_2 = 0.47 \pm 0.05$. The Alfrey-Price Q and e values for TAVBI were also calculated: $Q = 0.88$, $e = 0.31$. This introductory work indicates that TAVBI has potential for the preparation of a wide variety of reactive polymers.

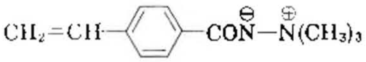
INTRODUCTION

Earlier, the preparation, homo- and copolymerization properties of trimethylamine methacrylimide (TAMI) were reported by this laboratory.[1] Continuing our studies, we now report on the preparation and polymerization studies of trimethylamine-4-vinylbenzimide (TAVBI).



$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-CO\overset{\ominus}{N}-\overset{\oplus}{N}(CH_3)_3$$

TAMI



TAVBI

It has been amply demonstrated by various research papers that pyrolysis of trimethyl aminimides gives isocyanates.[2-5] For example, pyrolysis of TAMI gives an excellent yield of isopropenyl isocyanate.[2] As previously suggested, it is apparent that monomers such as TAMI and TAVBI should have utility in the preparation of a wide variety of new, interesting and potentially useful "reactive" polymers.

The present work was undertaken to prepare TAVBI and study some of the homo- and copolymerization characteristics of this new monomer and obtain an estimate of its Alfrey-Price Q and e values.

EXPERIMENTAL

The NMR spectra were obtained on a Varian A-60 spectrometer with tetramethylsilane as internal standard, and the infrared spectra were obtained by using a Perkin-Elmer Model 237B spectrophotometer. The melting points, uncorrected, were obtained on a Thomas-Hoover capillary melting point apparatus.

Monomers

Trimethylamine-4-vinylbenzimide (TAVBI). The monomeric aminimide was prepared from 4-vinylbenzoic acid[6] by using the procedures previously reported.[2–5] The acid chloride was prepared by treatment of the carboxylic acid with an excess of thionyl chloride for 48–60 hr at room temperature. After removal of the thionyl chloride with a rotary evaporator under reduced pressure, the yellow oil was used directly.

The acid chloride was also prepared by treatment of sodium *p*-vinylbenzoate with oxalyl chloride in benzene.[7]

1,1-Dimethyl-2-(4-vinylbenzoyl)hydrazine. The acid chloride, 4-vinylbenzoyl chloride, was prepared from 5 g (0.034 mole) of 4-vinylbenzoic acid and 6 ml of thionyl chloride. The crude acid chloride was dissolved in Skelly F, and the milky solution was filtered through filter aid to remove the polymeric material. Removal of the Skelly F solvent gave 5.4 g (88%) of the acylhalide.

The acid chloride dissolved in 10 ml of Skelly F was added dropwise to a solution of 6 g of 1,1-dimethylhydrazine in 100 ml of Skelly F maintained at 10°C. After addition (35 min) the mixture was stirred at room temperature for an additional 19 hr. The mixture was filtered and the collected solid washed with Skelly F and then dried. The solid was washed with water to remove the 1,1-dimethylhydrazine hydrochloride and dried under reduced pressure to obtain a 4.14 g (68%) yield of product, mp 122–125°C. Recrystallization from benzene gave a white, crystalline solid, mp 125.5–126°C. The infrared spectrum (halocarbon mull) exhibited the expected bands for NH at 3210 cm^{-1}. The NMR spectrum ($CDCl_3$, τ) showed a singlet at 7.33 ppm, vinyl multiplet between 4.80 and 4.00 ppm, a broad singlet at 3.00 ppm, and a quartet between 2.67 and 2.17 ppm, in an expected ratio of 6:3:1:4, respectively.

ANAL. Calcd for $C_{11}H_{14}N_2O$: C, 69.45%; H, 7.42%; N, 14.72%. Found: C, 69.40%; H, 7.39%; N, 14.62%.

1,1,1-Trimethyl-2-(4-vinylbenzoyl)hydrazinium tosylate. In a 300-ml flask was placed 5 g (0.026 mole) of 1,1-dimethyl-2-(4-vinylbenzoyl)-hydrazine, 6 g of methyl *p*-toluenesulfonate and 125 ml of anhydrous acetonitrile. The solution was heated to reflux and a trace of hydroquinone added after $^1/_2$ hr. After heating at reflux for an additional 5 hr, the solution was cooled and allowed to stand at room temperature for 12 hr. The crystals that formed were collected by suction filtration to obtain a 5.3 g yield of tosylate. Concentration of the mother liquor gave an additional 3.0 g. Recrystallization of the combined fraction from a methanol–benzene solution gave 8.1 g (82%) yield of analytically pure, white crystalline tosylate, mp 166–168°C. The infrared spectrum exhibited the expected bands for the NH grouping at 3150 cm^{-1}, N—CH grouping at 2780 cm^{-1}, vinyl at 1625 cm^{-1}, and the carbonyl grouping at 1675 cm^{-1}. The NMR spectrum ($CDCl_3$, τ) showed a singlet at 6.10 ppm, singlet at 7.70 ppm, vinyl multiplet at 4.70–4.07 ppm, and complex multiplets between 3.50 and 2.25 ppm in the expected ratio of 9:3:3:9.

ANAL. Calcd for $C_{19}H_{24}N_2O_4S$: C, 60.61%; H, 6.44%; N, 7.44%. Found: C, 60.78%; H, 6.53%; N, 7.43%.

Trimethylamine-4-vinylbenzimide (TAVBI). A solution of 7.2 g (0.0196 mole) of 1,1,1-trimethyl-2-(4-vinylbenzoyl)hydrazinium tosylate in 35 ml of anhydrous methanol was titrated to the phenolphthalein endpoint with 1.108*N* alcoholic KOH requiring 16.9 ml, 96% theoretical base. The mixture was chilled in an ice bath, potassium tosylate filtered from the solution, and the methanol removed on a rotary evaporator. The product was taken up in chloroform, dried over sodium sulfate and filtered. Removal of the chloroform solvent yielded a solid which was dissolved in hot benzene. Cyclohexane was added to the hot solution until a gummy yellow material precipitated. After decanting the hot solution, more cyclohexane was added until turbid. Cooling gave white, fluffy needles, 3.30 g (79.5%), mp 122–124°C. The infrared spectrum (halocarbon mull) exhibited bands for the vinyl grouping at 1630 cm^{-1} and the carbonyl grouping at 1575 cm^{-1}. The NMR spectrum ($CDCl_3$, τ) showed a singlet at 6.55 ppm, the vinyl multiplet between 4.75 and 2.70 ppm, and a quartet centered at 2.16 ppm, in the expected ratio of 9:3:4.

ANAL. Calcd for $C_{12}H_{16}N_2O$: C, 70.57%; H, 7.90%; N, 13.72%. Found: C, 70.58%; H, 8.00%; N, 13.47%.

Comonomers. The monomers methyl methacrylate and styrene (commercially obtained) were purified by distillation under nitrogen through a 12 in. Vigreux column immediately before use. The hydroxypropyl methacrylate was used as received from Rohm and Haas Company.

Solvents and Initiators

All of the solvents used in the polymerizations were purified according to standard procedures. Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol.

DTA and TGA

Differential thermal and thermogravimetric analyses were obtained on finely divided samples by use of a du Pont 900 DTA and 950 TGA unit. Alumina was employed as a reference material, and the analyses were performed under nitrogen from 0 to 500°C with a heating rate of 20°C/min.

Titration

The nonaqueous titration procedure used in this work is a standard procedure developed for amine titration. The amine is titrated in a suitable nonaqueous solvent (such as glacial acetic acid) with standardized perchloric acid with gentian violet indicator. The aminimide functional group is neutralized according to the following equation:

$$—\mathrm{CO}\overset{\ominus}{\mathrm{N}}—\overset{\oplus}{\mathrm{N}}(\mathrm{CH_3})_3 + \mathrm{HClO_4} \rightarrow \mathrm{CONH}—\overset{\oplus}{\mathrm{N}}(\mathrm{CH_3})_3\ \mathrm{ClO_4}^{\ominus}$$

Therefore, from a knowledge of the weight of polymer titrated and equivalents of perchloric acid used, the TAVBI unit fractions in the copolymers may be calculated. The titrations performed herein used a 50:50 glacial acetic–acetic anhydride mixture, 0.1054*N* perchloric acid, and gentian violet indicator.

Polymerizations

Homopolymerization (Trial 1, Table I). The polymerization solution was poured into 50 ml of acetone, forming a gummy mass. The liquid was decanted, and 50 ml of additional acetone was added; a brittle, powdery solid was formed. The infrared spectrum of a film cast from methanol showed no vinyl grouping absorption and showed absorption at 1575 cm^{-1} due to the carbonyl. Thermogravimetric analyses (TGA) shows the polymer losing 95% of theoretical trimethylamine between 180 and 220°C. A film cast from chloroform, when heated at 180°C for 1 hr showed disappearance of the 1575 cm^{-1} aminimide band and appearance of the isocyanate infrared absorption band at 2250 cm^{-1}.

Homopolymerization (Trial 2, Table I). The polymerization solution was reduced to a gummy mass on the rotary evaporator, the residue dissolved in 10 ml of methanol and precipitated from acetone. The results were the same as for trial 1.

Homopolymerization (Trial 3, Table I). After the 48-hr heating period, most of the polymer had precipitated as a heavy oil. The heavy oil was dissolved in 25 ml of methanol and precipitated from ether. The hard solid was washed with ether and collected by filtration, giving 8.0 g of solid. A sample was redissolved in methanol, reprecipitated from ether, dried, and analyzed. The infrared spectrum (halocarbon mull) showed the expected aminimide carbonyl absorption band at 1575 cm^{-1} and the NMR spectrum showed no vinyl protons. Further, thin-layer chromatography (TLC) showed no remaining monomer. The DTA curve exhibited a strong exotherm at 180°C, and the TGA curve showed a weight loss of 1.45 mg in a 5.10 mg sample between 180 and 220°C [calcd for $\mathrm{N(CH_3)_3}$ loss: 1.57 mg].

TAVBI–Styrene Copolymerization (Trial 4, Table I). The polymerization solution was poured into 400 ml of ether and the polymer collected. After washing with ether and five 50 ml portions of 2% $\mathrm{CHCl_3}$ in ether, the polymer was shown to be free of monomer by TLC. The infrared spectrum (halocarbon mull) showed carbonyl absorption at 1575 cm^{-1} and aromatic hydrogens. The NMR spectrum ($\mathrm{CDCl_3}$) showed no vinyl

TABLE I
General Polymerizations (TAVBI)[a,b]

Monomer, g (mole)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7
Methyl methacrylate	—	—	—	—	—	16	2.(0.02)
Styrene	—	—	—	8(0.077)	8(0.077)	—	—
Hydroxypropyl methacrylate	—	—	—	—	—	3(0.02)	—
TAVBI	0.5(0.0025)	0.5(0.0025)	10(0.049)	4(0.020)	4(0.020)	3(0.015)	0.2(0.00098)
Solvent, ml							
Distilled water	10	—	10	—	—	—	—
Methyl ethyl ketone	—	10	—	—	—	—	—
Acetonitrile	—	—	40	40	40	30	—
Initiator (AIBN), g[c]	0.04	0.04	0.2	0.08	0.2	0.2	0.02
Polymerization conditions							
Time, hr	16	16	48	22	72	55	48
Temp., °C	100	60	70	70	70	70	70
Conversion, %	—	—	80	42	70	90	50

[a] All polymerizations were carried out under nitrogen in sealed serum bottles with AIBN initiator, unless otherwise indicated.

[b] All polymers were checked for absence of TAVBI by TLC. The TLC method employed silica-gel coated plates, methanol solvent, and I_2 developer.

[c] The AIBN was dissolved in 1 ml of AR acetone and the initiator solution added to the aqueous polymerization systems.

protons. The elemental analysis indicated that the polymer consisted of about 1.7 styrene to 1 TAVBI unit (calcd: N, 5.14%; found: N, 5.16%).

The DTA curve exhibited an exotherm at 185°C. The TGA curve indicated a weight loss of 0.21 mg [calcd for $N(CH_3)_3$ loss, 0.23 mg.] between 170 and 220°C, which was in good agreement with the other analyses.

TAVGI–Styrene Copolymerization (Trial 5, Table I). The polymerization solution was poured into 400 ml of ether and the polymer collected. The analyses results were the same as in trial 4.

TAVBI—Methyl Methacrylate–Hydroxypropyl Methacrylate Terpolymer (Trial 6, Table I). The polymerization solution was diluted with 30 ml of acetonitrile and precipitated from 2% ethanol in ether. After decanting the ether solution from the gummy mass, the addition of 200 ml of additional ether caused the polymer to solidify, forming a brittle granular solid. The polymer was ground in a mortar and pestle and washed with ether. After air drying, 18 g of solid was isolated. No monomer was present as indicated by TLC. The infrared spectrum (film) showed hydroxyl absorption bands at 3510 and 3420 cm^{-1} and carbonyl absorption bands at 1720 cm^{-1} (ester) and 1575 cm^{-1} (aminimide). The analysis indicated that the polymer contained 15% of aminimide (calcd: N, 1.87%; found: N, 2.02%). The monomer ratio in the polymer was estimated at 5:1:1, methyl methacrylate:hydroxypropyl methacrylate: TAVBI. Differential thermal analysis (endotherm maximum 223°C, onset 170°C) and TGA indicated that the polymer lost trimethylamine (0.25 mg on a 5.49 mg sample), in good agreement with the expected loss (calcd: 0.3 mg).

A film cast from chloroform solution was heated at 180°C for 2 hr, and the infrared spectrum showed the disappearance of the 1575 cm^{-1} aminimide carbonyl absorption band and the appearance of the band at 1720 cm^{-1} attributable to the formation of the urethane linkage.

TAVBI–Methyl Methacrylate Copolymerization (Trial 7, Table I). The polymerization solid wax dissolved in 20 ml of chloroform and precipitated from methanol. After two additional precipitations from methanol, the white solid, after drying *in vacuo*, was obtained in a 1.1 g yield. The infrared spectrum (film from chloroform) indicated ester at 1725 cm^{-1}, aromatic ring at 1600 cm^{-1}, and aminimide carbonyl at 1575 cm^{-1}. The DTA curve showed onset of exotherm at 160°C, and the TGA curve showed a weight loss of 1.2 mg [calcd. for $N(CH_3)_3$ loss, 1.0 mg] on an 18.2-mg sample over a temperature range of 160–225°C.

The elemental analysis indicated that the polymer consisted of about 4 methyl methacrylate to 1 TAVBI unit (calcd: N, 2.45%; found: N, 2.38%).

TAVBI–Styrene Copolymerizations (Table II). Polymerizations were terminated by pouring the contents of each serum bottle into a large volume of ether. The precipitated polymers were collected, washed several times with ether, and checked for purity by TLC. All polymers showing traces

TABLE II
Reactivity Study of TAVBI

Run no.[a,b,c]	TAVBI, mole	Styrene, mole	Mole ratio	N, %	TAVBI, wt-% (by %N)	TAVBI, wt-% (by titration)	TAVBI, mole-% polymer[d]	$F = M_1/M_2$ (mole ratio polymer)
I	0.01	0.09	$^1/_9$	3.50	25.20	24.90	14.97	0.1760
II	0.02	0.08	$^1/_4$	5.51	40.00	38.99	24.90	0.3316
III[e]	0.03	0.07	$^3/_7$	7.09	51.50	51.17	34.91	0.5036
IV[e]	0.04	0.06	$^2/_3$	8.59	62.50	60.95	45.07	0.8191
V[e]	0.05	0.05	$^1/_1$	9.47	69.00	69.38	53.38	1.1450
VI	0.06	0.04	$^3/_2$	10.46	76.50	77.35	62.94	1.6983
VII	0.07	0.03	$^7/_3$	11.14	81.5	81.61	62.27	2.2541
VIII	0.04	0.01	$^4/_1$	11.66	85.5	85.58	75.09	3.0144

[a] Copolymerizations run under nitrogen in acetonitrile solvent (60 ml, run 8 had 50 ml) at 70 ± 0.5°C for 3 hr in 100-ml serum bottles with AIBN initiator (0.11 g run, 8 had 0.08 g).

[b] Due to isolation and purification problems, conversions are estimated for all runs at <15%.

[c] All polymers were checked for purity, i.e., absence of TAVBI, by TLC. The TLC method employed silica-gel coated plates, methanol solvent, and I_2 developer.

[d] TAVBI mole-% values were calculated from the average of the two TAVBI wt-% values determined from the %N and titration data.

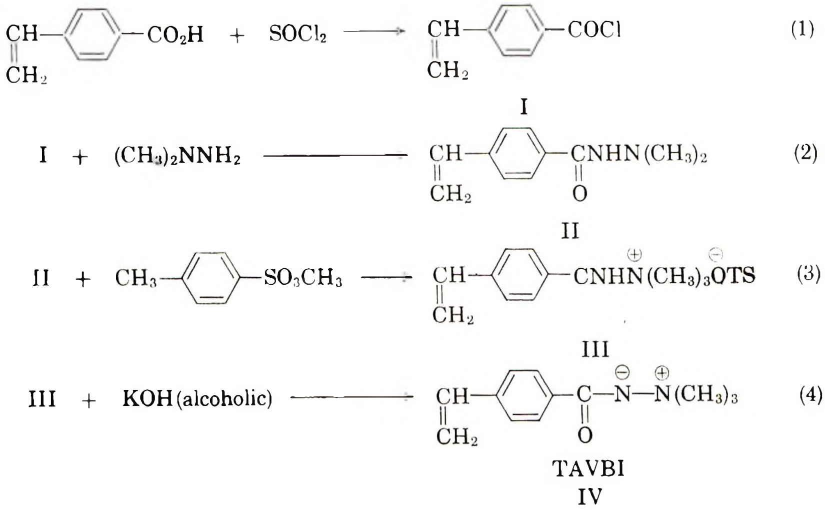
[e] Runs 3, 4, and 5 gave polymers with inherent viscosities of 0.05, 0.04, and 0.09, respectively, in CH_3CN (25°C; 0.05 g/100 ml).

of TAVBI were extracted with ether until TLC gave a negative indication of TAVBI. All polymers were dried *in vacuo* (0.1 mm Hg) for 24 hr and analyzed for TAVBI content by both per cent nitrogen determination and titration of the aminimide functional group (Table II). The values (see Table II, columns 6 and 7) determined by the two analysis procedures were in close agreement.

RESULTS AND DISCUSSION

Monomer Synthesis and Monomer Properties

Trimethylamine-4-vinylbenzimide (TAVBI) was prepared in fair yields according to the reaction scheme shown in eqs. (1)–(4).



Trimethylamine-4-vinylbenzimide (IV) exhibits excellent solubility in water, alcohols, acetonitrile, chloroform, dimethylsulfoxide and tetrahydrofuran, similar to the solubility properties previously reported for trimethylamine methacrylimide.[1]

Trimethylamine-4-vinylbenzimide has good thermal stability and long shelf life. For example, there is no evidence of polymer formation after long periods of storage in the dark at room temperature. The monomer can be recrystallized from benzene–cyclohexane mixtures or sublimed *in vacuo* without apparent polymerization or decomposition. Differential thermal and thermogravimetric analysis indicates that the monomer starts to decompose at ca. 175°C and decomposes rapidly at 200°C.

Polymerization

Some of the results from the initial homo- and copolymerization screening experiments on TAVBI are shown in Table I.

Homopolymerization of TAVBI was accomplished in both aqueous and nonaqueous solutions with AIBN as initiator. Both the infrared and

NMR spectra of the polymers showed no C=C double bonds but the presence of the aminimide moiety. Differential thermal and thermogravimetric analysis indicates the homopolymer starts to decompose, i.e., to lose trimethylamine, at ca. 170°C. TGA indicated further the polymer lost ca. 29% of its weight when heated from 170 to 200°C (theory, 30.8%).

Initial experiments (Table I) indicate that TAVBI can be copolymerized with a variety of other vinyl monomers to give water-soluble, low molecular weight polymers. The presence of the aminimide group $[\text{—CO}\overset{\ominus}{\mathrm{N}}\overset{\oplus}{\mathrm{N}}(\mathrm{CH_3})_3]$ in the copolymers was well established by nitrogen determination, infrared, NMR, and TGA analyses. On the basis of determinations of nitrogen content, these initial copolymerization experiments suggest that TAVBI is more reactive than methyl methacrylate and has approximately the same reactivity as styrene. Differential thermal and thermogravimetric analysis indicate that the copolymers start to lose trimethylamine at ca. 175°C.

Determination of Monomer Reactivity Ratios

The composition of the monomer feeds and the copolymers obtained, for the TAVBI–styrene system, are summarized in Table II. From these results, the monomer reactivity ratios were obtained by the method of Fineman and Ross:[8] $r_1 = 0.63 \pm 0.07$, $r_2 = 0.47 \pm 0.05$.

In Figure 1 the M_1 (TAVBI) in the monomer feed is plotted against the

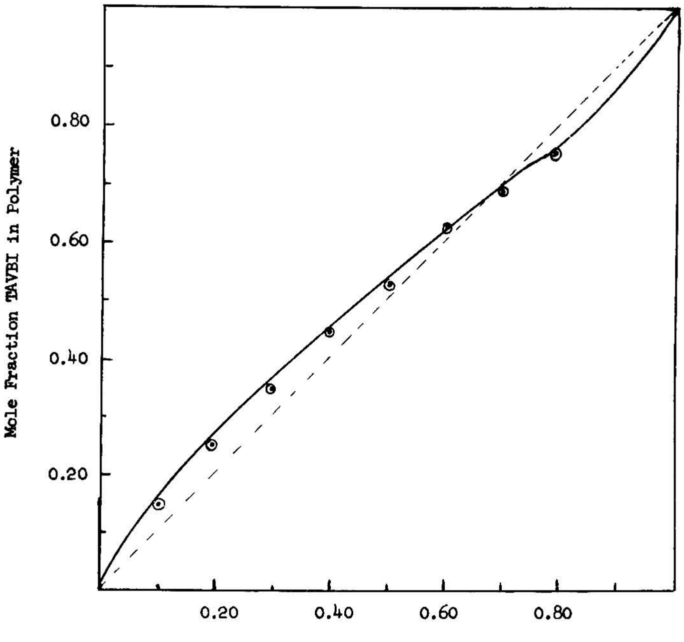


Fig. 1. Copolymer composition curve in the copolymerization of TAVBI–styrene.

corresponding molar content of m_1 in the copolymer. The line in the figure was calculated from the monomer reactivity ratios and the spots were from experimental data.

The Alfrey-Price Q and e values[9] for TAVBI were obtained from the monomer reactivity ratios in the copolymerization with styrene: $Q = 0.88$, $e = 0.31$. The Q and e values of styrene[10] used in the calculations were $Q = 1.0$, $e = -0.8$.

The Q and e values of some other modified styrene monomers are listed, along with those for TAVBI, in Table III. The introduction of the *para* $[\text{—CO}\overset{\ominus}{\text{N}}\text{—}\overset{\oplus}{\text{N}}(\text{CH}_3)_3]$ group has a mild deactivating influence on the general reactivity of the styrene monomer. Further, the introduction of the strong electron-withdrawing group changes the sign of the e value of styrene from a -0.9 to 0.31. The change in sign of the e value and its magnitude are quite in line with values for the other substituted styrene monomers.

Strong alternation occurs in the TAVBI–styrene copolymer, as predicted by the r_1 and r_2 values and supported by the crossover on the copolymer composition curve (Fig. 1). This is expected for two monomers, one of which can give rise to a radical of high electron density and one having a double bond of low electron density.

The TAVBI monomer was used to prepare a terpolymer consisting of TAVBI, methyl methacrylate, and hydroxypropyl methacrylate. The presence of hydroxyl and aminimide moieties in the terpolymer was established by infrared analysis. In addition, nitrogen determination and TGA also demonstrated the presence of the aminimide group. It was demonstrated that the polymer could be deposited as a coating and crosslinked with heat. Changes in the infrared spectra of the heated films supported the assumption that crosslinking occurred by formation of urethane bonds. This brief introductory work lends credence to the suggestion that TAVBI should have utility in the preparation of "reactive" polymers.

TABLE III

Q and e Values of TAVBI and Other Styrene Monomers

Monomer	e	Q
p-Dimethylaminostyrene	−1.37	1.51
p-Methoxystyrene	−1.11	1.36
p-Acetylaminostyrene	−0.98	1.43
p-Methylstyrene	−0.88	1.10
Styrene	−0.80	1.00
p-Iodostyrene	−0.40	1.17
p-Chlorostyrene	−0.33	1.03
p-Cyanostyrene	−0.21	1.86
p-Sulfonamidostyrene	0.37	1.62
p-Nitrostyrene	0.39	1.63
Trimethylamine-4-vinylbenzimide	0.31	0.88

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Heterogeneity Parameters by Light Scattering for Statistical Copolymers Incorporating Long Side-Chain Comonomers

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Synopsis

Heterogeneity parameters were obtained by light scattering for a series of statistical copolymers incorporating long side-chain comonomers, by employing the method of Bushuk and Benoit. These copolymers were selected to exhibit varied compositional drift as required by copolymerization theory. The magnitude of the parameters found agreed qualitatively with the heterogeneity expected from the drift in composition with conversion. This was calculated using the treatment of Skeist, as modified by Kruse. However, values greater than the limit of unity were found in two instances for the heterogeneity index, $Q/Q_{\max}$, which relates the compositional drift constant Q to the maximum value obtained for mixtures of homopolymers. These anomalies were attributed to the insensitivity of the method for heterogeneous copolymers having small differences in the refractive increments of their respective homopolymers. The magnitude and sign of P, which reflects molecular weight effects on composition, was questionable because of experimental error. Both effects appear to be general deficiencies of the method, which limit its practical use. For solvents with high values of dn/dc (≈ 0.1), the observed weight-average molecular weight approached the true value.

INTRODUCTION

It is well known[1] that the intensity of light scattered by copolymers increases anomalously at low values of the refractive increment. Consequently, the observed weight-average molecular weights increase as refractive increment is lowered in a series of solvents. This was first attributed[2] to the distribution of the values of dn/dc with the variable composition present in both the instantaneously formed copolymer,[3] and as composition drifts with conversion.[4] The phenomenon was first treated theoretically by Stockmayer[5] from a consideration of azeotropic copolymers. This theory was later extended by Bushuk and Benoit[6] to provide a convenient means of determining heterogeneity in copolymers. The latter work provided parameters characterizing compositional drift resulting from both molecular weight distribution and reactivity differences between the comonomers, as well as yielding the true weight-average molecular weight of the copolymer, and of the components of the copolymer. Experimental data obtained by the method have, so far, been limited essentially to copolymers of styrene and methyl methacrylate, but these included statistical copolymers,[6–8] graft copolymers,[9–11] block copolymers[6,7,12,13] and mixtures of homopolymers.[6,7] Other systems studied were a styrene–acrylonitrile azeotropic copolymer[14] and a statistical ethyl acrylate–methyl methacrylate copolymer.[15] Both showed little heterogeneity by the method.

In this work the effect of increasing compositional heterogeneity and broad molecular weight distribution was evaluated by the method for a series of statistical copolymers containing long side-chain comonomers. Copolymers employed were *n*-octadecyl acrylate with, respectively, styrene, *n*-butyl acrylate, and vinyl acetate and *N*-*n*-octadecylacrylamide with, respectively, vinylidene chloride and acrylonitrile. Because Price-Alfrey parameters were available for both of the long side-chain comonomers[16,17] the drift in composition with conversion could be computed.[4] Batch copolymerization to high conversions and branching through the side-chain were expected to cause extensive molecular weight broadening. These factors, coupled with variation in the refractive increment differences between the homopolymer pairs, were expected to impose a severe test of the practical utility of the method.

EXPERIMENTAL

Preparation of the Long Side-Chain Monomers

N-*n*-Octadecylacrylamide was prepared as described.[18] *n*-Octadecyl acrylate was obtained under special purchase from Monomer-Polymer Corporation and its physical properties have been described.[19] The amide and ester were, respectively, 98.5% and 95% pure by gas–liquid chromatography. The ester was 99% pure by ester number; its impurities appeared to be the lower homologs, principally C_{16}. Other vinyl monomers were the purest available commercially and were distilled just before use.

Polymerization Procedure

The copolymers containing *n*-octadecyl acrylate were prepared as follows. The styrene series were copolymerized in bulk at 60°C and were initiated with 0.2 mole-% of azobisisobutyronitrile (AIBN); the vinyl acetate series were copolymerized in benzene in a mole ratio of one, based on total monomers, and were initiated with 0.4 mole-% of AIBN; the *n*-butyl acrylate series were copolymerized in benzene at 63°C at a mole ratio of solvent to monomer of four, based on total monomer and were initiated with 0.2 mole-% of AIBN and regulated with 0.1 mole-% of *n*-dodecyl mercaptan. The copolymers incorporating *N*-*n*-octadecylacrylamide were prepared as follows; the vinylidene chloride series, through a feed composition of 25 mole-% of amide, were copolymerized in dispersion at 60°C with the use of a 0.5% polyvinyl alcohol solution (2 ml/g based on total monomer) containing 1.5 wt-% powdered magnesium carbonate (based on water) as a dispersing agent. The initiator was 0.1 mole-% of benzoyl peroxide. The balance of the vinylidene chloride copolymers were copolymerized in *tert*-butanol, with a solvent to total monomer ratio of 3 and were initiated with 0.4 mole-% of benzoyl peroxide. The acrylonitrile copolymers were prepared and purified as described.[18] All of the solution- and bulk-polymerized copolymers were isolated by precipitation in a nonsolvent and freed of monomer by repeated extractions. Hot methanol was used for all of the copolymers, except the vinyl acetate rich copolymers, which were extracted at room temperature in either hexane or hexane–methanol mixtures. Samples were freed of solvent by evaporation from thin layers, usually in vacuum at <50°C. The purification of the dispersion copolymer has been described.[19]

Refractive Increments and Light-Scattering Molecular Weights

Solvents used for light scattering were of the purest available commercially and were distilled before use through an efficient column. All refractive increment measurements were made at 30 ± 1°C with the use of a Brice-Phoenix differential refractometer which had been modified electronically by Dr. Brice for facile read-out of the solvent and solution values. A small glass correction factor calibrating the divided measuring cells, also provided by Dr. Brice, was applied to the readings. The light source was the 5360 Å mercury line. Each polymer or copolymer was measured at two of the concentrations to be used for the measurement of molecular weight, and the average quotient was taken as dn/dc. Deviations were always small. The same procedure was followed for the homopolymers and copolymers used in Table I. The value found for NBS broad molecular weight polystyrene in toluene at 30°C was 0.114; the literature value in this solvent was 0.109–0.111 at 25–30°C.[20] A compilation of refractive increment values is available[20] for comparison with other values in Table I.

Light-scattering measurements were made with a Sofica light-scattering photometer, Model Number 701. The light source was the green mercury line at 5360 Å, and the calibration standard was pure dust-free benzene. All measurements were made at 30 ± 1°C. Sample concentrations c were diluted to $0.75c$, $0.50c$, $0.33c$, and $0.25c$. The initial concentration was increased as scattering intensity decreased and ranged from 2.0 g/l when dn/dc was 0.1 to 0.2, to 15 g/l when dn/dc was 0.01 or less. Curvature of the virial slope was not found. Solvents and solutions were dedusted by filtering each concentration through a Millipore filter assembly directly into the solution cells, which were protected by slotted dust shields. Filter designation GSWP 0.22μ was used with most solvents; when these were soluble (with tetrahydrofuran and n-butyl acetate) filter designation NRWP 1 μ, was used. With the latter porosity, however, some dust or microgel was present as evidenced by a marked downward drift of the Zimm plot at low angles. The data were treated by the method of Zimm[21]

TABLE I
Refractive Increments and Observed Molecular Weights

Experiment[a]	Solvent	ν_a	ν_b	ν	$M_{app} \times 10^{-5}$
1 (OA + BA)	Tetrahydrofuran	0.0651	0.0702	0.0634	3.681
	Hexane	0.0885	0.1096	0.0997	3.186
	Chlorobenzene	−0.0525	−0.0682	−0.0575	3.101
	Benzene	−0.0292	−0.0505	−0.0337	4.053
	Toluene	−0.0239	−0.0425	−0.0280	3.074
2 (OA + STY)[b]	Hexane	0.1972[d]	0.1292	0.1588	10.31
	Tetrahydrofuran	0.1926	0.0898	0.1332	10.41
	Carbon tetrachloride	0.1518	0.0114	0.0714	10.31
	Benzene	0.1123	−0.0269	0.0253	15.44
	Chlorobenzene	0.0848	−0.0489	0.0007	638.0
3 (OA + STY)[c]	Hexane	0.1972[d]	0.1292	0.1585	15.32
	Tetrahydrofuran	0.1926	0.0898	0.1016	17.41
	Chlorobenzene	0.0848	−0.0489	−0.0324	19.61
	Carbon tetrachloride	0.1518	0.0114	0.0409	21.53
4 (OM + VCL)	Hexane	0.1579[d]	0.1168	0.1322	6.078
	Tetrahydrofuran	0.1263[d]	0.0898	0.1028	6.031
	Cyclohexane	0.1145[d]	0.0651	0.0797	6.901
	Toluene	0.0665[d]	−0.0154	0.0135	14.72
	Benzene	0.0607[d]	−0.0269	0.0059	73.53
5 (OM + AN)	Tetrahydrofuran	0.1244[d]	0.0898	0.0961	2.767
	Chlorobenzene	0.0039[d]	−0.0489	−0.0369	5.391
	Benzene	0.0072[d]	−0.0269	−0.0193	5.883
	Toluene	0.0236[d]	−0.0154	−0.0072	25.23
6 (OA + VA)	*n*-Butyl acetate	0.0716	0.0883	0.0812	5.755
	Tetrahydrofuran	0.0582	0.0723	0.0657	6.675
	Chlorobenzene	−0.0426	−0.0563	−0.0546	6.863
	Benzene	−0.0225	−0.0363	−0.0321	9.891
	Cyclohexanone	0.0083[d]	0.0175	0.0140	18.33
7 (OM)	Hexane			0.1292	7.649
	Tetrahydrofuran			0.0898	6.986
	Cyclohexane			0.0651	6.333
	Chlorobenzene			0.0489	6.214
	Benzene			0.0269	6.367
	Toluene			0.0154	7.952

[a] Letter combinations stand for the following: OM, *N*-*n*-octadecylacrylamide; OA, *n*-octadecyl acrylate; BA, *n*-butyl acrylate; STY, styrene; VCL, vinylidene chloride; AN, acrylonitrile; VA, vinyl acetate. The subscript *b* refers to the long side-chain copolymer.

[b] Weight fraction, *n*-octadecyl acrylate, 0.594.

[c] Weight fraction, *n*-octadecyl acrylate, 0.846.

[d] Extrapolated by using regression coefficients obtained by least-square fitting of values of ν and w_b for soluble copolymers.

for measurements at angles ranging from 30° to 150° for all five concentrations.

Osmometric Molecular Weights

Osmometric molecular weights were usually run in toluene at 37°C on a Mechrolab osmometer 501, following the procedure described previously.[18]

Calculations by Computer

The parameters of eq. (1) were evaluated by an IBM 1130 computer using program designation IBM POLRG and were carried through a five-degree polynomial. An F test, applied to the analysis of variance, revealed that the second-degree polynomial was the most significant, as required by theory.[6] The parameters of eq. (2) were evaluated by least-square fitting from a program calling subroutine SIMQ. A program solving the equation of Kruse[27] was written for insertion in a general calculation subroutine designated QREAD.

THEORY

The development of the theory has been described in detail elsewhere[5-7,22,23] and has been treated in reviews.[24-26] Consequently, only expressions pertinent to the present work will be discussed briefly here. Based on the assumption[6] of linearity between the refractive increment and the weight fraction of copolymer composition, an expression yielding the heterogeneity parameters P and Q and the true weight-average molecular weight $\bar{M}_w$ was derived and is given here as

$$M_{\text{app}} = \bar{M}_w + 2P(\nu_a - \nu_b/\nu) + Q(\nu_a - \nu_b/\nu)^2 \tag{1}$$

The weight-average molecular weights of the A and B component, M_a and M_b, respectively, are contained in the expression

$$M_{\text{app}} = (\nu_a\nu_b/\nu^2)\bar{M}_w + \nu_a(\nu_a - \nu_b)/\nu^2 w_a M_a + \nu_b(\nu_b - \nu_a)/\nu^2 w_b M_b \tag{2}$$

In both expressions M_{app} is the observed molecular weight, $\bar{M}_w$ is the true molecular weight, ν_a is the refractive increment of homopolymer A, ν_b is the refractive increment of homopolymer B, ν is the refractive increment, and w_i is the weight fraction for the copolymer. P and Q are defined by

$$2P = 2\sum \gamma_i M_i \delta w_i = w_b(\bar{M}_w - M_b) - w_a(\bar{M}_w - M_a) \tag{3}$$

$$Q = \sum \gamma_i M_i \delta w_i^2 = (w_a)(w_b)(M_a + M_b - \bar{M}_w) \tag{4}$$

where γ_i and M_i are, respectively, the relative concentration and molecular weight of species having composition w_i, while δw_i is the deviation in composition of these molecules from the average one. Thus P expresses the molecular weight influence on compositional heterogeneity, while Q indicates compositional drift produced in accordance with the kinetics of propagation in copolymerization. Limits of P and Q are

$$-w_a\bar{M}_w \leqslant P \leqslant w_b\bar{M}_w \tag{1a}$$

$$0 \leqslant Q \leqslant \bar{M}_w[1 - (w_a w_b)] \tag{2a}$$

For comparing data, the terms $P/\bar{M}_w$ and $Q/\bar{M}_w$ are convenient. An especially useful quantity is $Q/Q_{\max}$, where $Q_{\max}$ is the maximum value of the heterogeneity constant for a given system (i.e., the value obtained for a mixture of two homopolymers) and is defined as $(w_a w_b)\bar{M}_w$. $Q/Q_{\max}$, which has the limits $0 \leqslant Q/Q_{\max} \leqslant 1$, is thus a useful index of compositional heterogeneity.

RESULTS AND DISCUSSION

The observed molecular weight, M_{app} and the values found for the refractive increment are listed in Table I. In this work the b subscript always refers to the long side-chain homopolymer. The copolymers used and their lettered designations, in the order given in Table I, are: 1, *n*-octadecyl acrylate, OA, *n*-butyl acrylate, BA; 2,3 *n*-octadecyl acrylate, styrene, STY; 4, *N*-*n*-octadecylacrylamide, OM, vinylidene chloride, VCL; 5, *N*-*n*-octadecylacrylamide, acrylonitrile, AN; 6, *n*-octadecyl acrylate, vinyl acetate, VA. Experiment 7 (OM) shows molecular weight data for the homopolymer, *N*-*n*-octadecylacrylamide, in the same solvents used for the copolymers. Further reference to these systems will be by experiment number only. Because neither poly(vinylidene chloride) or polyacrylonitrile is soluble in any of these solvents, values of refractive increment versus weight fraction for a series of five copolymers, carried to high conversion, were fitted as first-degree polynomials, with the intercept yielding ν_a. This procedure was required with one solvent each for experiment 3 (hexane) and experiment 6 (cyclohexanone). Increase in the magnitude of the slope of this relation, $\nu_b - \nu_a$, is in the direction of increasing accuracy. For these experiments the relative magnitude of $\nu_b - \nu_a$ was: vinyl acetate, 0.11; butyl acrylate, 0.14; acrylonitrile, 0.34, vinylidene chloride, 0.51; styrene, 1.0. As had been observed before,[15] copolymers of similar structure had low relative values. The difference, $\nu_b - \nu_a$, was not constant for the solvent series of each experiment, as had been assumed for styrene and methyl methacrylate.[13] Surprisingly, it varied from positive to negative for the butyl acrylate and vinyl acetate system. This may reflect the influence of the long side-chains on dn/dc in these two examples where the slopes are already low.

In Table II are listed the reactivity ratios r_a and r_b and the mole fractions of the long side-chain comonomers in, respectively, the feed f_{b0}, the initial copolymer, F_{b0}, and the final copolymer, F_b. This last value was estimated from the relation of Skeist[4] and was read from plots using the simplified calculations of Kruse,[27] which were solved by computer. With the aid of these plots, the ratio of the experimental drift of F_b with conversion p compared to the maximum value at $p = 1.0$ was obtained as the ratio of areas in accordance with the relation

$$A/A_{\max} = n[F(n)] - \int_0^n f(p)dp/F(1) - \int_0^1 f(p)dp \tag{5}$$

The areas were measured from the plots with a planimeter and were given the designation $A/A_{\max}$. This ratio therefore, represents the extent of drift for each system. In similar fashion, A_{rel} (Table II) relates the hetero-

TABLE II

Reactivity Ratios and Calculated Initial and Final Copolymer Compositions

	Expt 1 (OA + BA)	Expt 2 (OA + STY)	Expt 3 (OA + STY)	Expt 4 (OM + VCL)	Expt 5 (OM + AN)	Expt 6 (OA + VA)
r_a	1.0	0.646	0.646	0.440	4.394	0.048
r_b	1.0	0.120	0.120	1.257	0.140	7.312
f_{b0}	0.350	0.300	0.600	0.250	0.350	0.400
F_{b0}	0.350	0.300	0.452	0.378	0.105	0.846
F_b[a]	0.350	0.300	0.560	0.315	0.230	0.455
F_b'[b]	0.157	0.320	0.638	0.357	0.380	0.340
w_b[b]	0.320	0.594	0.846	0.649	0.789	0.660
Conversion, %	89.0	94.8	91.3	66.9	83.1	93.8
$A/A_{\max}$	0	0	0.635	0.342	0.415	0.830
A_{rel}	0	0	0.29	0.11	0.31	1.00

[a] Calculated by the method of Kruse.[27]

[b] Calculated from the refractive increment data. w_b, calculated from the elementary analysis, was: expt 1, 0.574; expt 2, 0.567; expt 3, 0.827; expt 4, 0.642; expt 5, 0.783; expt 6, 0.701.

geneity of each experiment to the one having the greatest heterogeneity (experiment 6). F_b' and the corresponding weight fraction w_b were computed from the refractive increments of the homopolymers and copolymer. Similar values were obtained by elementary analysis. The values found for F_b' generally indicated greater compositional drift and more heterogeneity for the experiments than were estimated from the Kruse relation. However, large errors arise in determining copolymer compositions by elementary analyses.[28] Because error is also considerable in the Kruse relation, which depends on reactivity ratios,[28] these observed differences and apparent anomalies can be expected. Although composition estimates for copolymers by refractive increment probably involves less error than by the other methods, uncertainties in the determination can be large, arising mostly from impurities in the polymer and solvents.[29] This might be the cause of the low value of F_b' in experiment 1. In this case, however, the value of F_b' by elementary analysis seems to be correct. Reactivity ratios were calculated, the values for N-n-octadecylacrylamide, $Q = 0.66$, $e = 1.13$ being used,[17] except for experiment 5 (see below) and for n-octadecyl acrylate, $Q = 0.43$, $e = 0.80$, as estimated from reference 16. Other values of Q and e were from Young.[30]

The parameters, evaluated by computer, for eqs. (1) and (2) are listed in order of increasing heterogeneity in Table III. Equation (1) describes a parabola in which the magnitude of Q indicates the degree of curvature, the slope at $\nu_a - \nu_b/\nu = 0$ indicates the value and sign of P, and the intercept is $\overline{M}_w$. Relative heterogeneity is best expressed as $Q/\overline{M}_w$, while the fraction of the maximum heterogeneity attainable (realizable for mixtures) is given as $Q/Q_{\max}$. Consequently, for comparison with the data in Table II it is convenient but only qualitatively proper to compare A_{rel} and $Q/\overline{M}_w$,

TABLE III
Molecular Weights and Compositional Heterogeneity Parameters

	Expt 1 (OA + BA)	Expt 2 (OA + STY)	Expt 3 (OA + STY)	Expt 4 (OM + VCL)	Expt 5 (OM + AN)	Expt 6 (OA + VA)
$\bar{M}_w \times 10^{-5}$ [eq. (1)]	3.342	9.397	15.75	6.622	2.945	6.703
$\bar{M}_v \times 10^{-5}$ [eq. (2)]	3.248	11.29	14.69	6.445	2.863	5.135
$P \times 10^{-4}$	−1.03	4.88	5.13	−4.37	−3.29	56.28
$s_p \times 10^{-4}$	±4.72	±0.89	±1.08	±0.997	±1.11	±46.36
$Q \times 10^{-4}$	0	0.121	3.49	3.64	6.30	44.00
$s_q \times 10^{-4}$		±0.009	±0.83	±0.13	±0.39	±10.79
$P/\bar{M}_w$		0.052	0.033	−0.066	−0.112	0.840
$Q/\bar{M}_w$	0	0.0013	0.022	0.055	0.214	6.57
$Q_{\max} \times 10^{-5}$		2.307	2.176	1.522	0.500	1.405
$Q/Q_{\max}$	0	0.0053	0.160	0.239	1.26	31.3
$M_a \times 10^{-5}$	−1.823	4.252	6.114	2.549	2.976	114.1
$M_b \times 10^{-5}$	−1.991	7.078	9.609	5.440	3.698	48.18
$\bar{M}_n \times 10^{-5}$	1.017	3.609	3.813	1.722	1.232	1.076
$\bar{M}_w/\bar{M}_n$	3.29	2.60	3.99	3.85	2.39	6.23

with a value of one arbitrarily assigned to the latter parameter in experiment 6. Actually, if the limit of heterogeneity is assumed for experiment 6 [see relation (2a)], $Q/\bar{M}_w$ is then approximately 0.78, yielding for experiments 1–5 relative values for $Q/\bar{M}_w$ of respectively 0, 0, 0.03, 0.07, 0.27. The quantities $A/A_{\max}$ and $Q/Q_{\max}$ have different meanings, of course, and cannot be compared. In general, the values in Table III for Q, $Q/\bar{M}_w$ and $Q/Q_{\max}$ are in the expected order as required by their kinetic parameters r_a and r_b and are qualitatively in harmony with the calculated values of Table II. For example, in the two special cases of equal comonomer reactivity (experiment 1) and azeotropic feed composition (experiment 2) where both comonomers enter at equal rates, the values of the parameters are reasonable. Because these data seem to indicate that the reactivity ratios are correct, the value for $Q/\bar{M}_w$ in experiment 3 seems to be too low. Both the extent of drift, $A/A_{\max}$, and the quantity A_{rel} indicate the presence of considerable heterogeneity. In contrast, in experiment 4 there is better correspondence between the constants of Tables II and III.

Two divergent Q and e parameters exist for the *N*-*n*-alkylacrylamides,[17,31] leading to different predictions of reactivity and of homogeneity for the *N*-*n*-octadecylacrylamide–acrylonitrile system (experiment 5). The values r_a and r_b listed in Table II[31] predict much heterogeneity, while the other[17] values (r_a = 0.836, r_b = 1.191) indicate very little. Because $Q/\bar{M}_w$ and especially $Q/Q_{\max}$ were both large, the former values were considered to be correct and were listed. Some reservations exist however. The compositions of all copolymers of *N*-*n*-octadecylacrylamide with acrylonitrile have always been found at this laboratory to equal the monomer feed in either *tert*-butanol or benzene, where copolymerization occurs heterogeneously. Anomalies are known to exist which affect the kinetic parameters of copolymerization under heterogeneous conditions,[32] being especially severe with acrylonitrile copolymers. Conceivably heterogeneity could be present that was not reflected in the copolymer analysis.

The extreme heterogeneity found for the *n*-octadecyl acrylate–vinyl acetate system (experiment 6) is predictable from the reactivity reactivities in view of $A/A_{\max}$. However, the ratio $Q/Q_{\max}$ is far in excess of the theoretical limit of unity, for this system and, to some extent, for the previous one. For vinyl acetate this may be related to the small value of $\nu_b - \nu_a$ (Table I) coupled with the low value of ν used to calculate M_{app} in benzene and in cyclohexanone. By setting P equal to zero and using $Q_{\max}$, $\bar{M}_w$, and found values for the ratio $\nu_a - \nu_b/\nu$, values of M_{app} were calculated which were close to values found for the first three solvents in experiment 6, but which differed widely for the last two. Although this explanation may be an oversimplification, similar results were found for experiment 5.

The magnitude and sign of P reflects the shift in composition of the A or B species into the higher molecular weight fractions of the copolymers [eq. (3)]. In these systems, a negative value for the constant indicates a shift of the long side-chain monomers into the high molecular weight fractions; a positive value indicates the opposite. While specific trends in Table III may be rationalized, it is considered that the large error (values of s) in P make such rationalizations speculative. The errors in literature values of P and Q showed similar trends when all available data[6,7,9,10,13] were recalculated by the computer methods used for this work. With statistical copolymers, the data indicated greater heterogeneity than would be expected from the respective reactivity ratios.

Values of $\bar{M}_w$ from eq. (2) agree fairly closely with those of eq. (1) (Table III), while values of M_a and M_b, when inserted in eq. (3) yielded reasonable values of P. Credence is thus lent to the above remarks by the parameters of eq. (2).

SUMMARY AND CONCLUSIONS

In this work, several copolymers of increasing heterogeneity were prepared at high conversions from monomers selected to produce compositional drift in accordance with copolymerization theory. Molecular weight broadening was obtained by batch polymerization and through branching. It was shown that, in general, the heterogeneity index followed the kinetic predictions but that indices of heterogeneity higher than those theoretically possible were observed in two cases, one case being extreme. These facts, together with uncertainties with respect to the magnitude and sign of P, lead to the conclusion that experimental quantitation depends on the differences in value for the refractive increments of the two homopolymers. Insensitivity becomes particularly severe when $\nu_b - \nu_a$ is low and where ν_a and ν_b are of opposite sign. In this situation ν is extremely low, casting doubt on the validity of M_{app}. It is under these circumstances that M_{app}

attains its highest values and so exerts the greatest influence on Q and P. When the copolymer is homogeneous, the effect is negligible (experiment 1), but when heterogeneity is present (experiments 5 and 6) the effect is greatly magnified, leading to the anomalies observed. When $\nu_b - \nu_a$ is high and heterogeneity is low (experiment 2) the sign of ν_a and ν_b can be opposite and ν quite low while still yielding data leading to reasonable values of P and Q, even though in experiment 3 the value of Q seems low. Approximate values of $\bar{M}_w$ can be obtained by using solvents giving high values of dn/dc, ($\approx$0.1), for the copolymers. In this situation, the ratio of $\nu_a - \nu_b/\nu$ approaches zero where $M_{\text{app}} = \bar{M}_w$. Considerable data on a much wider variety of copolymer systems will be required to definitively characterize this light-scattering method.

The author is indebted to Dr. C. Roland Eddy for the computer program used to evaluate eq. (2) and to Miss Virginia Martin and Mrs. Ruth Zabarsky for the computations of the constants. He also thanks Mr. John W. Pensabene and Miss Andrea G. Shuman for the preparation of most of the copolymers used in this study.

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Evidence for Several Species of Active Sites in Ziegler-Natta Catalysts

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Synopsis

The kinetics of isoprene polymerization catalyzed by VCl_3 and Et_3Al were studied by measuring fractional conversions, polymer composition, and molecular weight distributions at a series of reaction times and temperatures. The rate of polymerization plotted against temperature shows an inflection point with a minimum and maximum in the 60–90°C range. The isomeric composition of the polymer changes with temperature but not with reaction time, while the molecular weight distribution undergoes substantial change with both of these variables. The rate of polymerization at sites producing low molecular weight polymers was measured, and the activation energy calculated to be about 10 kcal/mole. The active sites were found to deactivate at different rates. The results support the hypothesis that several species of active sites are present in the system and that these exhibit characteristic polymerization behavior.

INTRODUCTION

The presence of more than one type or species of active site on the surface of Ziegler-Natta catalysts has been known for some time. The dissimilarities between species may arise from a difference in the oxidation state of the transition metal, or from the environment of the transition metal atom on the crystal surface, or both. Evidence for species which differ in the oxidation state of the transition metal has been given by Overberger[1] and Schindler.[2] The latter examined the polymerization of ethylene by $TiCl_4$ in the presence of deuterium, and found the deuterium content of the polymer to be dependent upon whether the transition metal of the polymerization site was Ti(III) or Ti(IV). Fractionation showed that the molecular weight of polyethylene produced at Ti(III) sites was several times greater than that produced at Ti(IV) sites.[3] Polyisoprene prepared from $TiCl_4$ and $(i\text{-}Bu)_3Al$ possesses a molecular weight distribution which has been attributed to a multiplicity of active sites.[4] The existence of several species of active sites having the same oxidation state was postulated by Boor to account for the effect of electron-donating compounds on the polymerization of propylene by $TiCl_3$ and Et_2Zn.[5] These species differ in their ability to coordinate with electron donors, reflecting the chemical and structural variations which exist among them.

On the basis of this work one can postulate that each species of active site enjoys an existence which is independent of the other species present. Typically, Ziegler-Natta catalysts incorporate several species of active sites which, in the presence of monomer, produce polymer simultaneously. The study of these catalysts will be simplified as ways of examining the active species in isolation are found. This paper reports a study of the polymerization of isoprene with VCl_3 and Et_3Al. The results indicate the presence of several species of active sites and it has been found possible to take some initial steps toward their study on an individual basis.

EXPERIMENTAL

Polymerization Technique

Polymerizations were carried out in a 2-liter, steam-heated, water-cooled glass reactor fitted with a stainless steel headplate. Temperature control, to ±1°C, was achieved by the action of a thermistor through a bridge circuit and relay on a solenoid valve in a steam line. Rapid cooling was obtained by manual operation of a cold water valve. During operation, the reactor temperature could be changed within 2 min from any temperature in the 60–90°C range, to any other temperature in that range. VCl_3 powder was weighed into the reactor from a stainless steel tube which could be screwed into the reactor and discharged by opening a $^1/_4$-in. ball valve. The amount of other reagents required was calculated from the weight of vanadium trichloride added to the reactor, with the order of addition being: VCl_3, benzene, Et_3Al, isoprene, and, where appropriate, electron-donor compound. A positive pressure of nitrogen was maintained in the reactor at all times. Samples of polymer were collected in ice-cold flasks containing methanol under a nitrogen atmosphere. The polymer was recovered by pumping off the volatiles at a temperature below 40°C and storing them under nitrogen in a refrigerator until needed. The yield of polymer was obtained by direct weighing. An allowance for the catalyst residues was made by taking samples at zero time, before any polymer had been formed, and removing the volatiles exactly as in the case of samples containing polymer.

All VCl_3 manipulations were carried out in a nitrogen-filled dry box. Oxygen was removed from the box by flushing with at least five volumes of nitrogen, thereby reducing its concentration to less than 0.1%. The presence of oxygen was tested for by means of a 3-V lamp from which the glass envelope had been removed. If the lamp burned without smoking, the concentration of oxygen was deemed to be acceptably low. The nitrogen in the box was dried by circulation over open dishes of P_2O_5.

Chemicals

VCl_3 from Stauffer Chemical Co. was extracted for 16 hr at 80°C with dry benzene, washed twice with fresh dry benzene, pumped dry, ball-milled for 6 hr, and stored in a desiccator in the dry nitrogen box until required. The same batch of VCl_3 was used for all the experiments.

Et_3Al from Texas Alkyls was received as a solution in benzene and used without purification. Phillips Polymerization Grade isoprene was distilled under nitrogen and stored over activated alumina at 0°C until used, within three days of distillation. Benzene (Phillips Pure Grade) was dried over 3A molecular sieves and deaerated by nitrogen bubbling. Hi-Pure Grade nitrogen gas, from Liquid Carbonic, was used as received for most experiments. The nitrogen gas for a few experiments was obtained from high purity dry grade liquid nitrogen manufactured by Union Carbide. Methyl hydrate grade methanol was bubbled with nitrogen to remove dissolved oxygen and used without further treatment. Anhydrous diethyl ether from Fisher Scientific Co. was used without purification. Diisopropyl ether, Fisher Certified Reagent Grade, was purged with nitrogen to remove oxygen, dried with sodium metal, and distilled under nitrogen.

Structural Analysis of the Polymer

The structure of the polyisoprenes prepared was determined by the nuclear magnetic resonance method.[6] The absorption due to methyl group protons relative to tetramethyl silane (TMS) occurs at 1.66 ppm in *trans*-1,4-polyisoprene, 1.79 ppm in *cis*-1,4-polyisoprene, and 0.9 and 1.8 ppm in cyclized polyisoprene. Because of the absorption at 1.8 ppm it is not possible to obtain a reliable estimate of the *cis*/*trans* ratio in the presence of cyclized polyisoprene. Protons of the terminal CH_2 groups in 3,4-polyisoprene absorb at 4.84 ppm. The spectra were run in solutions of deuterated benzene in which solvent absorption by impurities was at a minimum. The small amount of benzene present, absorbing at 7.20 ppm relative to TMS, served as an internal reference. The percentage of each polyisoprene was determined by measuring the area under the appropriate absorption peak. In the absence of cyclization, the error in the *cis*/*trans* ratio is less than 1%, but the error in total *trans* content and in the 3,4-polyisoprene content is ±3%.

Molecular Weight Distribution Measurements

Molecular weight distributions were determined with a Waters gel permeation chromatograph containing columns with pore sizes of 5×10^6, 3×10^6, 1×10^5, and two of 3×10^4 Å. The initial theoretical plate count was 854, but it fell to 339 at the end of the experiments with most of the loss occurring in the 3×10^4 Å columns. The solvent was cyclohexane at 58°C; *trans*-1,4-polyisoprene was injected as a 0.5% solution in cyclohexane.

The chromatograph was calibrated with *trans*-1,4-polyisoprene fractions prepared in a large-scale Baker-Williams column[7] employing ethylene dichloride as the solvent and methyl ethyl ketone as the nonsolvent. The intrinsic viscosity of the fractions was determined in toluene at 30°C, and the molecular weight calculated from Cooper's relationship:[8]

$$[\eta] = 4.37 \times 10^{-4} M^{0.65}$$

The fractions were run in the chromatograph and a trial calibration curve of log M_v against the elution volume in count numbers was prepared. Next, the chromatographic trace of each fraction was divided into segments, $\bar{M}_v$ for each segment was read from the graph, and the viscosity-average molecular weight for each fraction was calculated from[8,9]

$$\bar{M}_v = \left[\frac{\sum N_i M_i^{(1+0.65)}}{\sum N_i M_i}\right]^{1/0.65}$$

The calibration curve of log $\bar{M}_v$ versus count number was redrawn, the count numbers corresponding to the calculated $\bar{M}_v$ of each fraction being used. This process was repeated until no significant change in the calibration curve occurred with further iteration. Weight-average and number-average molecular weights were calculated from,[9]

$$\bar{M}_w = \sum N_i M_i^2 / \sum N_i M_i$$

$$\bar{M}_n = \sum N_i M_i \sum N_i$$

No allowance was made for broadening of the distribution due to imperfect resolution in the columns; the final calibration curve was: log $\bar{M}_v$ = 10.620 − 0.160 (count number).

Experimental reproducibility was estimated by running the same sample through the chromatograph a number of times, and by re-reading the same trace a number of times. Reading errors were negligible but the error from re-running the same sample was ±12% in $\bar{M}_w$ and ±8% in $\bar{M}_n$. The low molecular weight peaks found in most samples were not included in the molecular weight calculations. A cut-off was made in the region of count number 40 and the low molecular weight end of the distribution drawn in by hand. We estimate the precision of the measurements to be ±20% in $\bar{M}_n$ and ±15% in $\bar{M}_v$ and $\bar{M}_w$. The absolute error, due to concentration and other effects, is liable to be much greater.

EXPERIMENTAL RESULTS

Temperature Dependence of the Rate

The time dependence of fractional conversion, molecular weight distribution, and chemical composition was measured at 60, 70, 80, and 90°C. In each case the initial concentration of the reactants in benzene was $0.70M$ isoprene, $0.004M$ VCl_3 (slurry), and $0.008M$ Et_3Al. The fractional conversions are given in Figure 1 for reaction periods of up to 10 hr and in Figure 2 for periods of up to 10 days. The run-to-run experimental error is typified by the fractional conversions of two experiments at 70°C as seen in Figure 1. It is surprising to note that the rate of reaction at 80°C is less than that at 70 and 90°C. Natta found that the rate at which propylene is polymerized by VCl_3 and Et_3Al reaches a maximum at 70°C,[10] but our results with isoprene, plotted as fractional conversion at 4 hr against temperature, show an inflection point with a minimum and a maximum in

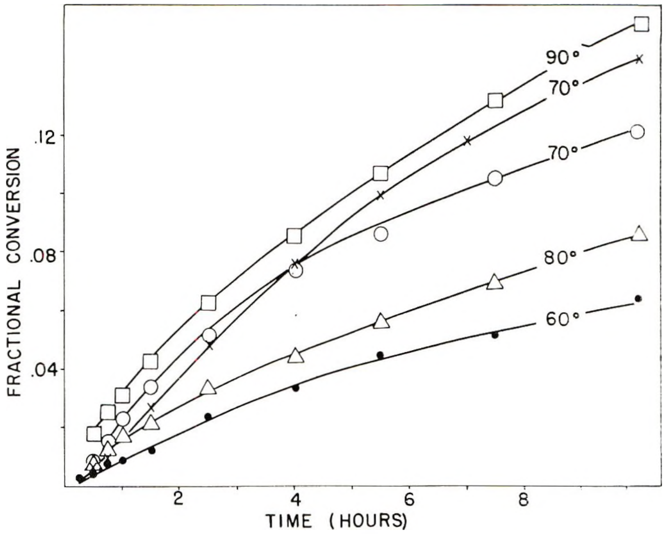

Fig. 1. Fractional conversion of isoprene at different temperatures. Concentrations in benzene: C_5H_8, 0.70M; VCl_3 (Slurry), 0.004M; Et_3Al, 0.008M.

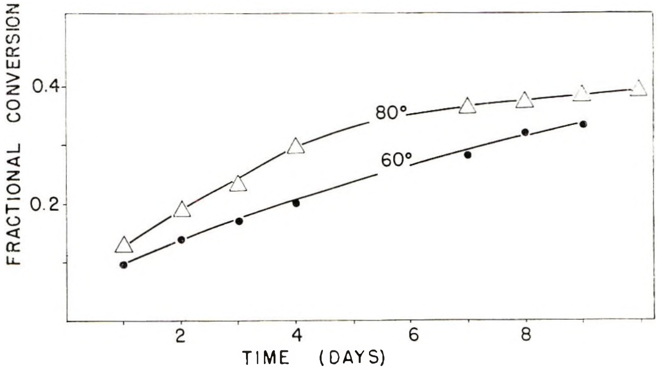

Fig. 2. Fractional conversions of isoprene at different temperatures. Concentrations as in Fig. 1.

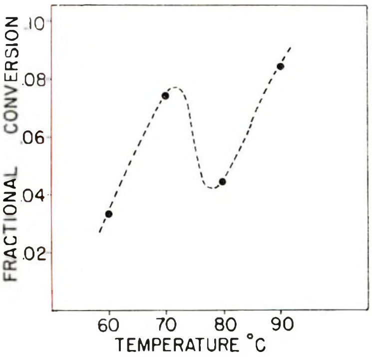

Fig. 3. Fractional conversion after reaction for 4 hr. From Fig. 1.

the 60–90°C interval (Fig. 3). Confirmation of the results in Figure 1 was obtained by changing the temperature of the reactor during the course of a run and observing the change in slope of the conversion curve. The increase in rate observed as the temperature is increased from 80 to 90°C is verified by the results in Figure 4 from which it is evident that the slope of the 90°C portions of the curve is higher than the 80°C portions. The maximum in the rate between 60 and 80°C is confirmed by the results in Figure 5. The latter experiments were done in 30-oz crown-cap bottles over a period of 3 days in order to demonstrate that the rate differences found at short reaction times were also found at longer times.

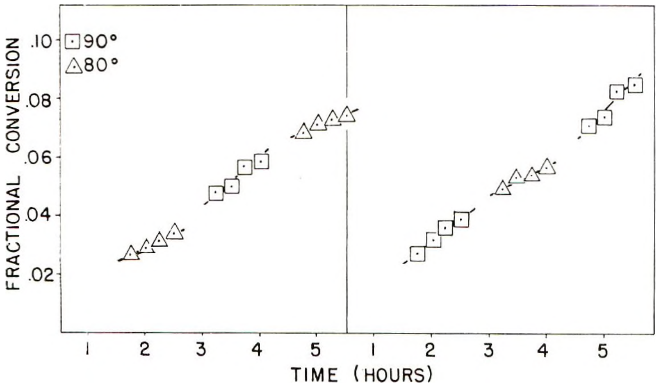

Fig. 4. Changes in the rate of conversion with temperature. Concentrations as in Fig. 1.

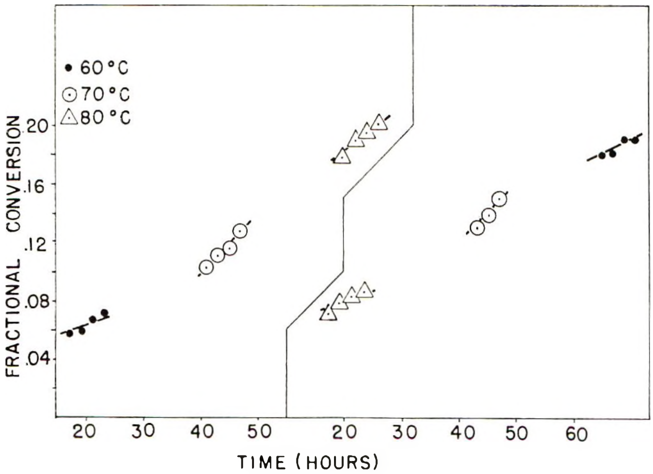

Fig. 5. Changes in the rate of conversion with temperature. Left side: Temperature varied from 60 to 70 to 80°C. Right side: Temperature varied from 80 to 70 to 60°C. Concentrations as in Fig. 1.

Molecular Weight Distributions

Changes in the molecular weight distribution with reaction time at 70 and 80°C are presented in Figures 6 and 7 respectively. The results are given as the change in refractive index, as a function of the elution volume expressed in count numbers, where one count number corresponds to 5 ml of eluted solution. The distributions have not been normalized to a common area; they are cumulative, not instantaneous, at the time indi-

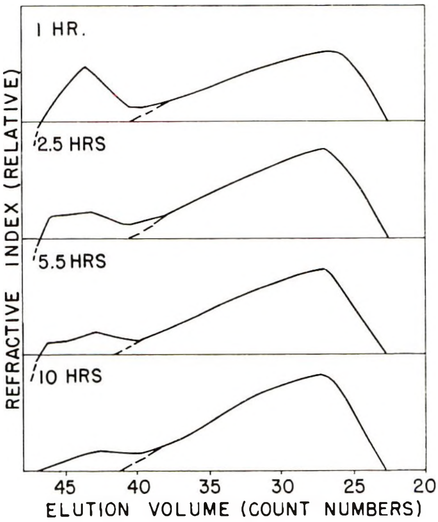

Fig. 6. Molecular weight distributions at 70°C. Concentrations as in Fig. 1.

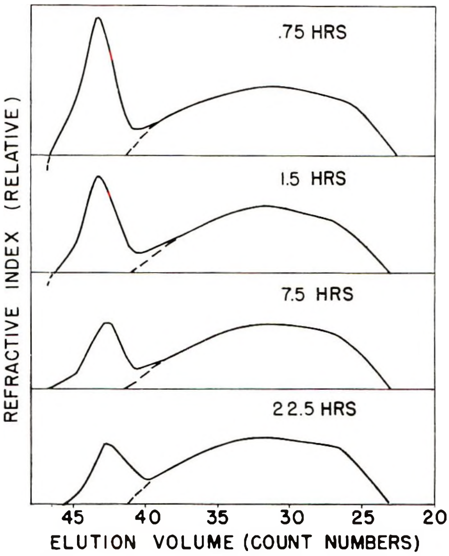

Fig. 7. Molecular weight distributions at 80°C. Concentrations as in Fig. 1.

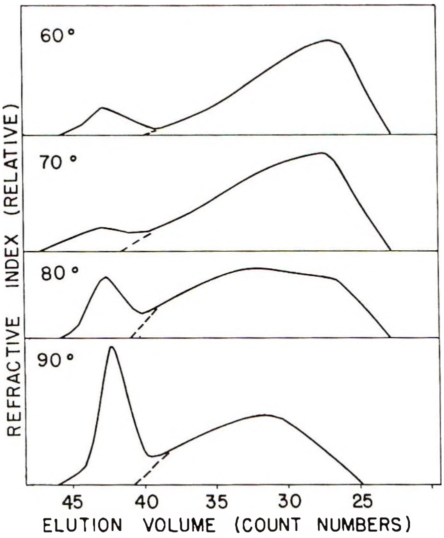

Fig. 8. Molecular weight distribution as a function of temperature after more than 9 hr reaction time. Concentrations as in Fig. 1.

cated. The changes undergone by the molecular weight distribution with reaction time at 60 and 90°C are similar to those at 70 and 80°C.

The distributions are distinctly nodular: for example, the 10 hr sample in Figure 6 exhibits five nodes at count numbers of 46, 43, 36, 31–33, and 27. The relative amount of low molecular weight polyisoprene decreases as the reaction proceeds indicating its formation occurs during the early stages of the polymerization. There are at least three overlapping nodes of high molecular weight polymer with maxima at count numbers 36, 31–33, and 27. The relative amount of polymer at these nodes does not, within the experimental resolution, change with the length of the reaction period.

Molecular weight distributions obtained after nine or more hours of reaction at 60, 70, 80, and 90°C are given in Figure 8; little change in the distribution is observed after the first 8 or 9 hr of reaction. The percentage of low molecular weight polymer clearly increases with the reaction temperature. In addition, the relative intensity of the nodes at count numbers 31–33 and 27 is changing; at 60°C virtually all of the polymer appears at count number 27, while at 90°C the most intense nodes are at 31–33 and 36, and the node at 27 has nearly disappeared. All of the nodes are evident at 70 and 80°C. Molecular weights were calculated for the combined nodes at 27, 31–33, and 36. These nodes overlap too much to be resolved. The contribution from the low molecular weight tail of these nodes was estimated by drawing in the dotted lines shown in Figures 6–8. Weight, number and viscosity-average molecular weights calculated from the chromatograms in Figures 6–8 are given in Tables I and II. The decline in molecular weight with increased temperature occurs because the inten-

TABLE I
Molecular Weights as a Function of Reaction Time

Temp, °C	Time, hr	$\bar{M}_w \times 10^{-6}$	$\bar{M}_n \times 10^{-6}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_v \times 10^{-6}$	$\bar{M}_w/\bar{M}_v$
70	1	1.5	0.23	6.5	1.2	1.2
	$2^{1}/_{2}$	1.4	0.26	5.4	1.1	1.3
	$5^{1}/_{2}$	1.2	0.19	6.6	1.0	1.3
	10	1.3	0.20	6.4	1.0	1.3
80	$^{3}/_{4}$	1.0	0.11	9.5	0.7	1.4
	$1^{1}/_{2}$	0.9	0.11	7.7	0.7	1.3
	$7^{1}/_{2}$	0.9	0.12	7.6	0.7	1.3
	$22^{1}/_{2}$	0.9	0.12	7.7	0.7	1.3

sity, relative to the whole polymer, of the high molecular weight node at count number 27 is decreasing. The ratio, $\bar{M}_w/\bar{M}_n$, passes through a maximum between 60 and 90°C due to the existence of several prominent nodes in this temperature range. Within the experimental error, $\bar{M}_w/\bar{M}_v$ does not change with temperature.

TABLE II
Molecular Weights at Various Temperatures

Temp, °C	$\bar{M}_w \times 10^{-6}$	$\bar{M}_n \times 10^{-6}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_v \times 10^{-6}$	$\bar{M}_w/\bar{M}_v$
60	1.7	0.32	5.3	1.4	1.2
70	1.3	0.20	6.4	1.0	1.3
80	0.9	0.12	7.7	0.7	1.3
90	0.5	0.11	4.4	0.4	1.3
90	0.4	0.08	5.2	0.3	1.3

Structural Analysis of the Polymer

The structure of the polymer sampled after various periods of reaction at a series of temperatures with and without diisopropyl ether was determined by NMR. Within the experimental error, there are no changes in compo-

TABLE III
Composition of the Polyisoprenes

Temp, °C	*Cis*, wt-%	*Trans*, wt-%	3,4-, wt-%	Cyclized, wt-%
60[a]	0	97 ± 3	3 ± 3	0
70[a]	0	97 ± 3	3 ± 3	0
80[a]	4	93 ± 3	3 ± 3	0
90[a]	3	92 ± 3	5 ± 3	0
70[b]	0	94 ± 3	6 ± 3	0
90[b]	9	83 ± 3	8 ± 3	0

[a] Concentrations as in Figure 1.

[b] Concentrations as in Figure 9.

sition with reaction time, but changes with temperature and catalyst composition do occur and these are given in Table III. Between 3 and 5% of 3,4-polyisoprene is formed at all temperatures investigated, and if diisopropyl ether is present, 6–8% is formed. Generally speaking, 3,4-polyisoprene seems to be concentrated in the low molecular weight polymer, but it is not possible at present to relate polymer composition to any particular node in the molecular weight distribution. Cyclization, if it occurs, appears to be a post-reaction phenomenon. Under all reaction conditions studied, some *cis*-1,4-polyisoprene is found at 80 and 90°C but not at 60 and 70°C. The amount increases if diisopropyl ether is used in the catalyst.

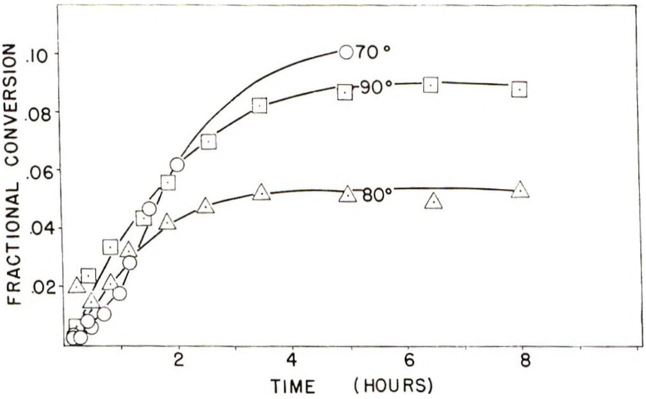

Fig. 9. Fractional conversion with diisopropyl ether. (□) Concentrations as in Fig. 1, $0.012M$ i-Pr$_2$O.

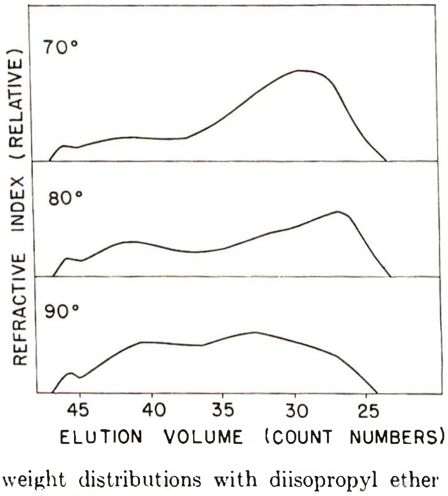

Fig. 10. Molecular weight distributions with diisopropyl ether after more than $2^1/_2$ hr reaction time. Concentrations as in Fig. 9.

Effect of Electron Donors

Experiments in which diethyl ether or diisopropyl ether was added to the catalyst have been carried out. At concentrations in benzene of 0.70M isoprene, 0.008M Et_3Al, 0.004M VCl_3 (slurry) and 0.004M diethyl ether the rate of polymerization increased by a few per cent, and there was no evident change in the molecular weight distribution. The time–conversion curves obtained when diisopropyl ether is present in the catalyst are given in Figure 9. As for the experiments without ether, the rate of conversion at 80°C is less than that at 70 and 90°C. The reaction terminates after 3–5 hr, although in the absence of ether termination occurs only after several days. The molecular weight distributions at 70, 80, and 90°C are given in Figure 10. Again the nodularity and its changes with temperature are evident.

DISCUSSION

The results described in this paper can be interpreted in terms of the presence of several distinct species of active polymerization sites on the VCl_3 catalyst. The ratio of the rates of chain growth and termination, factors which control the molecular weight, are characteristic of the species as is the rate at which the sites form and deactivate. The nature of the polymer, whether *cis*, *trans*, 3,4-, or some mixture of them is also a feature of the particular species. The concept of the independent nature of each species can be supported by the results presented in this paper.

In the reactions discussed so far, the catalyst components and isoprene were brought together at the same time. If the catalyst components are brought together before introducing isoprene, some surface reduction to VCl_2 will occur,[11] resulting in changes in the polymerization behavior. VCl_3 and Et_3Al were allowed to react for 2 hr at 90°C before isoprene was added to the reactor; the rate and conversion were greatly reduced and the

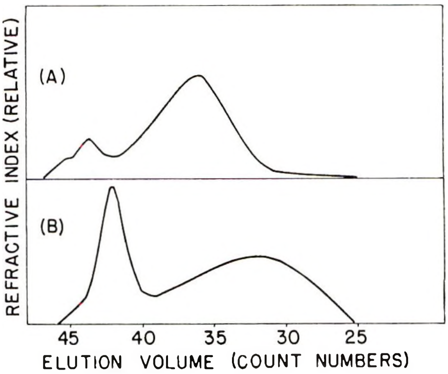

Fig. 11. Molecular weight distribution after catalyst aging at 90°C: (*a*) catalyst aged 2 hr, conversion 0.2% after 6 hr., (*b*) Not aged. Conversion 5% after 6 hr. Concentrations as in Fig. 1.

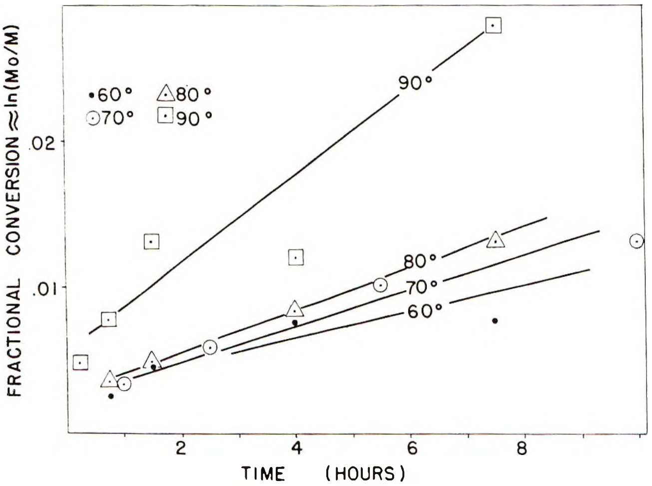

Fig. 12. Fractional conversion to low molecular weight polymer. Reaction conditions as in Fig. 1.

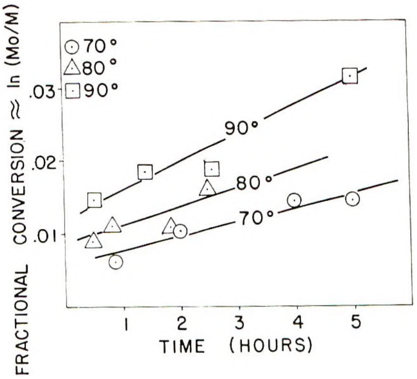

Fig. 13. Fractional conversion to low molecular weight polymer with diisopropyl ether. Reaction conditions as in Fig. 9.

molecular weight distribution altered substantially (Fig. 11). The sites yielding polymer at count numbers 31 and 27 were suppressed, but those giving polymer at count number 36 were not, an indication of the independence of these sites.

The experimental results have shown that *cis*-1,4-polyisoprene is produced at 80 and 90°C and that it is in this region that the active sites producing polymer of count number 27 are deactivating relative to those producing polymer of count numbers 31–33 and 36. Hence, *cis*-1,4-polyisoprene may be associated with one of these nodes and since the node at 31–33 is quite evident at 70°C, at which temperature there is no *cis* polymer, it seems likely that the *cis*-1,4-polyisoprene is concentrated in the node at count number 36. It is not known whether the *cis* isomer appears in a copolymer or homopolymer.

The polymer from each species of active site would be expected to possess a molecular weight distribution in which $\bar{M}_w/\bar{M}_n \simeq 2$. At all temperatures there is substantial overlapping of the polymer from more than one species of active site and $\bar{M}_w/\bar{M}_n$ is greater than two. The nodes overlap too much to resolve with confidence.

Because each species exhibits the characteristics of a simple reaction, the rate of polymerization due to a single species can be determined. The yield of polymer from a given species can be obtained by measuring the ratio of its area under the molecular weight distribution curve to the total area and multiplying by the total yield of polymer. Thus, conversion from sites of interest can be calculated as a function of reaction time. The active sites which yield nodes at count numbers 27 and 31 overlap too much to separate accurately, and further, the node at 27 appears to be undergoing deactivation in the temperature range studied. The low molecular weight peak at count number 43 does not suffer from these limitations and the fractional conversion to low molecular weight polymer as a function of time and temperature has been calculated. The results obtained without any electron donor and with diisopropyl ether are given in Figures 12 and 13, respectively. Due to the accumulation of experimental error, the points do not fall on good straight lines, but it is fair to say that the rate of polymerization to low molecular weight polymer increases as the temperature increases. The results have been examined by the Arrhenius equation,

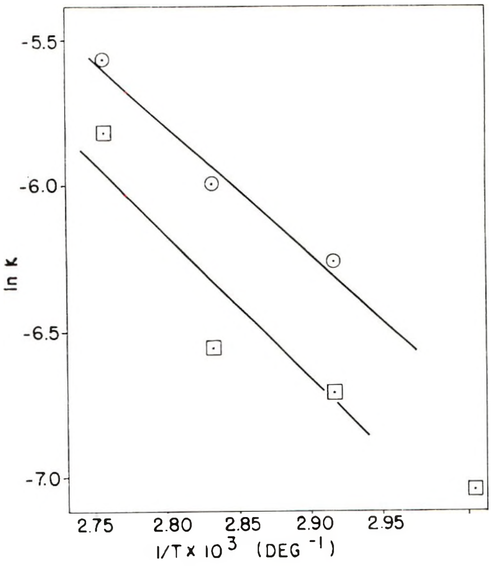

Fig. 14. Temperature dependence of the rate constant. (⊙) diisopropyl ether; (⊡) no electron donor.

$$\ln k = \ln A - (\Delta H^*/RT)$$

where k is a pseudo first-order rate constant, A is the Arrhenius factor, ΔH^* is the activation energy, R is the gas constant, and T the temperature. The constants k and A contain a term giving the concentration of active sites. A graph of ln k versus $1/T$ is presented in Figure 14 for polymerizations with and without diisopropyl ether. The experimental points are scattered too much to permit one to identify a difference, if any, in A and ΔH^* for the two reactions. From Figure 14, $\Delta H^* \simeq 10$ kcal/mole and $A \simeq 10$ min^{-1} for both reactions.

Cooper[11] has shown that the rate at which isoprene is polymerized by VCl_3, Et_3Al, and diisopropyl ether follows the same path with time as does the reduction of VCl_3 in the same system, without isoprene. This parallel may arise because the active site is an intermediate in the reduction process which probably occurs through the alkylation of vanadium by Et_3Al, followed by reduction when the unstable V—C bond ruptures. The V—C bond is probably a major feature of the active site, and polymerization possibly occurs during its transient existence. The possibility that divalent vanadium is required for the active site is unlikely as reduced VCl_3 exhibits very low activity. It seems therefore, in agreement with Cooper,[12] that the increased rate of polymerization observed when diisopropyl ether is added to the catalyst is due to an increase in the rate of formation of V—C bonds, and therefore in the rate of active site formation. The decline of the node at count number 27 with temperature is possibly related to deactivation by reduction, as Natta[10] suggests is the case in the polymerization of propylene. The subsequent increase in the overall rate at higher temperatures results from increased activity at those sites which yield polymer of count numbers 31–33 and 36.

The results described in the paper are consistent with the hypothesis that the polymerization of isoprene with VCl_3 and Et_3Al proceeds simultaneously at several independent species of catalyst sites, and that these species can be characterized by their chemical behavior. The deactivation of certain species with temperature may be the result of conversion to some other species of active site rather than conversion to an inactive site.

We wish to thank Messrs. J. Hulme and D. Wooden for the molecular weight and chemical composition measurements, respectively, and Dr. J. F. Henderson for his comments during the course of this work. The permission of Polymer Corporation Limited to publish this paper is gratefully acknowledged.

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Reduction of Disulfide Bonds in Keratin with 1,4-Dithiothreitol. I. Kinetic Investigation

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Synopsis

The kinetics of the reduction of disulfide groups in wool fibers with dithiothreitol has been investigated. The rate-controlling process appears to depend on the pH of the reducing solution and changes from diffusion control to reaction rate control as the pH is decreased from neutral to pH 3.50. Pseudo second-order kinetics, second-order with respect to the concentration of the disulfide groups in keratin, has been found to describe the experimental data at pH 3.50. An activation energy of 25 kcal/mole has been determined for the rate-controlling step at that pH value, as opposed to an activation energy of 13.4 kcal/mole for the diffusion-controlled process at neutral pH. Only about 85% of the disulfide groups are accessible to dithiothreitol under the conditions which were investigated.

INTRODUCTION

The reactivity and accessibility of disulfide groups to reducing agents in protein fibers has been investigated by a number of workers, and a considerable amount of evidence supporting conflicting theories has been reported.

Elsworth and Phillips[1,2] found that the reduction of wool with bisulfite solutions at pH 5.0 left a considerable amount of disulfide groups unreacted. A similar lack of completeness of reduction was reported by Harris and co-workers[3] when they reduced wool with thiolacetic acid. This evidence, and the results of other investigations, led Phillips and his co-workers[4–6] to postulate the existence of four fractions of disulfide groups in keratin differing in reactivity or accessibility. It has since been shown, however, that this theory is not necessarily valid and that some of the supporting evidence could be explained in terms of the equilibrium nature of the scission process.[7,8] Thompson and O'Donnell[9] showed that increases in the concentration of the reducing agent, mercaptoethanol, up to $4M$ resulted in nearly complete scission of the disulfide bonds. Similarly, the reduction with sulfite can be forced to completion if one of the reaction products is removed by reaction with an organo-mercurial compound.[7,10] Recently Leach and co-workers[11] described an elegant electrolytic method for the reduction of disulfide bonds in keratin in which small amounts of thiols were used to act as current carriers. These workers were able to achieve

100% reduction at pH 9 and over 90% reduction at pH 7, which seems to suggest that molecular accessibility is not involved in restricting reduction of disulfide bonds in keratin and that apparently the equilibria formed in the two-step reduction process determine the degree of reduction obtainable. The two steps of the reaction between the disulfide bonds and a thiol, in which the first step is the formation of a mixed disulfide, are shown in eqs. (1) and (2) where W stands for the wool residue:

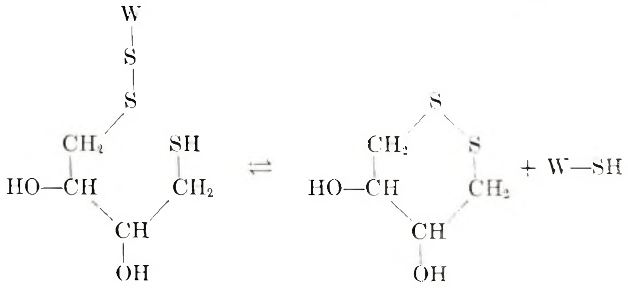
$$\mathrm{W{-}S{-}S{-}W + R{-}SH \rightleftharpoons W{-}S{-}S{-}R + W{-}SH} \tag{1}$$

$$\mathrm{W{-}S{-}S{-}R + R{-}SH \rightleftharpoons R{-}S{-}S{-}R + W{-}SH} \tag{2}$$

Both reaction steps lead to equilibria with equilibrium constants near unity, which explains why extremely high concentrations of the thiol (R-SH) are necessary to approach completion of the reaction. It would appear that a reducing agent which forms an energetically favored oxidized form would have a high equilibrium constant for the second step of this reaction and thereby shift the overall equilibrium to the side of the reduced disulfide group in keratin. A compound which has been shown to be promising in this respect[12] is 1,4-dithiothreitol (DTT), which has recently been introduced into protein chemistry as a protective reagent for SH groups by Cleland.[13]

In the first step (3) of the reaction sequence, DTT reacts with disulfides like a monothiol and forms a mixed disulfide. This step has an equilibrium constant near unity.

$$\mathrm{W{-}S{-}S{-}W + HS{-}CH_2{-}CH(OH){-}CH(OH){-}CH_2{-}SH \rightleftharpoons}$$
$$\mathrm{W{-}SH + W{-}S{-}S{-}CH_2{-}CH(OH){-}CH(OH){-}CH_2SH} \tag{3}$$



(4)

In the second step (4) the free SH group of the mixed disulfide reacts intramolecularly with the disulfide group forming combined cysteine and the cyclic disulfide 4,5-dihydroxy-1,2-dithiane. The geometrical requirements of the six-membered ring cause considerable distortion[14] of the normal dihedral 90° angle for an unstrained disulfide leading to a strain energy of at least 5 kcal in a 1,2-dithiane.[15,16] Nevertheless, this compound is remarkably stable, and an equilibrium constant of 1.3×10^4 has been reported by Cleland[13] for the second step of the reaction with cystine. This high equilibrium constant for the second step causes a shift of the overall equilibrium to the reduced form of the disulfide bond in the keratin. DTT is therefore a reducing agent which is not hampered by the usual equilibrium considerations connected with the reduction reaction, and causes a specific and symmetric scission of the disulfide bonds without producing any byproducts such as mixed disulfides. In other words, it is ideally suited for a kinetic investigation of the reduction reaction of disulfides in keratin fibers, and some of the results of this investigation are reported in this paper.

EXPERIMENTAL METHODS

Materials

The wool investigated was solvent-extracted, coarse, crimpless 40–44s, subsequently referred to as BA fleece wool. The ultraviolet spectrum of the oxidized cyclic form of DTT (Fig. 1) has a characteristic absorption maximum at 284 mμ with no interference from DTT itself, which proves extremely valuable in following the reduction reaction. The calibration of this method with authentic 4,5-dihydroxy-1,2-dithiane has been reported previously.[12]

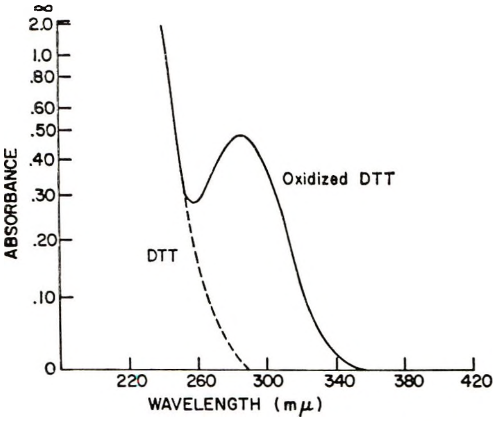


Fig. 1. Ultraviolet spectra of DTT and oxidized DTT in water.

Reduction of Wool with DTT

Wool samples of approximately 0.5 g were reacted in a constant-temperature bath with 100 ml solution of DTT under nitrogen with magnetic stirring. The stirring rate was maintained at approximately 250–300 rpm, and increases in the rate did not cause any changes in the rate of reduction. The reduction was followed by determining the increase in concentration of oxidized DTT in the solution surrounding the wool from absorbance measurements at 284 mμ in a Beckman DU spectrophotometer. The spectrophotometer cell was filled under nitrogen, and after measuring the absorbance, the solution was returned to the reaction vessel under nitrogen. For the investigation of the pH dependence of the reduction reaction, phosphate buffers of an ionic strength of $\mu = 0.183$ were used. These buffer solutions were adjusted with phosphoric acid to the lower pH values and differences in ionic strength were compensated for by the addition of a neutral electrolyte, sodium chloride.

Determination of Residual Disulfide

The applicability of this method of determining the degree of reduction was tested by determining the residual disulfide content in the fibers by the standard method of Folin and Marenzi[17] as modified by Zahn and Traumann.[18] The free SH groups of the combined cysteine were protected from reoxidation during this analysis by reaction with methyl iodide. The correlation of the degree of reduction as determined by the measurement of the concentration of oxidized DTT and as determined by analysis of residual disulfide content in the wool is shown for a number of cases in Figure 2. This correlation is quite satisfactory and demonstrates that the measurement of the oxidized DTT in the solution surrounding the wool proves an accurate way of determining the degree of reduction in the fibers.

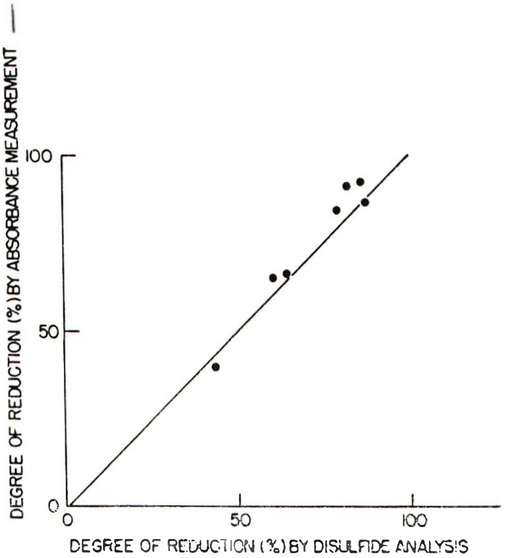


Fig. 2. Correlation of two methods for the determination of the degree of reduction (the line represents a 1:1 relation).

Titrimetric Determination of DTT

For the determination of DTT in a $5 \times 10^{-4}M$ solution surrounding the wool, 5 ml aliquots were withdrawn under nitrogen, injected into the cell of an automatic recording titrator (Radiometer Copenhagen), and adjusted to pH 8 by the addition of $0.1N$ NaOH. The pH of 3.5 used in these experiments had been obtained by adding $0.1N$ HCl to the reducing solution. The wool had been previously adjusted to the same pH value. A sufficient amount of sodium chloride was added to compensate for differences in ionic strength ($\mu = 0.183$) as compared to the experiments in buffered solutions. A 1 ml portion of a 0.1N $K_3Fe(CN)_6$ solution was then added, constituting a twofold excess of oxidizing agent resulting in an immediate drop of pH which is compensated for by the automatic recorded addition of 0.1N NaOH. The oxidation reaction can be written as:

$$R{-}(SH)_2 + 2K_3Fe(CN)_6 + 2NaOH \rightarrow 2K_3NaFe(CN)_6 + 2H_2O + RS_2 \qquad (5)$$

The reproducibility of this titration method was found to be quite satisfactory.

RESULTS AND DISCUSSION

Under the assumption that the overall rate of the reaction between DTT and the disulfide bond in wool, at least in unbuffered neutral (pH 5.9) solutions, is controlled by diffusion of DTT into the fibers, increases in the concentration of oxidized DTT in the solution can be taken as an indication of the rate of diffusion of DTT into the fiber. This would mean that the two other steps, reaction with the disulfide bonds forming oxidized DTT and the back-diffusion of oxidized DTT out of the fiber, are faster than diffusion of DTT into the fiber. This latter assumption appears justified, since the medium out of which the oxidized DTT has to diffuse is swollen due to reduction and should, therefore, offer less resistance to the back diffusion of oxidized DTT into the solution.

For the calculation of an approximate diffusion coefficient, an equation developed by Crank[19] was chosen which describes the diffusion from a stirred solution of limited volume into a cylinder:

$$\frac{M_t}{M_\infty} = 2\left[\frac{2}{\pi^{1/2}}\left(\frac{Dt}{a^2}\right)^{1/2} - \frac{1}{2}\frac{Dt}{a^2} - \frac{1}{6\pi^{1/2}}\left(\frac{Dt}{a^2}\right)^{3/2} + \ldots\right] \qquad (6)$$

M_t in this equation is the amount of solute in a cylinder of radius a after time t, and M_∞ is the corresponding amount after infinite time. In our case, M_t corresponds to the concentration of oxidized DTT in the solution C_t, and M_∞ can be equated to the maximum concentration of oxidized DTT in the solution C_∞, obtainable if all disulfide groups have been reduced. If C_t/C_∞ is plotted against the square root of time, as shown in Figure 3, the curves show a linear relationship for about 50–60% of the reaction, indicating that up to this degree of reduction the first term in the diffusion equation can be used. After this initial linear relationship, the curves level off at values of 0.9, indicating a degree of reduction of approximately 90%, which appears to be independent of the temperature.

This degree of reduction of 85–90% appears indeed to be the limiting value under these conditions as shown in Table I in which the degree of reduction as determined from absorbance measurements is compared with the degree of reduction determined from residual disulfide analyses in the wool samples after methylation of the free SH groups. An average residual amount of ~75 μmole/g of disulfide bonds is found in the keratin

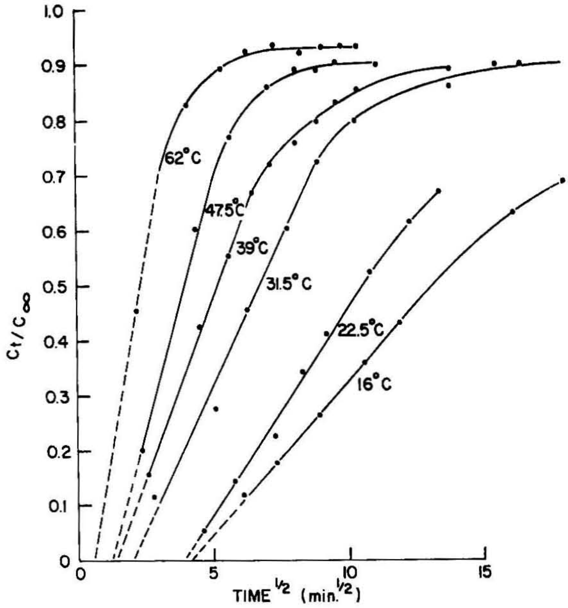


Fig. 3. Reduction of wool with DTT at different temperatures; 0.5 g wool, $10^{-2}M$ DTT, 100 ml solution.

even after exceedingly long times of reduction and at elevated temperatures. Occasionally the formation of oxidized DTT exceeds 90 or 100%, which must be attributed to secondary reactions which are not connected with the reduction of the disulfide bonds in the keratin and are probably due to incomplete elimination of oxygen from the system. To eliminate the possibility that preferential absorption of oxidized DTT would account for the apparent lack of completion of the reduction, the residual 15% disulfide bonds were isolated after total hydrolysis of an exhaustively reduced and subsequently methylated sample and identified as cystine by

TABLE I
Degree of Reduction and Residual Disulfide Content at Equilibrium in the Reaction with $10^{-2}M$ DTT Solution

Temp, °C	Time, hr	Degree of reduction, %[a]	Residual cystine content, μmole/g[b]	Degree of reduction, %[b]
29	30.5	104.4	78.2	84.1
29	46	90.7	74.3	84.9
29	70	107.3	69.7	85.8
39	6	91.8	59.9	88.0
47.5	6	90.6	80.5	83.6
62	6	92.2	66.6	86.4

[a] Determined from absorbance measurements.

[b] Determined from disulfide analyses in the wool sample.

paper chromatography. No trace of oxidized DTT could be found in the hydrolysate.

Approximate diffusion coefficients can be calculated from the slopes of the straight portions of the curves in Figure 3, using an average radius of the fibers of ~24 μ as determined by vibroscopic measurements.[20] These approximate diffusion coefficients for a concentration of $1 \times 10^{-2}M$ DTT are shown in Table II. By extrapolation of the straight lines put through the experimental points to $C_t/C_\infty = 0$, an initiation time, t_i, is determined which indicates the existence of a surface barrier to diffusion. This has been noted previously in experiments on the dyeing of wool fibers and has been identified with the epicuticle.[21]

TABLE II
Diffusion Coefficient of DTT in Wool ($1 \times 10^{-2}M$)

Temp, °C	$1/T \times 10^{-3}$, °K^{-1}	$D \times 10^8$, cm^2/min	t_i, min
16.0	3.459	0.355	17.7
22.5	3.383	0.643	15.2
31.5	3.283	1.268	4.0
38.5	3.209	1.975	2.0
47.5	3.119	3.616	1.4

From the temperature dependence of the diffusion coefficients, an activation energy of diffusion can be calculated according to the following equations:

$$D_t = D_0 e^{-E/RT} \tag{7}$$

$$\ln D_t = \ln D_0 - (E/RT) \tag{8}$$

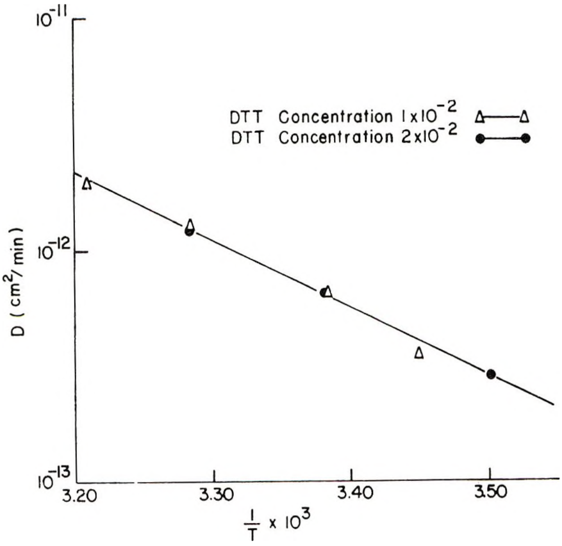


Fig. 4. Temperature dependence of the diffusion coefficient of DTT in wool.

where D_t is the observed diffusion coefficient at a temperature T, and D_0 is a constant. If $\ln D_t$ is plotted as a function of the reciprocal of the absolute temperature, the points should lie on a straight line. In Figure 4 the diffusion coefficients have been plotted in this way, and an activation energy of 13.4 kcal/mole has been calculated from the slope of the straight line put through the experimental points. This value compares favorably with activation energies for the diffusion within wool fibers of various solute molecules which range from 11 to 14 kcal/mole,[22] providing good support for the assumption that diffusion is the rate-controlling step.

Concentration Dependence

The concentration dependence of the diffusion coefficients can be seen in Table III. At lower concentrations the diffusion coefficient is independent of concentration; however, it increases significantly at higher concentrations of reducing agent.

TABLE III
Concentration Dependence of Diffusion Coefficients of DTT in Wool

Concentration $\times 10^2$, mole/l	Temp, °C	$D \times 10^8$, cm^2/min	t_i, min	$t_{1/2}$, min
1	16.0	0.355	17.7	173
1	22.5	0.643	15.2	142
2	12.5	0.290	21.1	214
2	22.5	0.646	11.6	144
2	31.5	1.26	7.3	55
9.4	8.0	0.834	21.2	108
9.4	10.5	1.25	10.1	67
9.4	16.0	2.17	7.3	40

Similar behavior of independence of concentration up to a certain critical concentration and subsequent sharp increases in diffusion coefficients have been observed in dyeing[23] and in the oxidation of wool with potassium permanganate.[24]

pH Dependence

A series of phosphate buffers ranging from pH 3.49 to 8.20 was used for the investigation of the pH dependence of the reduction of disulfide bonds in wool with DTT. To compensate for differences in ionic strength of the buffer solutions, sodium chloride was added as required. As shown in Figure 5, the rate of reduction is strongly affected by changes in pH. Plots of C_t/C_∞ against the square root of time still show considerably long straight portions even at low pH values. The pH dependence of the apparent diffusion coefficients, as determined from the straight portions of these curves, is shown in Figure 6. Also shown in Figure 6 is the pH dependence of $t_{1/2}$, the time necessary to accomplish reduction of 50% of

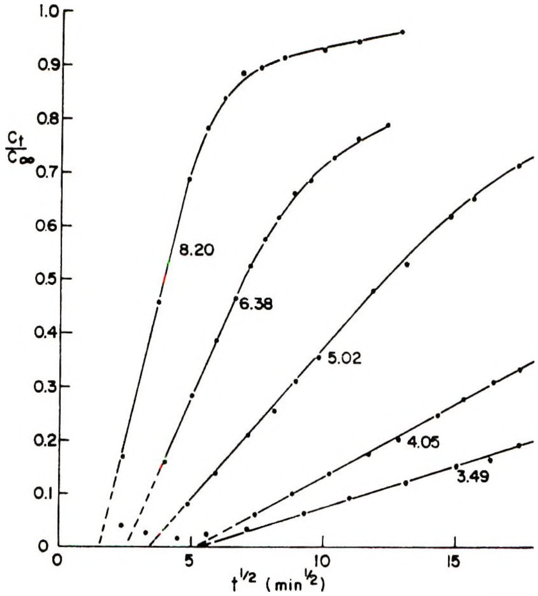


Fig. 5. Reduction of wool with DTT at different pH values; 0.5 g wool, $2 \times 10^{-2}M$ DTT, 24°C.

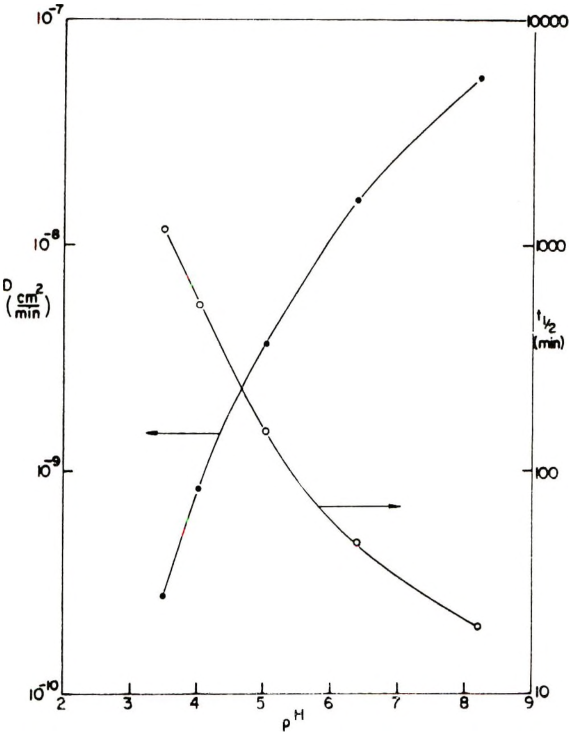


Fig. 6. pH dependence of apparent diffusion coefficients of DTT in wool and of half times of reaction.

all disulfide bonds present in the keratin. The only way in which diffusion may be expected to depend on pH is through differences in swelling of the fibers, since the penetration of neutral molecules through the fiber structure should be unaffected by changes in electrical charges on the surface and within the fiber. As shown by the work of Alexander and co-workers[25] on the pH independence of the reaction rate between chlorine and wool over wide ranges of pH values, swelling seems to have a negligible effect. Herrmann[26] investigated the pH dependence of the time necessary for complete penetration of keratin fibers by various thiols and found relatively small effects of thiols containing no ionizable groups other than SH. These observations suggest that the strong pH dependence of the rate of reduction with DTT (Fig. 6) indicates a change in the mechanism of the rate-controlling step from diffusion to the reaction rate itself as the pH is decreased. The rate of the reaction is expected to decrease rapidly with decreasing pH, since the concentration of the reacting mercaptide ions is controlled by the pH-dependent dissociation equilibrium:

$$\mathrm{HS{-}R{-}SH} \rightleftharpoons \mathrm{HS{-}R{-}S^{(-)}} + \mathrm{H^{(+)}} \tag{9}$$

A single pK value of 9.15 for DTT has been determined by titration with sodium hydroxide solution in an automatic recording titrator. Eventually the reaction rate will be slower than the diffusion in the fiber and then become the rate-determining step. In this case one might expect a change in the activation energy at low pH values.

Kinetic Analysis

If the reaction sequence of the reduction reaction is expressed as shown in eqs. (10) and (11)

$$\underset{\mathrm{A}}{\mathrm{W{-}S{-}S{-}W}} + \underset{\mathrm{B}}{\mathrm{HS{-}R{-}SH}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathrm{C}}{\mathrm{W{-}S{-}S{-}R{-}SH}} + \underset{\mathrm{D}}{\mathrm{W{-}SH}} \tag{10}$$

$$\underset{\mathrm{C}}{\mathrm{W{-}S{-}S{-}R{-}SH}} \overset{k_2}{\rightleftharpoons} \underset{\mathrm{E}}{\mathrm{R{-}S_2}} + \underset{\mathrm{D}}{\mathrm{W{-}SH}} \tag{11}$$

it can be shown that the rate expression which can be derived for the formation of the cyclic disulfide appears as that of a pseudo first-order reaction:

$$dE/dt = k_1^*(A_0 - E) \tag{12}$$

which can easily be solved to give the following expression:

$$k_1^* = (1/t) \ln [A_0/(A_0 - E)] \tag{13}$$

This equation has been derived under the assumption that the reaction rate of step 1 is considerably slower than that of step 2 and, therefore, determines the rate of the overall reaction. In other words, the intermediate mixed disulfide reacts to form the cyclic disulfide and combined cysteine as soon as it is formed and never exists in an appreciable concentration. If this assumption is correct, the amount of cyclic disulfide formed should be equal to the amount of DTT that has reacted and therefore disappeared from the reaction mixture. The amount of the cyclic disulfide formed can be determined easily by the measurement of absorbance at 284 mμ and the residual DTT in the solution can be determined by oxidation with excess potassium ferricyanide and titration of the acid generated in the reaction. Since the sample is not returned to the reaction vessel, a valid reaction rate cannot be determined from these experiments. The amount of oxidized DTT formed and the amount of DTT lost, however, should still be equal under the above mentioned assumption. The results of the determinations of DTT and oxidized DTT are shown in Table IV, and the differences between these two values are expressed as ΔC and listed in the last column. The low ΔC values indicate that the mixed disulfide does not exist in an appreciable concentration at any time under these conditions. It can, therefore, be concluded with some justification that the first reaction is slower than the second and that it is rate-controlling.

TABLE IV
Reduction of Wool with DTT at pH 3.5.

Time, hr	DTT, Concn. mmole/l	Calculated concn. oxidized DTT, mmole/l[a]	Concn. oxidized DTT, mmole/l	ΔC, mmole/l
0	4.73	0	0	—
$^1/_2$	4.65	0.08	0.02	−0.06
1	4.60	0.13	0.04	−0.09
$3^1/_3$	4.60	0.13	0.08	−0.05
5	4.51	0.22	0.21	−0.01
$5^5/_6$	4.38	0.35	0.31	−0.04
9	4.11	0.62	0.64	+0.02
12	3.89	0.84	0.93	+0.09
25	3.35	1.38	1.58	+0.20
29	2.99	1.74	1.93	+0.19

[a] Calculated from the decrease in the concentration of DTT.

TABLE V
Reduction of Wool with DTT in Unbuffered Solution (pH 5.9)

Time, min	Concn. DTT, mmole/l	Calculated concn. oxidized DTT, mmole/l[a]	Concn. oxidized DTT, mmole/l	ΔC, mmole/l
0	4.77	0	0	—
40	4.55	0.22	0.36	+0.14
110	3.70	1.07	1.09	+0.02
170	3.14	1.63	1.61	−0.02
280	2.44	2.33	2.32	−0.01
480	2.04	2.73	2.90	+0.17
1200	1.01	3.76	3.93	+0.16

[a] Calculated from the decrease in the concentration of DTT.

A similar experiment was conducted in an unbuffered solution without addition of sodium chloride or hydrochloric acid at a pH of 5.9 resembling the conditions of the initial series of experiments under which conditions the rate-controlling step appears to be diffusion of DTT in the fibers. The results are shown in Table V, and again very low ΔC values are found. This observation provides evidence for the previously made assumption that, under these conditions, diffusion of DTT in the wool is the rate-controlling step, all following steps being considerably faster.

To investigate the applicability of the derived expression for pseudo first-order kinetics at lower pH values, an experiment at pH 3.5 and with a DTT concentration of 2×10^{-2} mole/l was chosen. This concentration constitutes an approximate eightfold excess of reducing agent over the available disulfide bonds and at least in the initial phase of the experiments the changes in the concentrations of DTT can be neglected. In Figure 7 ln $[1/(1 - x^1)]$ is plotted against time, where x^1 represents the degree of reduction and is equal to E/A_0. There is considerable deviation from the linear behavior which would be expected if pseudo first-order kinetics were applicable. This is also borne out in Table VI which shows the reaction rate constant k_1*. Over no significant time period could a constant value be obtained, as already indicated by the corresponding curve in Figure 7. At all four temperatures which were investigated it could be shown that eq. (13) does not describe the experimental data and that the

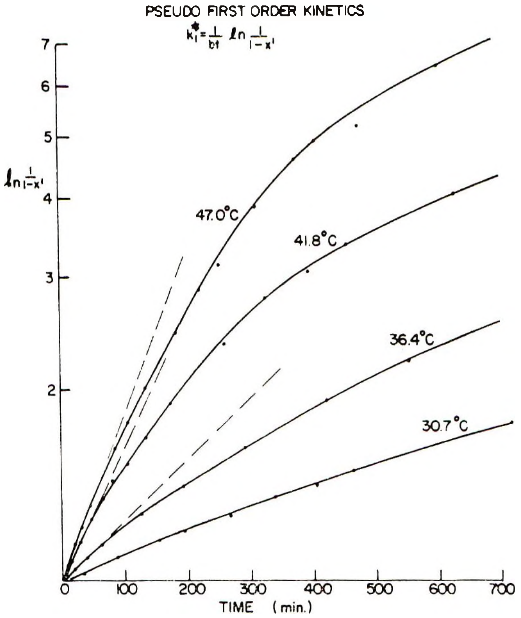


Fig. 7. Pseudo first-order kinetics for the reduction of wool with DTT at pH 3.50.

TABLE VI

Reduction of BA Fleece Wool (~0.5 g) with 2×10^{-2} *M* DTT at pH 3.50 and 36.4°C

Time, min	Absorbance	Reduction, %	$k_1^* \times 10^3$, min^{-1}	$k_2^* \times 10^3$, l/mole min
20	0.026	4.3	2.22	3.59
40	0.048	8.0	2.09	3.47
63	0.073	12.2	2.07	3.52
128	0.130	21.7	1.91	3.46
193	0.176	29.4	1.80	3.44
291	0.230	38.4	1.66	3.42
421	0.288	48.1	1.56	3.51
556	0.329	54.9	1.43	3.49
744	0.373	62.3	1.31	3.54
1271	0.438	73.1	1.03	3.41
1734	0.470	78.5	0.886	3.36
2711	0.504	84.1	0.678	3.11

reaction obviously does not follow simple pseudo first-order kinetics. If, however, pseudo second-order reaction is considered and it is assumed that the reaction is second-order with respect to the concentration of the disulfide bond A, the following expression for the reaction rate constant is obtained:

$$k_2^* = (1/A_0t)[1/(1 - x^1) - 1] \tag{14}$$

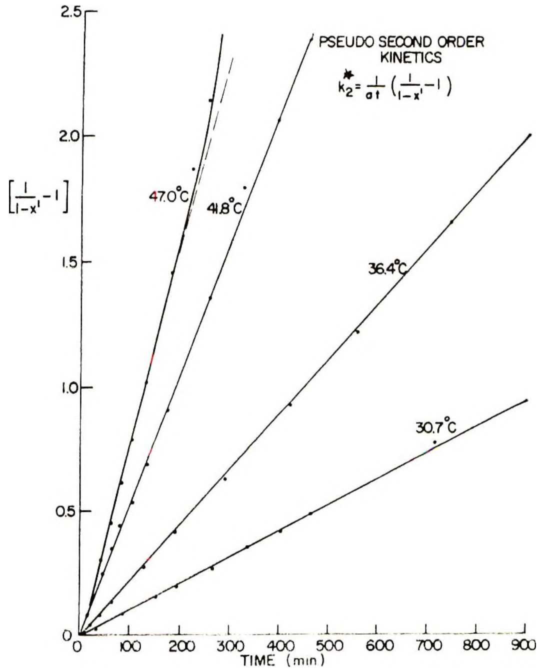


Fig. 8. Pseudo second-order kinetics for the reduction of wool with DTT at pH 3.50.

This equation seems to represent a much better description of the experimental data as the constant values of k_2^* in the last column of Table VI indicate. The initial concentration of cystine in the wool was calculated under the simplifying assumption of a uniform distribution of cystine throughout the fiber using the apparent density of wool in water at 25°C given by King.[27] A concentration of cystine of 0.625 mole/l was obtained this way. It is interesting to note that this reaction rate constant decreases significantly at the critical reduction values of 80–85%, at which point no further reduction of the disulfide bonds in the keratin can be accomplished as was pointed out above. Accordingly, a plot of $[1/(1 - x^1) - 1]$ against time, representing pseudo second-order kinetics as shown in Figure 8 for four different temperatures, shows linear portions of the curves over a considerable time range. For all four temperatures which were investigated a satisfactory constancy of k_2^* has been found over most of the reaction range until the values dropped as reduction of 80–85% had been reached. Average values of the rate constant were determined from the slopes of the curves in Figure 8. The temperature dependence of these data is shown in Figure 9, where the natural logarithm

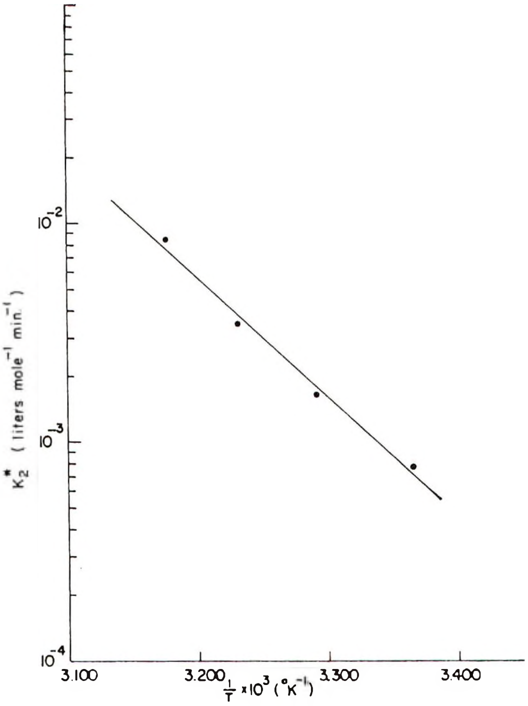


Fig. 9. Temperature dependence of pseudo second-order rate constant at pH 3.50 for reduction of wool with DTT.

of k_2^* is plotted against the reciprocal of absolute temperature according to an Arrhenius equation:

$$\ln k_2^* = \ln K - (E/RT) \qquad (15)$$

If these data are assumed to follow a linear relationship as is indicated at least over this narrow temperature range, an activation energy of ∽25 kcal/mole can be calculated from the slope of this line. This activation energy is twice the value that has been found for the unbuffered solution

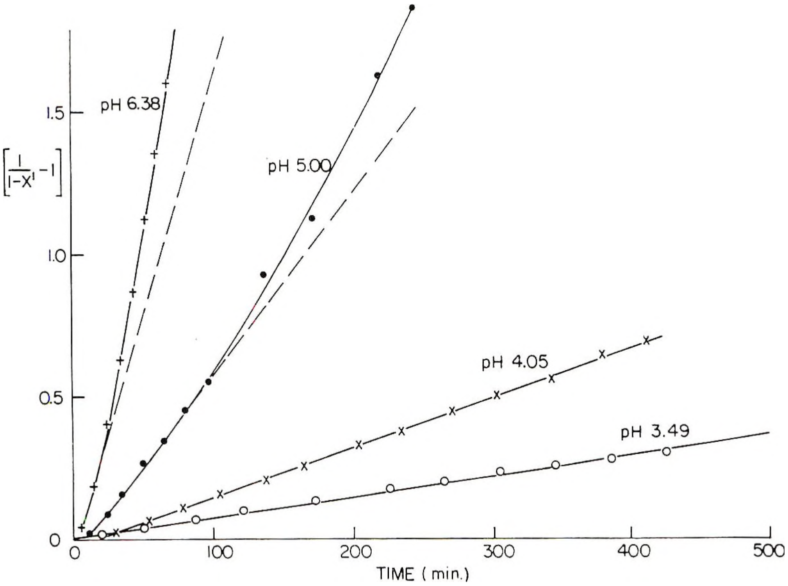


Fig. 10. Pseudo second-order kinetics for the reduction of wool with DTT at 24°C.

which has been described above and which presumably represents a diffusion controlled rate of reduction. This change in activation energy indicates that there is indeed a distinct difference in the mechanism of the rate controlling step of reduction in neutral solution as opposed to reduction at lower pH values. If an attempt is made to fit the experimental data at higher pH values into the pseudo second-order kinetics, deviations from the linear behavior occur (Fig. 10). This indicates that pseudo second-order kinetics do not describe the behavior at approximately neutral pH values, and it seems reasonable to assume that the low activation energy observed under these conditions is indeed the activation energy of a diffusion-controlled process. Further experimental data are currently being obtained, and until these data are available no attempt will be made to speculate about the surprising observation that a pseudo second-order kinetics describes the experimental data more satisfactorily than the expected pseudo first-order kinetics.

SUMMARY

Approximately 85% of the disulfide bonds in keratin are uniformly accessible to DTT and can be reduced under very mild conditions with small excess of reducing agent. The residual 15% could not be reduced under the conditions investigated.

The rate of reduction of disulfide bonds in wool with an unbuffered neutral solution of DTT appears to be controlled by the rate of the diffusion of the reducing agent into the fiber. An activation energy of 13.4 kcal/mole has been determined for this process.

With decreasing pH, a change in the mechanism of the rate controlling step is observed. At lower pH values the reaction rate itself apparently is slower than the rate of diffusion and becomes rate controlling. An activation energy of 25 kcal/mole has been determined at pH 3.5.

Pseudo second-order kinetics, second-order with respect to the disulfide bonds in keratin, has been found to describe the experimental data at pH 3.5.

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Polymerization of 2-(Chlorinated Methyl)-4-Methylene-1,3-Dioxolanes*

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Synopsis

The polymerizations of the novel 2-(chlorinated methyl)-4-methylene-1,3-dioxolanes derived from mono-, di-, and trichloroacetaldehyde were investigated. Poly-2-trichloromethyl-4-methylene-1,3-dioxolane was of particular interest because of its high hydrolytic stability and nonflammability. The monomers could be polymerized with cationic catalysts via the methylene functions without cleavage of the dioxolane rings. This selectivity was due to the acetal-stabilizing negative substituents and to the use of Lewis acid complexes of low reactivity as catalysts. In contrast to previously reported poly-4-methylene-1,3-dioxolanes, the title polymers were high-melting colorless solids of good to excellent fire resistance.

INTRODUCTION

Polymeric derivatives of halogenated aldehydes have been based on participation of the carbonyl in making up the polymer backbone.[1] They are known to possess limited hydrolytic and thermal stability.[2] One example in which derivatives of chlorinated aldehydes were components of carbon-chain polymers was the polyketene acetals.[3] Attempts to capitalize on the unusually high stability of acetals of chloral by using them as a polymer backbone have failed, since no synthesis route for diol-derived polyacetals has been found.[2,4] Since cyclic acetals of chloral are quite accessible,[4] it was thought interesting to attach them to a carbon polymeric chain, expecting to obtain hydrolytically stable high-melting fire-resistant plastics and, by analogy to polyvinyl butyral, for example, plastics with good adhesiveness and transparency. As model reactions the syntheses and polymerizations of 4-methylene-1,3-dioxolanes were chosen. Their polymerization is initiated by cationic catalysts, as expected for the vinyl ether type of monomer. However, the acetal bonds in 1,3-dioxolanes are easily cleaved by electrophilic catalysts. Therefore, various degrees of ring-opening have been reported to accompany carbon-chain polymerization of 4-methylene-dioxolanes.[5,6] Because of the high hydrolytic stability of chloral acetals[4] it was hoped that the unreported 2-trichloromethyl-4-methylene-1,3-dioxolane would undergo carbon-chain polymerization with-

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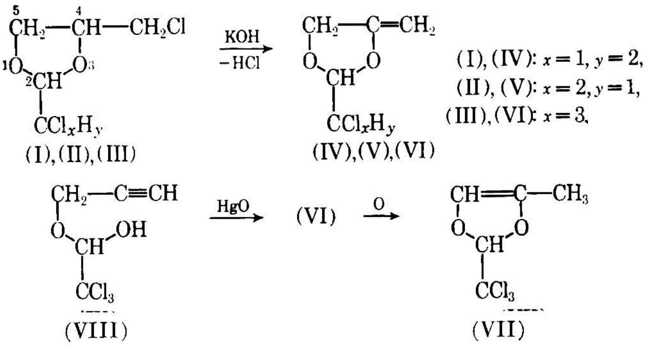
* Part of this paper was presented at the Meeting of The American Chemical Society, Spring 1967.

out acetal cleavage. The also unreported analogues from mono- and dichloroacetaldehyde were included in this study.

RESULTS AND DISCUSSION

Two synthesis routes for the monomers and also a side reaction are summarized below:

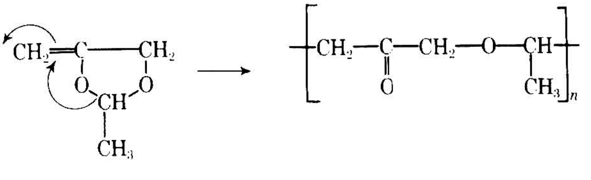


(I), (IV): $x = 1, y = 2$,
(II), (V): $x = 2, y = 1$,
(III), (VI): $x = 3$.

The removal of hydrogen chloride in the 4 positions was unusual, since the 2 hydrogen was expected to be more acidic. The monomer syntheses, the elimination mechanism, and some interesting spectral properties of these compounds will be discussed in a separate paper.

It has been reported that frequent discolorations, the presence of carbonyl groups and ether linkages in the backbone, and the absence of unsaturation and of crosslinking in poly-4-methylene-1,3-dioxolanes is due to simultaneous openings of the carbon double bond and the acetal ring during the cationic polymerization.[6]

coupled vinyl and ring-opening polymerization:



The occurrence of ring-opening polymerization even at −78° indicated little differences in the activation energies of both types of propagation. It was therefore necessary to search for highly selective catalysts, to avoid participation of the acetal group.

In contrast to haloketene-acetals[3] it was found that both free-radical (tri-*n*-butylboron + cumene hydroperoxide or benzoyl peroxide) and anionic (*n*-butyllithium) catalysts did not initiate polymerization of (IV), (V), or (VI) at temperatures ranging from −78° to 100°. Free-radical catalysts caused discolorations and viscosity increases at the higher temperatures. Monomer (IV) was converted to a black solid with formation of water and of hydrochloric acid after 12 hr. of reaction with 0.1% of benzoylperoxide at

100°. Protic and most Lewis acids and their etherates were either ineffective or produced dark oils or black resins, often in violent reactions accompanied by carbonization. The infrared spectra of these resins indicated the presence of carbonyl groups and of unsaturation. The formation of water and hydrochloric acid was detectable. Similar results were obtained when a cationogenic catalyst (iodine) or carbonium salts were used (adducts of triphenylmethyl chloride with bismuth trichloride, mercuric halides, and cadmium chloride in various solvents such as *p*-cresol or dimethyl sulfoxide). Alcoholic solutions of zinc chloride, reported to have converted several 4-methylene-1,3-dioxolanes to soluble polymers with little or no discolorations,[5] also resulted in the formation of black resins. When methanolic solutions of Lewis acids of different strengths were screened, it became apparent that the monomer reactivity of a given catalyst complex toward ring-opening as well as toward carbon-chain polymerization decreased markedly from (IV) to (VI); see Table I. The more reactive Lewis acid solutions were found to cause degradative ring-opening polymerization, as indicated by the dark colors of the polymers and by their infrared spectra. They were soluble, except for those in which partial carbonization had occurred. The catalysts are arranged in Table I according to their visually established decreasing reactivity, which resembles previous comparisons of relative reac-

TABLE I
Catalyst Screening, 1*M* Lewis Acids in Methanol

(IV) = 2-Chloromethyl-4-methylene-1,3-dioxolane
(V) = 2-Dichloromethyl-4-methylene-1,3-dioxolane
(VI) = 2-Trichloromethyl-4-methylene-1,3-dioxolane
Catalyst concentration: approximately 1 mole-%
Time: up to 72 hr.
O = no polymerization
C = carbon-chain polymerization, polymers colorless, negligible $C{=}O$ (by IR)
R = ring-opening polymerization, polymers dark, large $C{=}O$ (by IR)
The subscripts refer to times after which viscosity increases became noticeable: 1, instantaneous; 2, ≤ 24 hr.; 3, > 24 hr.

Lewis acid	IV		V		VI	
	25°	70°	25°	70°	25°	70°
BF_3 ether	R_1	—	R_1	—	R_2	—
$SnCl_4$	R_1	—	R_2	—	C_2	—
$FeCl_3$	R_1	—	R_3	—	O	R_2
$ZnCl_2$	R_1	—	$C_3 + R_3$	—	O	R_3
$SbCl_5$	R_2	—	R_3	R_3	O	O
$TiCl_4$	R_2	—	R_3	R_3	O	O
ZnI_2	C_2	—	O	R_3	O	R_3
$BiCl_3$	O	R_2	C_3	—	O	C_3
$CdCl_2$	C_3	—	C_3	—	O	O
$HgCl_2$	O	R_3	O	O	O	O
$AlCl_3$	O	O	O	O	O	O

TABLE II

Polymerization of VI with Ziegler Catalysts

Catalyst (1% by mole)	Solvent	Temp., °C.	Time, hr.	Yield, %	$\bar{M}_n$	T_s, °C.
$TiCl_4$ + $Al(i\text{-}C_4H_9)_3$,[a] ratio 3:1	—	25	19	explosive		
$TiCl_4$ + $Al(i\text{-}C_4H_9)_3$,[a] ratio 3:2	—	25	19	14	17,240	210–35
$TiCl_4$ + $Al(i\text{-}C_4H_9)_3$,[a] ratio 3:4	—	25	19	29	23,950	220–30
$TiCp_2Cl_2$ + $Al(C_2H_5)_2Cl$,[b] ratio 1:2	—	25	20	55 (2)	12,680	205–20
$Ti(On\text{-}C_4H_9)_4$ + $Al(C_2H_5)_2Cl$,[c] ratio 1:1	—	25	20	63.6	28,960	220–225
$Al(C_2H_5)_2Cl$ (1*M* in heptane)	toluene, 1 l./mole	−78 and 25	4 and 12	traces	—	—
$Al(C_2H_5)Cl_2$	" "	−78 and 25	4 and 12	49.5	43,100	220–225

[a] A 1*M* solution of $TiCl_4$ in dichloromethane was added to a 1*M* solution of $Al(i\text{-}C_4H_9)_3$ in heptane at room temperature with stirring. After 40 min. the flask was cooled to −40° and the monomer added and permitted to warm to 0°C. for 1 hr. thereafter to room temperature.

[b] Cp = cyclopentadienyl. A 1*M* solution of $Al(C_2H_5)_2Cl$ in heptane was added to a solution of $TiCp_2Cl_2$ in monomer at 0°C. The polymer was separated from 10–15% of insoluble material.

[c] A 1*M* solution of $Al(C_2H_5)_2Cl$ was added to the monomer, containing a 1*M* solution of $Ti(On\text{-}C_4H_9)_4$ in toluene.

tivities of Lewis acid catalysts.[7] The more negatively substituted the monomers were, the slower they reacted with a given Lewis acid solution in both normal and degradative types of polymerization. Thus, tin tetrachloride caused an explosive decomposition with (IV), a rapid (several hours) degradative reaction with (V), and a somewhat slower carbon-chain polymerization with (VI). This reflected the expected increasing stabilization of the acetal structure with increasing negative substitution in the 2 positions of (IV), (V), and (VI).

The infrared spectrum of poly(VI) prepared at −78° (Table II) was devoid of absorptions in the 5–6.5 μ range, indicating the absence of carbonyl and unsaturated groups. Other polymers listed in Tables II and III showed bands at about 5.9 and 6.15 μ of very weak intensity (well below one tenth of the relatively low intensity of C—H absorptions at 3.35–3.4 μ). These minor bands are ascribed to unsaturation and not to carbonyl groups, since the monomers showed absorptions in the same region (medium shoulder at 5.85, strong at 5.95, medium shoulder at 6.1–6.2 μ), while colored polymers obtained by degradative polymerization showed a sharp, strong band at 5.7 and a shoulder at 5.8 μ. The infrared spectra could thus be used to distinguish reliably between carbon-chain and degradative polymerizations.

TABLE III

Polymerization of IV, V, and VI with 1*M*-Lewis Acids in Methanol

Catalyst	(M/C)[a]	Temp., °C.	Time	Yield, %	$\bar{M}_n$[b] ($\times 10^{-3}$)	T_s, °C.[c]
(IV) ZnI_2	900:1	25	1 day	69	6.2	95–110
(IV) $CdCl_2$	900:1	25	14 days	58	16.0	100–130
(V) $ZnCl_2$	800:1	25	14 days	11	2.7	105–110
(V) $BiCl_3$	800:1	25	14 days	12	2.3	90–100 (y)
(V) $CdCl_2$	800:1	25	14 days	47 (9)	(11.5)	135–150
				(38)	(5.8)	130–150 (y)
(VI) $SnCl_4$	900:1	25	2 hours	13	13.0	210–225 (y)
(VI) $BiCl_3$	700:1	80	3 days	19 (5)	(6.9)	200–215 (y)
				(14)	(3.0)	187–195 (y)

[a] M, monomer; C, catalyst (moles).

[b] Based on polymer insoluble in methanol; data in parentheses refer to yields after fractional precipitation.

[c] Discolorations are indicated as "y" = yellow; the softening temperatures were determined on a Fisher-Johns melting-point apparatus.

The system tin tetrachloride–(VI), which favored carbon-chain reaction exclusively, was chosen for further study. The effects of added methanol on rates (followed by refractive index), yields, and molecular weights are summarized below for polymerizations carried out in bulk at 0–5°C. in nitrogen atmosphere:

(*1*) Polymerization occurred with tin tetrachloride in the absence as well as in the presence of methanol, with molar ratios of $CH_3OH/SnCl_4$ of 0, 1, 3, 4, and 10; practically no conversion took place with a molar ratio of 2 after slight initial reaction.

(*2*) Plots of refractive index versus time showed induction periods for molar ratios of 0 (over 3 hr.) and of 1 (0.5 hr.) and none or below (0.5 hr.) for other catalyst ratios. The rates during the first 1.5 hr. were proportional to the amount of added methanol. At later stages the plots acquired wavelike patterns, i.e., consecutive cycles of inhibition and polymerization, except for $CH_3OH = 0$; see Figure 1.

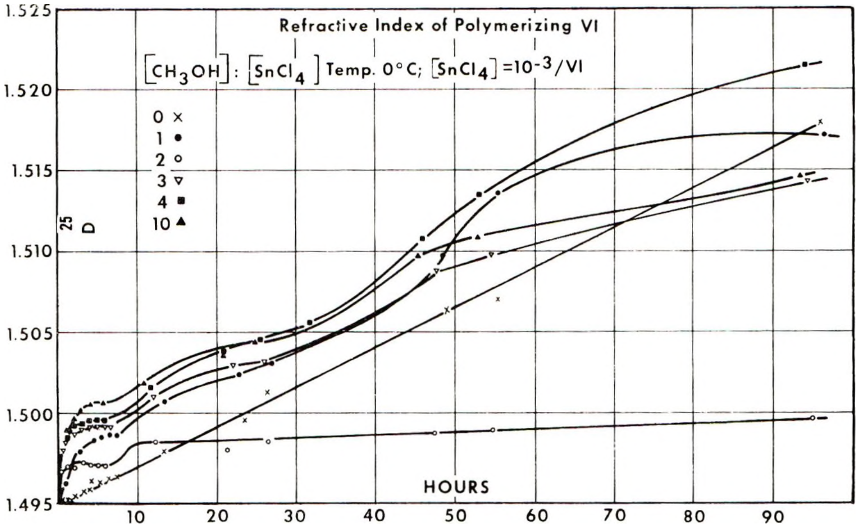


Fig. 1. Refractive index of polymerizing (VI).

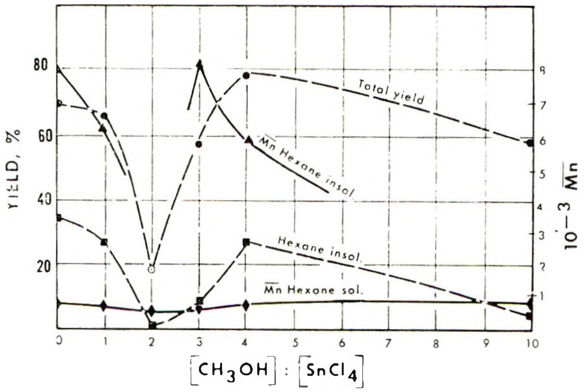


Fig. 2. Polymerization of (VI) at 0°C.; $[SnCl_4] = 10^{-3}$ monomer.

(*3*) Total yields, yields in high polymer, and molecular weights were highest for the methanol-free polymerization (Fig. 2). However, even in this case about one half of total yield was oligomer ($M_n \leq 1000$).

The analyses of the polymers showed a small excess of CH and deficiency in chlorine. This could not be explained by CH_3O endgroups, since the deviations were too large and independent of M_n. It was also noticed that the infrared and NMR spectra of the polymers indicated the presence of approximately one CH_3 group for every ten monomer units. This may be explained by assuming isomerization of the monomer to 2-trichloromethyl-4-methyl-1,3-dioxole (VII) and copolymerization of the latter. Although this isomerization was independently found to be catalyzed by weak bases, some dioxole was detected in residual monomers after workup of polymerization mixtures (see under "Experimental").

Interestingly, it was also found that Lewis acids, modified in the fashion of Ziegler-type catalysts, supported a carbon-chain polymerization of (VI) without affecting the acetal group (Table II). It is likely that they did not act by a Ziegler coordination mechanism, as indicated by the fact that aluminum alkylchlorides at low temperature effected polymerization in the absence of titanium compounds. The highest molecular weights (over 40,000) were obtained under these conditions.

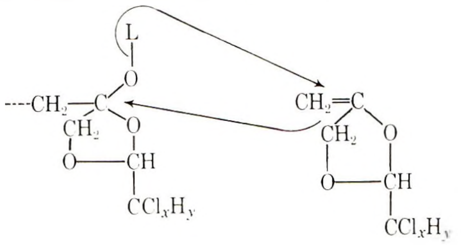
The polymers were white (trichloromethyl) or light yellow (di- and chloromethyl derivatives) powders, forming transparent, brittle films when cast from solution. They were soluble in common organic solvents except alcohols and aliphatic hydrocarbons. Their softening temperatures (see Table III) increased from polychloromethyl (100–130°C. for M_n = 16,000) to polydichloromethyl (135–150°C. for M_n = 11,500) to polytrichloromethyl-4-methylene-1,3-dioxolane (220–235°C. for M_n = 43,000). The higher-melting polymers showed slight yellowing after melting. The high softening temperatures contrast with those of previously known chlorine-free poly-4-methylene-dioxolanes, which soften well below 100°C.[5]

Polymers derived from chloro- and dichloromethyl-4-methylene-1,3-dioxolane supported combustion to varying degrees. Polytrichloromethyl-4-methylene-1,3-dioxolane, however, burned only partially on a red-hot spatula in a Bunsen burner, leaving considerable carbonized residue after 5 min. Whenever withdrawn from the flame, burning ceased instantaneously. The nonflammability of this polymer distinguished it from other polymeric derivatives of chloral, including polychloral.

The hydrolytic stability of poly(VI) was established by subjecting it to ASTM Procedure D-1376-58 for determining aldehydes in polyvinyl acetals. After 3 hr. of reflux the quantitatively recovered polymer was devoid of hydroxyl groups. Its infrared spectrum showed minor differences in the C—Cl region. Purification from acetone–methanol gave a 76% yield of poly(VI), which was identical in all respects to the starting material. It was concluded that no hydrolysis of poly(VI) had taken place under the conditions of the ASTM procedure, since the hydrolysis solution did not contain chloral hydrate, according to vapor-phase chromatography.

The current experiments were not designed to establish the mechanism of this reaction. Obviously, the characteristic features of cationic polymerizations are missing, such as fast rates at low temperatures and inhibition by more than cocatalytic amounts of alcohol. It is unlikely that dissociated carbonium ions are involved in the propagation. In this and other respects the observed phenomena are compatible with a "pseudo cationic" mechanism, such as that suggested by Plesch and his co-workers for the system styrene–water–perchloric acid[8] or styrene–water–titanium tetrachloride,[9] with an ester as a chain carrier. In the case of 4-methylene-1,3-dioxolanes the ester would possess a ketal structure linked to the Lewis acid complex, L. In the polymerization of (VI) with stannic chloride or aluminum alkyl chlorides alone the ester may be formed from impurities or by isomerization of some monomer during the induction period.

propagation on ketal ester of Lewis acid "L":



The C—OL bond would be much more reactive than the acetal structure, since noncyclic ketals such as 2,2-diethoxypropane are known to hydrolyze more than 10^4 times faster than cyclic acetals such as 2-methyl-1,3-dioxolane.[10] This would permit insertion of suitably polarized monomer to form the growing chain, P, with considerably greater ease than, say, styrene copolymerizes with 1,3-dioxolane.[11] Whether this insertion occurs via ionic transition states or in the fashion of a four-center reaction may be difficult to determine. If ionic species are involved, they are certainly not free ions in the conventional sense of the word.

The wavelike patterns observed in the polymerization of (VI) with stannic chloride and methanol (Fig. 1) were similar to those reported previously for stannic chloride–water–styrene.[12] The interpretation of these data involved the formation of inhibiting hydrochloric acid, followed by hydrochlorination of styrene and participation of the monomer chloride, together with stannic acid chloride, in the consecutive inhibition–retardation–initiation cycle. It was likely in the case of the 4-methylene-1,3-dioxolane (VI) that free hydrochloric acid with a methanol-solvated proton would have selected the acetal group rather than the double bond as its target. Thus, (VI) was found to undergo degradation with catalytic amounts of methanolic anhydrous hydrofluoric acid or sulfuric acid hydrate. The conversion patterns may, at least in this case, involve the previously discussed monomer ester, a possibility that had not been considered for styrene at that time.

EXPERIMENTAL

Purity of Monomers

The monomers were purified by distillation through a 36 in. spinning-band column under nitrogen. Vapor-phase chromatography showed the following impurities for 2-chloromethyl (IV), 2-dichloromethyl (V), and 2-trichloromethyl-4-methylene-1,3-dioxolane (VI):

% Monomer	No. impurities	No. distillations
(IV) 94.33	5	1
(V) 91.07	4	1
(VI) 98.09	2	4

Catalyst Screening

Catalysts were of reagent grade and used as such. Solutions (1*M*) were prepared from anhydrous solvents under nitrogen and transferred with baked syringes. In case of precipitates (such as $BiCl_3 + CH_3OH$) the supernatant liquid was used. Freshly distilled monomers, 5 ml. each, were transferred by means of baked syringes into baked nitrogen-flushed, 10 ml. vials, closed with serum stoppers. The polymerizations were observed over a 2 wk. period.

Polymerization of (IV), (V), and (VI)

The polymerizations were carried out under nitrogen in baked, two-necked, 50 ml. flasks, provided with a three-way gas inlet and magnetic stirring bars. Monomers followed by catalyst solutions were added from baked syringes.

The polymer mixtures were dissolved in acetone and twice precipitated into methanol as fine white powders. The filtrates from poly(VI), Table III, were evacuated, and the distillable residue (4%) was fractionated through a spinning-band column. The fraction boiling from 65–69°C. at 7.2 mm. consisted of a mixture of monomer with 2-trichloromethyl-4-methyl-1,3-dioxole (VII), according to its NMR spectrum.

Polymerization of 2-Trichloromethyl-4-methylene-1,3-dioxolane (VI) with Tin tetrachloride

Reagents. Nitrogen, Linde H.P. dry, led through 10 in. calcium hydride tower. Dichloromethane, stored over and distilled from Linde molecular sieve 5A under nitrogen. Tin tetrachloride, Fisher Scientific Co., No. T-140, used as such from fresh bottle.

Polymerization Procedure. Two-necked, 100 ml. flasks, provided with glass stopper, three-way stopcock, and magnetic stirring bar, were baked at 120°C., permitted to cool under nitrogen flush, and immersed in an ice bath. During stirring the following additions were made from baked syringes through the stopcock, with purging with nitrogen through its horizontal arm. Monomer (40.70 g., 0.2 mole) was followed by varying amounts of mixtures of methanol with 0.1 ml. dichloromethane, keeping the latter's concentration constant. This was followed by 0.1 ml. (2×10^{-4} mole) of a 2*M* solution of tin tetrachloride in dichloromethane. The added methanol corresponded to 0, 1, 2, 3, 4, and 10 molar multiples of tin tetrachloride. Stirring was continued for 30 min. after addition of catalyst.

The conversion was followed by measuring the refractive index of samples withdrawn every 30 min. during the first 8 hr. Later readings were less frequent. The refractive index of the monomer (n_D^{25} = 1.4950) seemed to be little affected by the small amounts of catalyst and solvents, ranging from 1.4945 to 1.4950. After 96 hr. in an ice bath the polymers were dissolved in 80 ml. of dichloromethane containing approximately 80 mg. of ethanolamine and precipitated twice into 800 ml. of hexane. The precipitates and residues obtained after evaporation of hexane were dried at 100°C. and 0.2 mm. Hg to constant weight.

ANAL. Calcd. for $(C_5H_5Cl_3O_2)_n$ (%): C 29.20, H 2.46, Cl 52.40. Found for hexane-insoluble polymer (%):

$CH_3OH:SnCl_4$ = 0 = C 30.71, H 2.77, Cl 51.8; mol. wt. 8090
1 = C 30.10, H 2.58, Cl 53.3; mol. wt. 6290
4 = C 29.89, H 2.66, Cl 52.1; mol. wt. 8285
10 = C 29.77, H 2.53, Cl 51.9; mol. wt. 5860

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The Emulsion Polymerization of Vinyl Acetate. Factors Controlling Particle Surface Area and Rate of Polymerization

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Synopsis

An emulsion polymerization system with uniform continuous addition of vinyl acetate monomer, Pluronic F68 surfactant, and persulfate initiator has been examined with variation of the surfactant concentration over a tenfold range. The particle surface area per unit weight of emulsion was found to vary directly as the surfactant/monomer ratio, as also did the emulsion viscosity. At constant polymer/emulsion weight the number of particles per unit emulsion weight varied directly as the cube of the surfactant concentration. It is shown that these relationships apply also to other monomers, such as styrene and methacrylate esters. The solubility of vinyl acetate in a range of Pluronic F68 aqueous solutions was determined, and it was shown that the rate of polymerization is dependent on the solubility of the monomer in the surfactant solution. It is concluded that when a water-soluble initiator is used, polymerization proceeds in the aqueous phase. The principal factors controlling the rate of polymerization in the emulsion polymerization of vinyl acetate are, consequently, the initiating system and the concentration of monomer in the aqueous phase. Solubilization characteristics indicate that the surfactant concentration will have a much greater effect on the less water-soluble monomers, such as styrene, than on the more soluble ones, such as vinyl acetate.

INTRODUCTION

Examination of the kinetics of emulsion polymerization has usually been carried out in one-stage processes in which all the ingredients are added at the start. In such a process both the overall concentration of monomer and the ratio of surfactant to monomer will vary during the polymerization. Since the particle size also changes during the reaction, it is possible for fortuitous correlations to be observed.

To reduce the number of the uncontrolled variables, the kinetics of the emulsion polymerization of vinyl acetate at high conversion was examined in a system involving continuous addition of monomer, surfactant, initiator, and alkali, a process that was expected to yield a narrow distribution of particle diameters. Non-ionic Pluronic F68 was selected as the sole surfactant because of its versatility as emulsifier and stabilizer and the added advantage that it is soluble in vinyl acetate and compatible with its polymer.

EXPERIMENTAL

The polymerizations were conducted under atmospheric pressure in a 16-liter FMB stainless-steel reactor suitably equipped with a stirrer, temperature recorder and means of adding three ingredients simultaneously at a steady rate and of taking samples. The basic formula used was as follows. Distilled water: The quantity of distilled water was adjusted to give a final theoretical nonvolatile content of 50.0% at complete conversion. Vinyl acetate (inhibited with 15 ppm hydroquinone): 100.00 parts by weight. Pluronic F 68: a block copolymer derived from propylene oxide and ethylene oxide; contains 5 ppm 2:6 di-*tert*-butyl-*p*-cresol (supplied by Wyandotte Corporation). Ammonium persulfate, reagent-grade, 0.24 parts by weight. Distilled water, 21.00 parts by weight. Sodium hydroxide, reagent-grade, 0.10 parts by weight. Distilled water, 20.00 parts by weight.

The first portion of distilled water was put in the reactor and was followed, with agitation, by 10% of the monomer–Pluronic F68 solution (made up at 27°C. and cooled back to room temperature) and 0.20 parts by weight of the persulfate initiator in 1.00 parts by weight distilled water.

The temperature was raised to 60°C. and then over 15 min. to 70–72°C., reflux being avoided by jacket cooling as necessary. The balance of the monomer–surfactant solution and the persulfate and NaOH solutions were added to the reactor continuously in separate streams at known uniform rates over about 4 hr., the temperature being kept 70–72°C. Small samples were taken every 0.5 hr. The polymerization of the sample was stopped by cooling immediately and saturating with air. The nonvolatiles were determined gravimetrically; the weight-average particle sizes, by a turbidimetric method.[1]

The quantity of Pluronic F68 was varied between 2.0 and 20.0 parts by weight on 100 parts vinyl acetate.

The number of polymer particles (N) was calculated by assuming a specific gravity of 1.198 for polyvinyl acetate. This value for the specific gravity was calculated from the density of the final polymer emulsion and compares well with previously published figures.[2,3] The particle diameter was calculated from light-transmission figures corrected for the surfactant content. The particle diameter distribution was checked in selected samples by electron microscopy and found to be similar to that noted by French,[4] i.e., log normal.

The solubility of vinyl acetate monomer in surfactant solutions was determined by shaking 10 ml. of the monomer with 100 ml. of the solution at 20°C. and allowing them to stand at this temperature overnight. The vinyl acetate concentration of the aqueous phase was then determined on a Perkin-Elmer 800 gas chromatograph with a differential flame-ionization detector. A 12 in. column was used with a 10% Reoplex 400 stationary phase at 69°C., the flame-ionization detector at 100°C., the injection port at 170°C., and the nitrogen carrier at 31.2 ml./min.

DISCUSSION

Particle Surface Area

In the present series, in which monomer, initiator, and surfactant were added continuously, the rate of polymerization was substantially constant, both during each experiment and with variation of the surfactant concentration over a tenfold range. Since both the particle diameter and the number of particles per unit weight of emulsion varied during the polymerization process, conclusions may be drawn concerning the dependence of these factors apart from the rate of polymerization.

From Figure 1 it is seen that at a given surfactant concentration the total particle surface area is directly proportional to the emulsion weight:

$$4\ \pi r^2 N \propto W \tag{1}$$

where r is particle radius, N is total number of particles, and W is emulsion weight.

In Figure 2 the slopes of the curves of Figure 1 are plotted against the surfactant concentration, and the total particle surface area per unit weight of emulsion is seen to vary directly as the surfactant concentration. A straight line is also obtained by using the mean values for total particle surface area per gram of emulsion given in Table I. Thus

$$4\ \pi r^2 N/W \propto [\mathrm{S}] \tag{2}$$

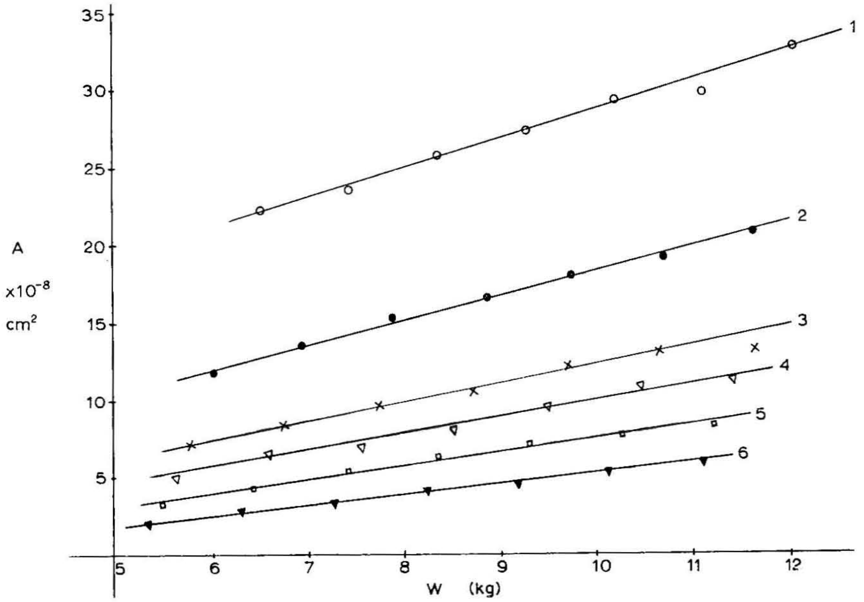

Fig. 1. Variation of total particle surface area A with weight W of emulsion at different surfactant–monomer ratios [S]: (○) 0.20; (●) 0.12; (×) 0.08; (▽) 0.06; (□) 0.04; (▼) 0.02.

TABLE I

Time sample taken after start of contin. addn., hr.	Nonvol., % wt. in emuls.	Polymer–emulsion wt. ratio	Wt.-avg. particle diam., μ	Tot. No. particles, N $\times 10^{-17}$	Tot. No. particles per g. emulsion, N/W, $\times 10^{-14}$	Tot. particle surface area per g. emulsion, cm.^{2}) A/W, $\times 10^{-4}$
Expt. 1 (ratio Pluronic F68 to monomer, 0.20):						
0.5	20.78	0.170	0.025	1133	173.7	34.0
1.0	26.26	0.215	0.034	648	87.0	31.6
1.5	30.81	0.252	0.041	487	58.2	30.8
2.0	34.58	0.284	0.048	379	40.8	29.6
2.5	37.78	0.311	0.054	321	31.4	28.8
3.0	40.24	0.331	0.062	246	22.1	26.6
3.5	42.32	0.348	0.064	254	21.1	27.2
Expt. 2 (ratio Pluronic F68 to monomer, 0.12):						
0.5	20.75	0.181	0.046	178	29.6	19.7
1.0	26.90	0.235	0.061	115	16.5	19.3
1.5	31.73	0.278	0.072	93.5	11.6	19.3
2.0	35.52	0.312	0.084	73.9	8.37	18.6
2.5	39.11	0.345	0.094	64.3	6.59	18.3
3.0	41.70	0.368	0.103	57.4	5.36	17.9
3.5	43.42	0.383	0.107	57.8	4.97	17.9
Expt. 3 (ratio Pluronic F68 to monomer, 0.08):						
0.5	22.56	0.206	0.085	30.9	5.34	12.1
1.0	28.78	0.263	0.108	22.5	3.33	12.2
1.5	33.61	0.308	0.124	19.9	2.57	12.4
2.0	37.25	0.341	0.143	16.2	1.86	11.9
2.5	40.59	0.372	0.150	17.0	1.75	12.4
3.0	42.89	0.393	0.162	15.7	1.47	12.1
3.5	44.96	0.413	0.180	13.2	11.3	11.5

Expt. 4 (ratio Pluronic F68 to monomer, 0.06):						
0.5	22.63	0.210	0.122	10.41	1.84	8.67
1.0	29.60	0.276	0.144	9.74	1.47	9.58
1.5	34.36	0.321	0.177	6.98	0.921	9.03
2.0	38.10	0.356	0.194	6.64	0.777	9.17
2.5	41.47	0.388	0.197	7.69	0.809	9.86
3.0	44.68	0.419	0.207	7.87	0.751	10.14
3.5	46.67	0.438	0.228	6.72	0.587	9.57
Expt. 5 (ratio Pluronic F68 to monomer, 0.04):						
0.5	23.03	0.219	0.190	2.80	0.509	5.75
1.0	30.15	0.287	0.217	2.89	0.448	6.62
1.5	36.11	0.345	0.240	2.94	0.397	7.19
2.0	40.49	0.387	0.260	2.94	0.352	7.45
2.5	43.19	0.413	0.280	2.79	0.300	7.38
3.0	46.16	0.442	0.300	2.67	0.260	7.36
3.5	48.10	0.461	0.312	2.70	0.241	7.38
Expt. 6 (ratio Pluronic F68 to monomer, 0.02):						
0.5	22.52	0.218	0.290	0.767	0.143	3.76
1.0	29.85	0.290	0.330	0.813	0.128	4.39
1.5	34.56	0.336	0.360	0.836	0.115	4.67
2.0	38.55	0.376	0.380	0.897	0.109	4.94
2.5	40.72	0.397	0.410	0.844	0.092	4.84
3.0	44.19	0.431	0.420	0.941	0.093	5.12
3.5	46.40	0.453	0.430	1.007	0.091	5.26

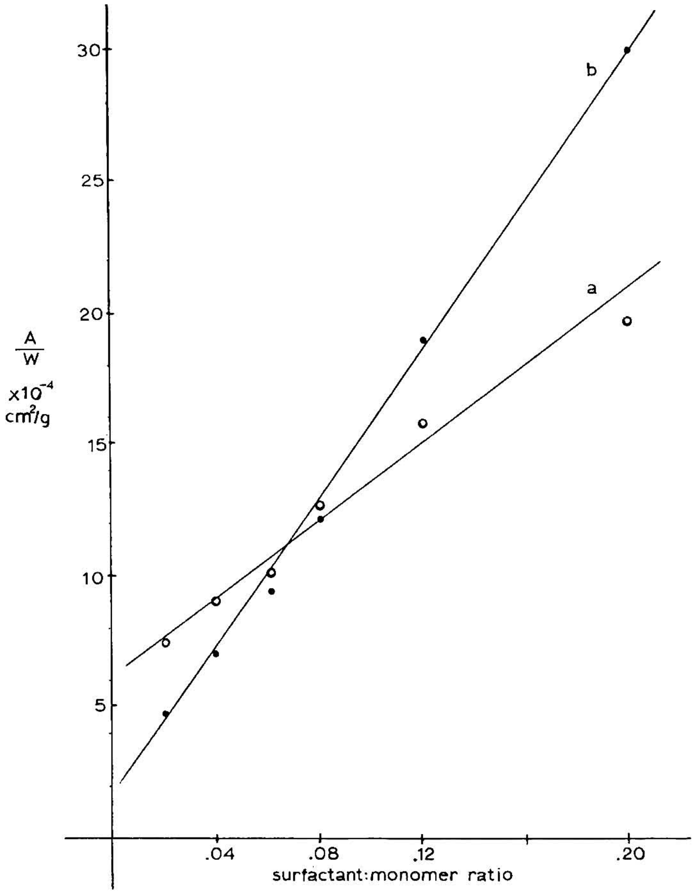

Fig. 2. Variation of particle surface area per unit weight of emulsion, A/W, with surfactant–monomer ratio [S]: (a) A/W from slopes of Figure 1; (b) A/W mean values from Table I.

where [S] is surfactant or stabilizer concentration as proportion of monomer. Therefore, at a constant polymer–emulsion weight ratio

$$^4/_3\ \pi r^3\ N/W = \text{constant} \tag{3}$$

$$r \propto [\mathrm{S}]^{-1} \tag{4}$$

as confirmed in Figure 3. Alternatively, from eq. (3)

$$r^2 \propto (W/N)^{2/3}$$

Thus, substituting for r^2 in relation (2) gives, at a constant polymer–emulsion weight ratio,

$$N/W \propto [\mathrm{S}]^3 \tag{5}$$

Relation (2) is in agreement with the assumption[5] that a minimum quantity of adsorbed surfactant per unit particle surface is necessary for stability and may be compared with other published results. Thus, French[4]

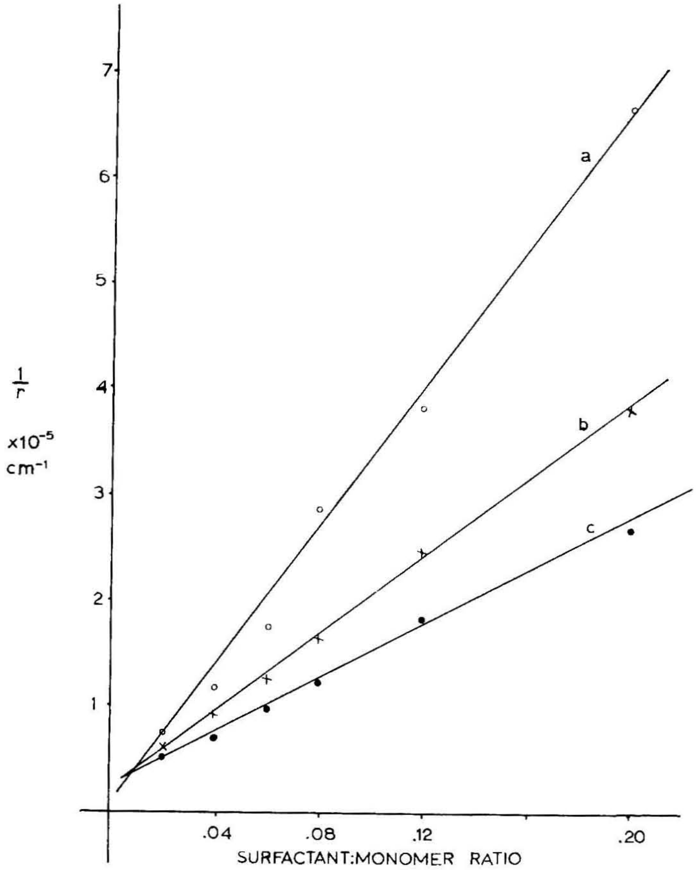

Fig. 3. Variation of reciprocal of particle radius ($1/r$) with surfactant–monomer ratio [S] at constant polymer–emulsion weight ratios: (a) 0.20; (b) 0.30; (c) 0.40.

investigated the emulsion polymerization of vinyl acetate in a one-stage process, using Pluronic surfactants. In a series in which Pluronic F68 was varied from 1.0 to 10.0 parts per 100 parts vinyl acetate a linear relationship was found, at a conversion of 0.97, between the total particle surface area per unit weight of polymer and the surfactant concentration that was similar to relation (2). French also found that the number of polymer particles per unit weight of polymer at an approximately constant polymer emulsion weight ratio varied as the cube of the surfactant–monomer ratio, much as in relation (5).

Previous results[6] (Fig. 4) have shown that the variation of total particle surface area with emulsion weight applies to vinyl acetate in a colloid-free formula containing other nonionic surfactants, with and without anionic surfactant.

The results of Brodnyan et al.[7] with methyl and *n*-butyl methacrylates in a one-stage process at constant monomer and initiator concentrations showed that the rate of polymerization (R_p) per "specific particle surface

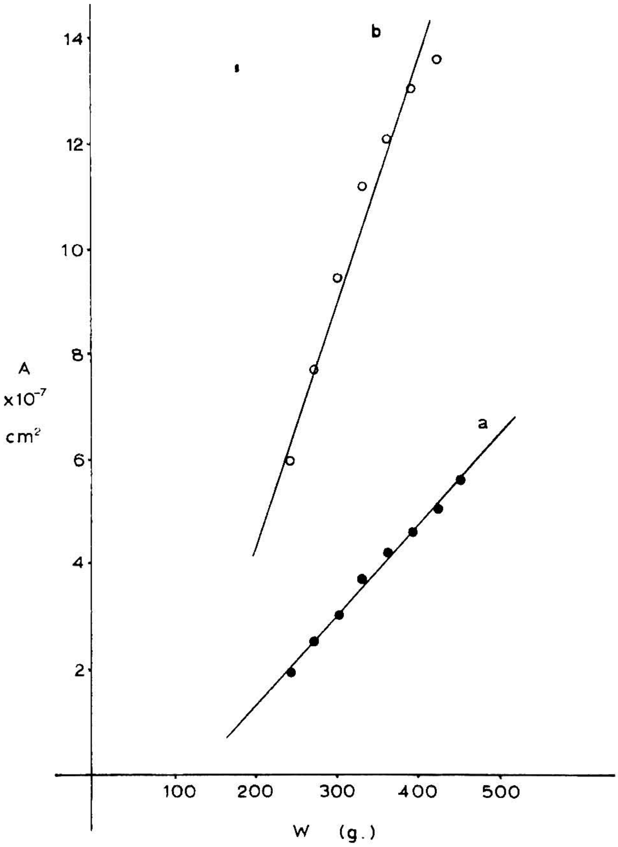

Fig. 4. Variation of total particle surface area A with weight W of emulsion: (a) non-ionic surfactant alone; (b) non-ionic with anionic surfactant.

area" was relatively constant, viz. $R_p \propto 4\pi r^2N/W$; from which those workers concluded that the particle surface could be the locus of polymerization as predicted by Medvedev.[8]

However, in a plot, Figure 5, of particle surface area per unit weight of emulsion versus surfactant–monomer ratio, taken from the published data, straight lines are obtained, and this result,

$$4\pi r^2N/W \propto [S]$$

may then be compared with relation (2).

It is then possible to explain the approximate variation found by Brodnyan et al. in the number of particles per unit volume with the cube of the anionic surfactant concentration by analogy with relation (5), by assuming an approximately constant polymer–emulsion weight ratio.

The results of Ewart and Carr[9] for styrene treated similarly (Fig. 6) lead to the relation

$$4\ \pi r^2N/V \propto [S][M]^{1.7} \tag{6}$$

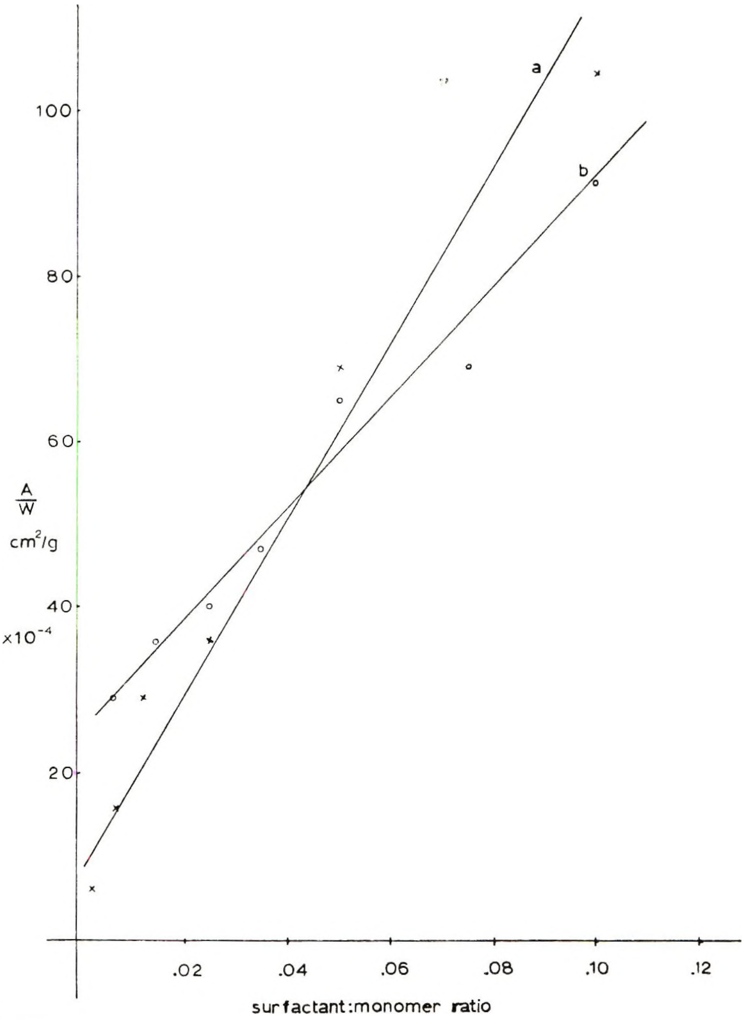

Fig. 5. Variation of total particle surface area per unit weight of emulsion (A/W) with surfactant–monomer ratio (data of Brodnyan et al.[7]): (×) methyl methacrylate; (○) n-butyl methacrylate.

where [M] is monomer concentration and V is volume of water, while Brodnyan et al.[7] have demonstrated that the dependence of particle number on the cube of the surfactant concentration also applies.

More directly, Berezhnoi et al.[10] and Vanderhoff et al.[11] have shown that for styrene the total particle surface area varies directly with the anionic surfactant concentration (viz. sodium laurate and sodium dihexyl sulfosuccinate, respectively); again, this may be compared with relation (2).

Relationships (4) and (5) also have been reported to apply to vinylidene chloride and vinyl chloride.[12]

The variation of particle surface area per unit weight (or volume) of emulsion with surfactant concentration is therefore covered by relation (2)

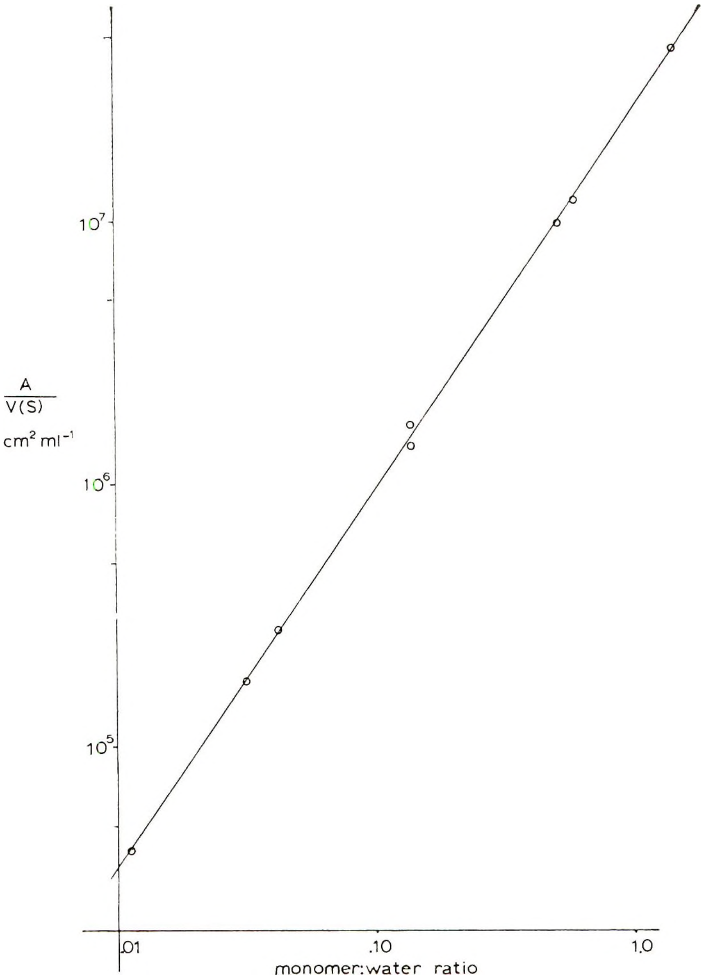

Fig. 6. Variation of total particle surface area per unit volume of emulsion per unit surfactant–monomer ratio ($A/V(S)$) with monomer–water ratio.

for a variety of monomer and surfactant types. Two results obtained with vinyl acetate and methyl acrylate,[13] and ethylene[14] indicate a different relationship, however:

$$N/V \propto [S] \qquad (7)$$

Although the results with ethylene may be due to its different solubility characteristics, it is not possible to explain Alexander's results[13] with vinyl acetate and methyl acrylate on the evidence presented.

The most probable explanation of the observation that particle surface area per unit weight (or volume) of emulsion varies as the concentration of surfactant is that the number of stable particles depends on the quantity of surfactant available for stabilizing a given surface area. In the system studied, 2.02×10^{13}–2.40×10^{13} molecules of Pluronic F68 were required to stabilize 1 cm.^{2} of polyvinyl acetate in emulsion at final theoretical polymer–emulsion weight ratios of 0.49–0.42.

From relation (2), since polymer weight P varies as r^3N, it may be shown that

$$r \propto (1/[S])(P/W) \tag{8}$$

The particle size is thus determined by the surfactant–monomer ratio and the polymer concentration.

On extrapolation of curve (b) of Figure 2 to zero surfactant concentration, the particle surface area per unit emulsion weight yields a value of 1.6 × 10^4 cm.^{2}/g. A similar value is obtained by extrapolation of Figure 4 in French's paper[4] and may be compared with values ranging between 0.24 × 10^4 and 2.07 × 10^4 cm.^{2}/ml. for persulfate-initiated polymerizations in aqueous solution in the absence of surfactant.[15] In the latter case, stabilization of the polymer particles presumably is effected by sulfate endgroups.

Rate of Polymerization

The comparative study[16] of the polymerization of a mixture of acrylate monomers by one-stage and continuous monomer addition processes has shown that in the latter the rate of polymerization was relatively constant, suggesting that the major controlling factor was the monomer concentration.

Patsiga et al.[17] have noted that the rate of polymerization of vinyl acetate in emulsion is independent of soap concentration. This is in agreement with other results from partially water-soluble monomers, viz., vinyl acetate[18] and methyl acrylate,[19] reported in the literature but not with those of O'Donnell et al.[20] which show that

$$R_p \propto [S]$$

for vinyl acetate stabilized with polyvinyl alcohol, nor with those of Dunn and Taylor,[21] who, using low concentrations of polyvinyl alcohol and vinyl acetate, reported that the rate of polymerization *decreased* with increase of the stabilizer.

The general independence of the rate of polymerization from the surfactant concentration for the more water-soluble monomers may be compared with results obtained by Medvedev and his co-workers[8,10] from styrene in a one-stage process with azobisisobutyronitrile as initiator and an anionic surfactant, when the polymerization rate was found to be dependent on surfactant concentration only below a surfactant monomer ratio of 0.15 (equal to 5% in the aqueous phase).

Berezhnoi et al. have suggested[22] that the rate of polymerization is determined by the concentration of emulsifier only up to the point at which the particle surface is saturated by emulsifier; Uchida and Nagao,[23] working with acrylonitrile and methyl methacrylate, have found the rate to increase with anionic surfactant concentration up to the critical micelle concentration.

Since from the consensus of data discussed above the particle surface area is determined by the surfactant concentration, it seems more reasonable that the rate of polymerization depends on the solubility of the monomer in the water phase, as proposed essentially by Okamura and Motoyama[18,24] and confirmed by Vanzo,[25] and that the constant rate observed by Medvedev[8,10] at a very high surfactant concentration represented the point at which the solubility of styrene in that water phase reached a maximum.

In support of this it may be noted that the solubility of vinyl acetate increases to a much lesser extent in 2% sodium dodecyl sulfate solution at 30°C. than does styrene.[18] Thus,

	Water	2% aq. sodium dodecyl sulfate
vinyl acetate:	2.3%	4.0%
styrene:	0.03%	0.12%

Similarly, the solubility of styrene increases substantially in 0.093*M* potassium palmitate solution:[26]

	Water	0.093*M* potassium palmitate
40°C.:	0.0320%	1.00%
50°C.:	0.0382%	1.45%

The relatively greater solubilization of the less water-soluble monomers is consistent with McBain and Richard's results[27] with organic liquids, some of which are quoted in Table II below.

It was shown by Uchida and Nagao[23] that the rate of polymerization of acrylonitrile in aqueous polyvinyl alcohol solution varied with the stabilizer concentration and that the solubility of acrylonitrile correspondingly increased with the concentration of polyvinyl alcohol.

In the present work it may be noted from Tables III and IV that Pluronic F68 has little effect on the solubility of vinyl acetate in water and that the mean rates of polymerization, which vary slightly over a tenfold increase of surfactant concentration, are proportional to the solubility of vinyl acetate in the surfactant solution, exhibiting a maximum at a surfactant concentra-

TABLE II

Solubility of Organic Liquids in Surfactant Solution[27]

	Water, % w/v	0.1 aq. potassium laurate, % w/v	Ratio of solubilities
n-Hexane	0.014	0.170	12.1
n-Octanol	0.059	0.444	7.53
Benzene	0.070	0.296	4.23
Methyl isobutylketone	1.820	3.020	1.66
Methyl *tert*-butyl ether	5.126	6.586	1.28

TABLE III
Rate of Polymerization (R_p) and Surfactant Concentration

Expt. No.	Mean concn. of Pluronic F68 in aqueous phase, w/w	Mean R_p (fraction of monomer addition rate)
1	0.109	0.92
2	0.071	0.91
3	0.050	0.90
4	0.038	0.94
5	0.026	0.98
6	0.013	0.93

TABLE IV
Solubility of Vinyl Acetate in Aqueous Solutions of Surfactant at 20°C.

Surfactant concn., g./ml.	Solubility of vinyl acetate, % w/v	
	Pluronic F68	Ethylan BCP[a]
0.16	2.42	—
0.08	2.36	5.33
0.04	2.37	4.83
0.02	2.63	2.94
0.01	2.52	3.12
0.005	—	2.42
Nil	2.22	2.22

[a] A commercially available nonylphenyl–ethylene oxide condensate, with 9–10 ethylene oxide units. The free polyethylene glycol content was 0.8%.

tion of 0.02–0.03 g./ml. A nonylphenol–enthylene oxide (9 unit) adduct is seen to be rather more efficient with vinyl acetate, but even at a concentration of 8.0% surfactant the solubility of vinyl acetate is only about 2.5 times that in water.

It seems probable, therefore, that the rate of polymerization is controlled essentially by the concentration of monomer in the water phase, assuming that the surfactant does not interfere with the initiator system, and that where the rate has been shown to depend on surfactant concentration or particle surface area this has been a reflection of the ability of the surfactant to increase the solubility of the monomer in the aqueous phase.

From the solubilization characteristics discussed above it follows that the rate of polymerization of the less water-soluble monomers will be more dependent on surfactant concentration. In considering the basic rate equation,

$$R_p = k_p[\mathrm{M}][\mathrm{R}\cdot]$$

where $[\mathrm{R}\cdot]$ is the concentration of radical, $[\mathrm{M}]$ has been assumed to represent the monomer concentration in the particles. Although this may be true when a polymer-soluble initiator is used, it is unlikely to apply to water-soluble initiators. The results presented in this paper suggest that the water phase is the main locus of polymerization, in which case [M] should be regarded as the monomer concentration in this phase.

In the presence of excess monomer the overall concentration of monomer liable to polymerize and, hence, the rate of polymerization will be determined by the solubility of the monomer in the aqueous surfactant solution. If the monomer is not in excess, R_p will depend on the proportion of monomer partitioned into the water phase.

Emulsion Viscosity

At a nonvolatile content of 50% there is a direct relation (Fig. 7) between the emulsion viscosity and the particle surface area per unit weight of emulsion; thus,

$$\text{emulsion viscosity} \propto 4\pi r^2 N/W \propto [S] \tag{9}$$

This relationship is different to that found by French,[4] which was that

$$\log(\text{emulsion viscosity}) \propto [S]$$

The difference could be due to the different methods of manufacture of the two series of emulsions or to the different methods of determination of the viscosity.

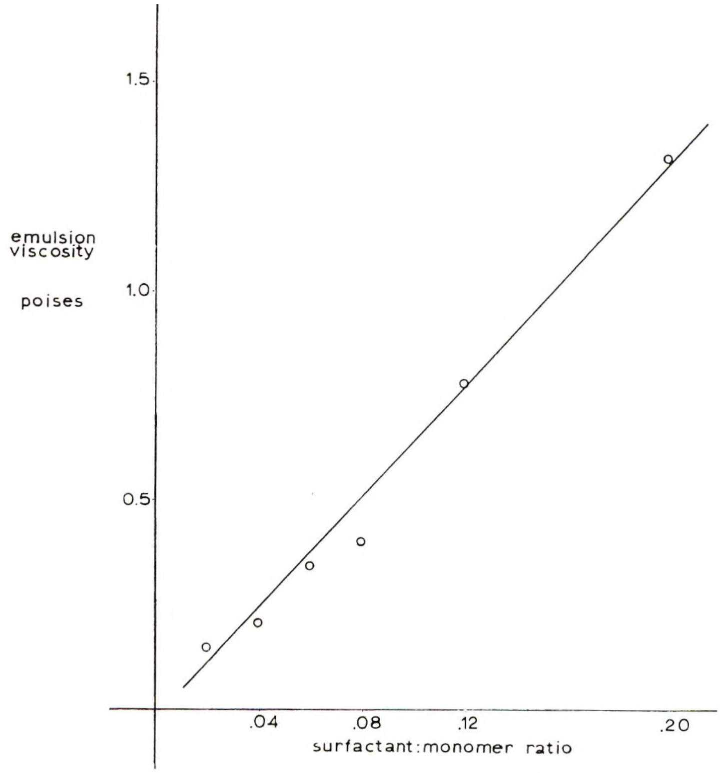

Fig. 7. Variation of emulsion viscosity with surfactant–monomer ratio.

TABLE V
Final Emulsion Properties

Expt. No.	Ratio Pluronic F68 to monomer, w/w	Nonvolatile, % wt. in emulsion	pH	Visc. at 25°C.,[a] poise	Wt. av. particle diam., μ	Surf. tens. at 21°C., dynes/cm.
1	0.20	48.1	5.0	1.31	0.08	42.7
2	0.12	48.5	5.0	0.78	0.12	42.4
3	0.08	48.9	5.1	0.40	0.17	41.6
4	0.06	49.3	5.1	0.33	0.21	42.9
5	0.04	49.0	5.1	0.20	0.27	43.0
6	0.02	49.4	4.8	0.14	0.33	42.6

[a] Measured on a Ferranti viscometer: VL/VMA speed 5 (shear rate, 161.8 sec.$^{-1}$)

CONCLUSIONS

In a continuous-addition process for the emulsion polymerization of vinyl acetate initiated by persulfate, the particle surface area of polymer per unit weight of emulsion varies directly as the surfactant monomer ratio. This relationship has been shown to apply to a number of monomers, irrespective of their solubility in water.

The particle size is determined by the surface area that the given concentration of surfactant is able to stabilize and by the polymer concentration.

In the system studied in the present work the rate of polymerization is dependent on the solubility of the monomer in the water phase, and it may therefore be deduced that the latter is the principal locus of polymerization.

The viscosity of a polyvinyl acetate emulsion stabilized with Pluronic F68 and prepared by a continuous-addition process, varies directly as the surfactant concentration at a given nonvolatile content.

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Some Properties of Poly-α-piperidone

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Synopsis

The high molecular weight polymer of α-piperidone, which had been unobtainable with the use of alkali metal, trialkyl aluminum, or Grignard reagent as catalyst, was prepared with M–AlEt$_3$, (where M is alkali metal), MAlEt$_4$ or KAlEt$_3$(piperidone) as catalyst and *N*-acyl-α-piperidone as initiator. From the determination of the behavior of the solution viscosity of poly-α-piperidone in *m*-cresol at 30°C. the value of 0.27 for the Huggins constant was obtained. Examination of the correlation between the number-average molecular weight, determined by endgroup titration, and the intrinsic viscosity gave a somewhat small value for the endgroup COOH. This may be considered due to the consumption of *N*-acyl-α-piperidone by a propagating polymer in the course of polymerization. The thermal stabilities of the polyamides, nylons 4, 5, and 6, was in the order nylons 6 > 5 > 4 according to differential thermal and thermogravimetric analyses, Poly-α-piperidone, which has a reduced viscosity of 0.7, shows a melting point of 270°C., which was expected from the zigzag pattern of the correlation between melting points and numbers of CH$_2$ groups for polyamino-acid polymers.

INTRODUCTION

In preceding papers[1,2] it was reported that MAlEt$_4$, or M–AlEt$_3$ (M = alkali metal), or KAlEt$_3$ (piperidone) had the ability to produce a high molecular weight polymer of α-piperidone. Since the method gave for the first time a high molecular weight poly-α-piperidone (nylon 5), the determination of several properties of this polymer in solution or in solid state is interesting not only in itself but also for comparison with the properties of nylons 4 and 6.

In this work the viscometric behaviors of the polymer in *m*-cresol and the thermal properties of the solid polymer were determined.

EXPERIMENTAL

Preparation of Polymers for Determination of Endgroups

A series of polymers having various degrees of polymerization was prepared by varying the polymerization time, the other polymerization conditions being constant at 2.5 mole-% of KAlEt$_4$, 2.0 mole-% of *N*-acetyl-α-piperidone, and 40°C.

The polymerization was terminated with water, and the precipitated polymer was kept standing in 5 wt.-% aqueous hydrochloric acid solution for 12 hr. and then was washed several times with water and methanol and dried under reduced pressure at 70°C.

Measurement of Intrinsic Viscosity

The viscosity measurement was carried out in an Ubbelohde viscometer at 30 ± 0.02°C., in a concentration range of 0.125–1.500 g. per 100 ml. The intrinsic viscosity was determined by graphical extrapolation of the reduced viscosity to concentration zero.

Measurement of Molecular Weight by Endgroup Determination

The carboxyl groups were determined by microtitration. They were titrated in benzyl alcohol at room temperature with 0.02*N* NaOH (10 ml. of water was added to 250 ml. of a solution in order to raise the solubility of NaOH) and phenolphthalein as indicator. Benzyl alcohol and chloroform were distilled in a nitrogen atmosphere and titrated as blanks before each use.

All the procedures for preparation of a colloidal solution of polymer in a mixed solvent of benzyl alcohol and chloroform and for titration were done in a stream of dry nitrogen. To 10 ml. of benzyl alcohol 0.100 g. of polymer was added and the mixture was heated for about 4 min., so as to dissolve completely. The solution was cooled in about 4 min., and then 10 ml. of chloroform was added with stirring. The resulting colloidal solution was titrated as soon as possible at room temperature.

Measurement of Melting Point of Polymer

The melting point of the polymer was determined in air with a Meihoh Thermo Analyzer and with a Yanagimoto Melting Point Apparatus.

Differential Thermal Analysis

DTA was carried out in a stream of dry nitrogen with a Shimazu DT-10. A "sandwich" technique was used, in which 0.200 g. of sample was placed between two layers of α-alumina. The sample was heated at a controlled rate of 8°C./min., and the differential temperature was recorded against the inert sample of α-alumina packed into the first compartment of the cell.

Thermogravimetric Analysis

TGA was carried out in air or nitrogen with an Automatic Recording Thermobalance Type ORK-B Oyorika Kogyo. The sampling of the polymer was 0.300 g. The weight losses of the samples were recorded to an accuracy of ±0.5% and the temperature to better than ±5°C. The temperature of the sample reached at a temperature in about 7.5 min. in every case.

RESULTS

Correlations between Reduced Viscosity, Intrinsic Viscosity, and Number-Average Molecular Weight

The behavior of the viscosity in various concentrations of polymer in *m*-cresol and the correlation between the intrinsic viscosity and the number-average molecular weight of the unfractionated poly-α-piperidone were examined.

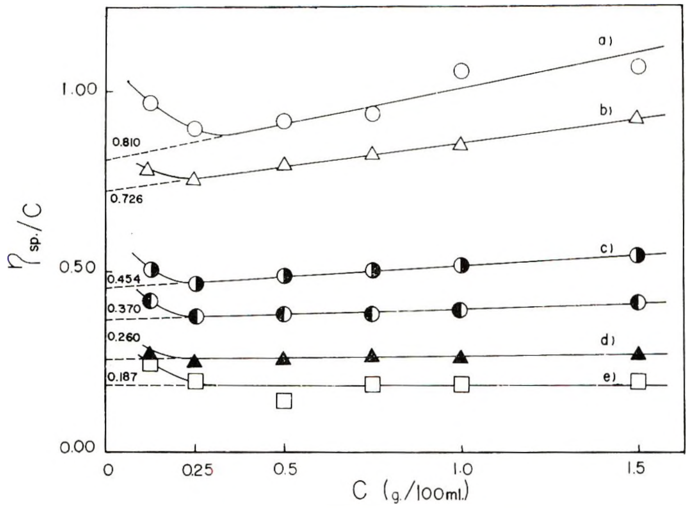

Fig. 1. Reduced viscosity versus concentration of α-piperidone polymer solution in *m*-cresol at 30°C.

The data for reduced viscosity versus concentration are given in Table I and plotted in Figure 1. Since the deviation of reduced viscosity was great below a polymer concentration of 0.25 g. per 100 ml., the usefulness of the viscosity formula is limited to the range of concentration from 0.25 to 1.50 g. per 100 ml.

TABLE I

Relationships between Reduced Viscosities and Concentrations of Polymer (Nylon 5) Solutions

Sample No.	[η]	Reduced viscosities of α-piperidone polymer[a] at concentration of polymer (g. per 100 ml. of *m*-cresol)					
		1.5	1.0	0.75	0.50	0.25	0.125
816	0.810	1.07	1.06	0.94	0.92	0.90	0.97
ate-3/2	0.726	0.94	0.87	0.83	0.80	0.76	0.77
Li-LiAl	0.454	0.55	0.52	0.51	0.49	0.47	0.51
ate-3/26	0.370	0.42	0.40	0.39	0.39	0.38	0.42
ate-2/15	0.260	0.28	0.27	0.27	0.26	0.26	0.28
ate-2/11	0.187	0.20	0.19	0.19	0.14	0.20	0.25

[a] Measured by Ubbelohde viscometer in *m*-cresol at 30°C.

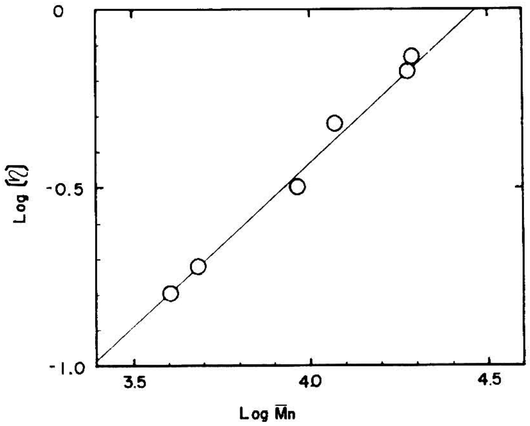

Fig. 2. Log–log plot of reduced viscosity versus number-average molecular weight.

The formula chosen[3] for correlating the data with $k = 0.27$ at 30°C. was

$$\eta_{sp}/C = [\eta] + k[\eta]^2C$$

In the case of poly-ε-capramide the Huggins constant k in *m*-cresol was 0.47 at 20°C., reported by Liquori and Mele[4] and 0.37 at 25°C., reported by Hoshino and Watanabe.[5] The equation

$$[\eta] = (3/C)^3\sqrt{\eta_{rel}}-1$$

was also used, which had been presented by Leopelmann.[6]

A log–log plot of $[\eta]$ versus $\bar{M}_n$ is shown in Figure 2 and Table II. The slopes of the lines give the value of a in the equation

$$[\eta] = K\bar{M}_n{}^a$$

The values obtained for a and K are 0.92×10^{-5} and 7.76×10^{-5}, respectively. A detailed discussion of the values of a and K for the polymer in *m*-cresol is difficult now, because there is a remarkable consumption of *N*-acyl-α-piperidone at the propagating polymer and during alkaline poly-

TABLE II
Data on Endgroups

η_{sp}/c	$[\eta]$	log $[\eta]$	COOH,[a] eq./g. ($\times 10^{-4}$)	$\bar{M}_n$ ($\times 10^{3}$)	log $\bar{M}_n$
0.16	0.16	−0.796	2.58	4.03	3.61
0.20	0.20	−0.722	2.08	4.81	3.68
0.33	0.32	−0.495	1.08	9.25	3.97
0.53	0.48	−0.319	0.85	11.8	4.07
0.73	0.67	−0.174	0.53	18.9	4.28
0.81	0.74	−0.131	0.51	19.6	4.29

[a] Average values of two runs.

merization of α-piperidone, which might not give the correct number for the carbonyl group in the endgroup measurement.

Correlation between Melting Point and Reduced Viscosity

The melting point of nylon 5 has been reported to be 259°C., but the degree of polymerization of the polymer used was comparatively low ($[\eta] = 0.246$ dl./g. in *m*-cresol at 30°C.).[7]

The melting point of nylon 4 derived from α-pyrrolidone by alkali-metal-catalyzed polymerization at low temperature was reported to be 251 and 260–265°C. by Murahashi et al.[8,9] Nagaoka et al. have investigated the dependence of the melting point of poly-α-pyrrolidone on the intrinsic viscosity and indicated that the polymer having an intrinsic viscosity higher than 0.7 dl./g. in *m*-cresol at 25°C. melted at 260–263°C.[10]

We examined the thermal behavior of nylon 5 having reduced viscosities of 0.18–0.81 by differential thermal analysis and ordinary melting-point measurement; the results are given in Table III and Figure 3.

The thermogram of nylon 5 in Figure 3 exhibits a well-defined peak position and peak area; the position of the fusion point was taken as the melting point of the polymer.[11] The fusion peak in DTA appeared at a somewhat higher temperature than that measured with the naked eye, but it rose exactly in accordance with the increase in reduced viscosity.

The effect of the heating rate on the position of fusion point was determined as shown in Table IV. T_2 appeared broadly at about 233°C. at

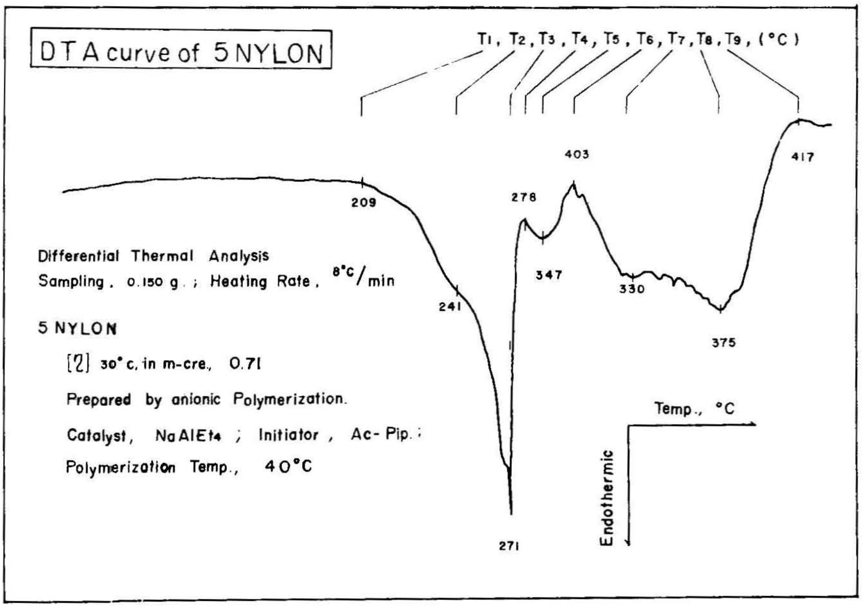

Fig. 3. Differential thermal analysis of nylon 5; sampling, 0.150 g.; heating rate 8°C./min.

TABLE III
Differential Thermal Analysis of Nylon 5

Polymn. time,[a] days	η_{sp}/C[b]	Melting point, °C.		Endothermic peak, °C.								
		([c])	([d])	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8	T_9
1	0.17	253	254	211	240	252	260	268	279	—	330	419
2	0.22	259	—	207	243	265	273	278	283	337	371	440
5	0.38	264	—	207	241	262	272	283	291	327	377	411
10	0.50	266.5	267	210	243	269	277	284	301	335	380	424
20	0.72	270	269–270	209	243	271	278	287	301	335	365	402
25	0.76	267	268–269	209	242	271	278	287	301	335	375	417

[a] Catalyst $NaAlEt_4$, initiator *N*-benzoyl-α-piperidone, polymerization temperature 40°C.

[b] Reduced viscosity of a solution of 0.5 g. of polymer in 100 ml. of *m*-cresol at 30°C.

[c] Measured by Meihoh Thermo Analyzer.

[d] Measured by Yanagimoto Micro Melting Point Apparatus.

TABLE IV
Effect of Heating Rate on DTA Curves[a]

Heating rate, °C./min.	T_2, °C.	T_3, °C.
1–2	233	259–262
4–5	243	267
9–10	243–244	266–267

[a] Nylon 5; $\eta_{sp}/C = 0.50$.

heating rate of 1–2°C./min., T_2 was obtained as a shoulder of the peak T_3 at a heating rate of 4–5 or 9–10°C./min., and T_3 rose somewhat with heating rate. T_2 might be considered to be the melting point of a low molecular weight polymer.

Thermal Stability of Nylons 4 and 5

The thermal gravimetric analysis of nylons 4 and 5 was carried out with a thermobalance in air or nitrogen. Figures 4 and 5 show the effect of experimental temperature on the degradation of polymer. The temper-

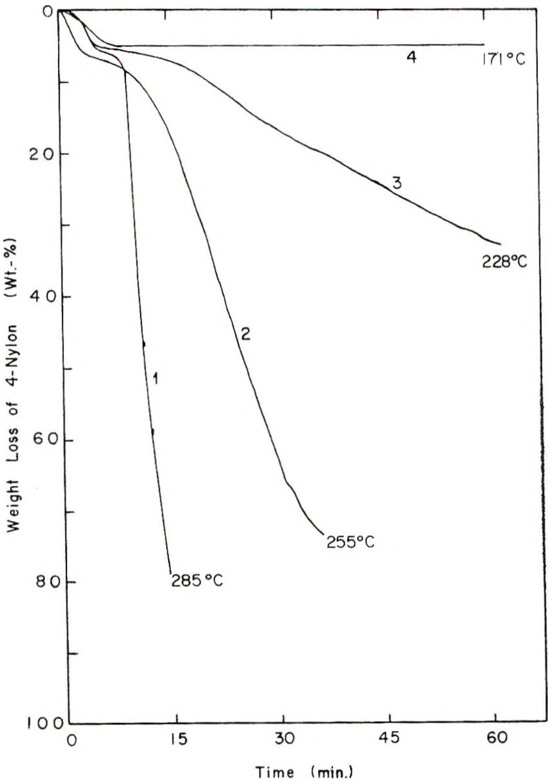

Fig. 4. Thermogravimetric analysis of nylon 4 by thermobalance: effect of temperature on weight loss: $[\eta] = 1.25$ in *m*-cresol at 30°C.

ature of the sample could be made to rise to a given temperature in 7.5 min. in all cases. The first stage of the curves indicates that water in the polymer was evolved continuously up to a temperature of 150°C. From the experimental data it may be recognized that the thermal stability of nylon 5 is superior to that of nylon 4 in the polymer untreated after polymerization. No weight loss was observed in nylon 6 at 250°C. during 60 min., but the degradation leading to almost an α-pyrrolidone for nylon 4 and to the formation of a yellow (in nitrogen) or a black (in air) block of nylon 5 were observed in the same condition.

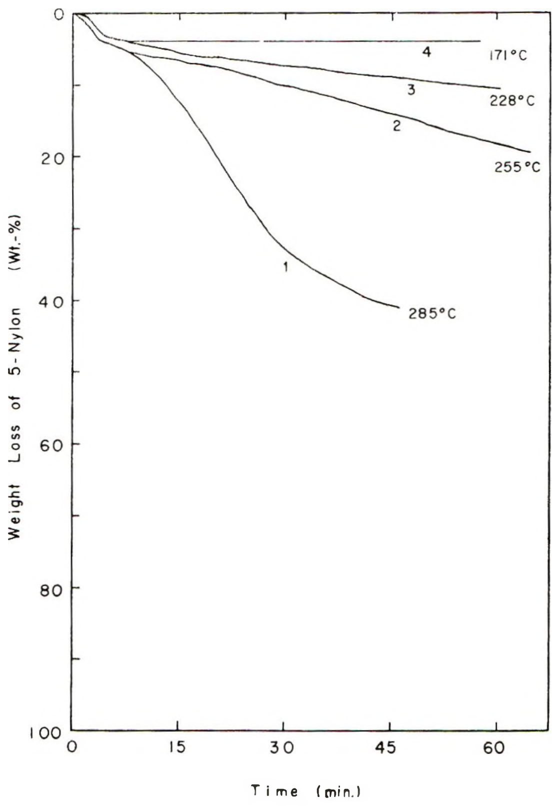

Fig. 5. Thermogravimetric analysis of nylon 5 by thermobalance: effect of temperature on weight loss; $[\eta]$ = 0.66 in m-cresol at 30°C.

The correlation between the viscosity of the polymer and the degradation behavior was examined; see Figure 6 and 7. No obvious effect of the degree of polymerization on the degradation was observed in either nylon 4 or nylon 5. These results might not support the consideration that the thermal degradation of nylon 4 occurs only at the polymer end. A partial ring closure in the main chain of the polymer may also be considered.

DISCUSSION

The determination of the change in the reduced viscosity of polymer treated at temperatures from 180 to 230°C. indicates that the decrease in the viscosity of nylon 4 was more predominant in the higher molecular weight samples; see Figure 8. Such thermal behavior is not explained only by considerations of the thermal degradation at the polymer ends and the depression in polymerizability of α-piperidone. A formation of ring lactam by ring closure from polymer chain is considered to be more predominant in nylon 4 than in nylon 5. The thermal degradation appeared at about 287°C. for nylon 4 and at 330°C. for nylon 5, and nylon 6 was stable at 330°C. under the condition of a heating rate of 8°C./min.; see Figure 9.

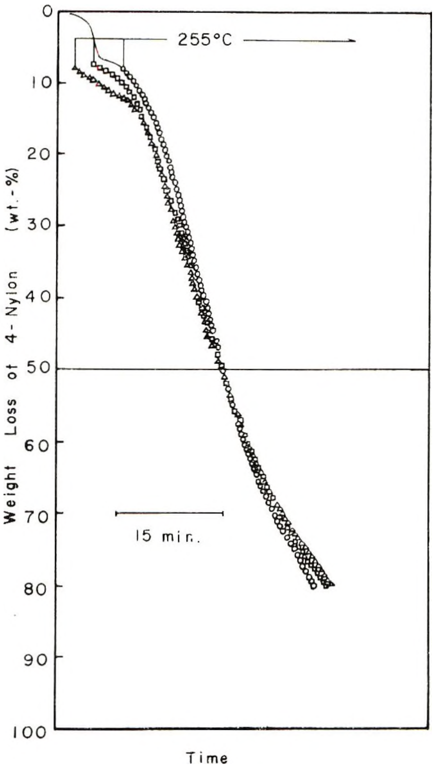

Fig. 6. Thermogravimetric analysis of nylon 4 by thermobalance: effect of reduced viscosity on weight loss at 255°C. in air. Values of η_{sp}/C: (○) 0.15; (□) 0.33; (△) 0.60 and 0.96.

The melting point of nylon 5 rose with increasing viscosity and reached the constant value of 270°C. (judged the naked eye); at this point the fusion peak in DTA curves indicated a temperature of 271°C.; see Figure 10.

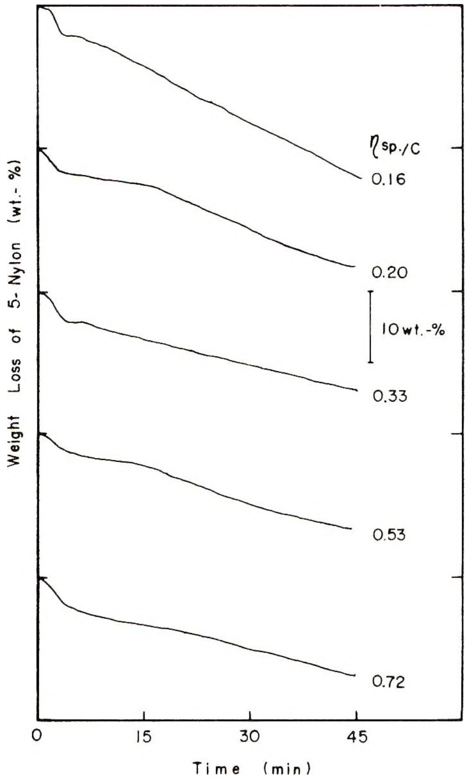

Fig. 7. Thermogravimetric analysis of nylon 5 by thermobalance: effect of reduced viscosity on weight loss at 255°C. in air.

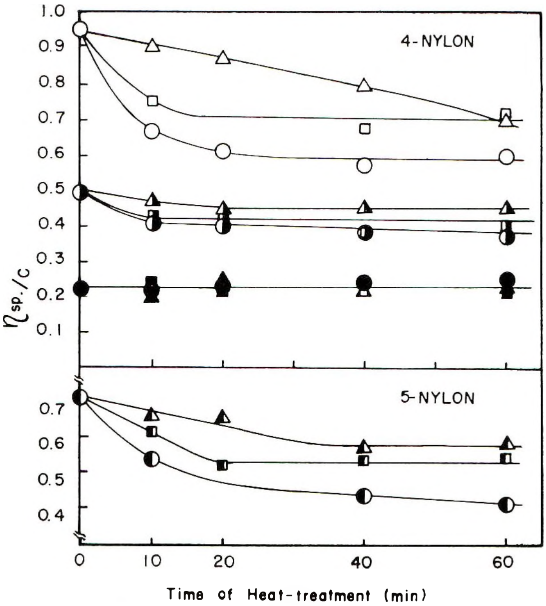

Fig. 8. Effect of heat treatment on reduced viscosity of nylons 4 and 5 in nitrogen atmosphere. Temperature of heat treatment: (circles) 230°C.; (squares) 200°C.; (triangles) 180°C.

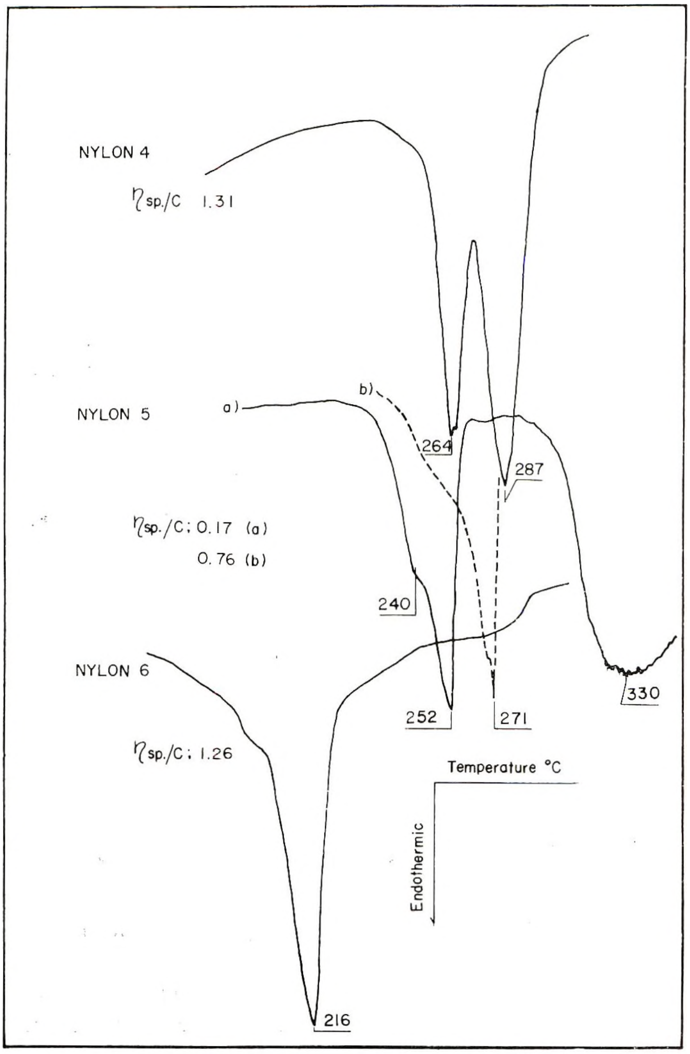

Fig. 9. Differential thermal analysis of nylons 4, 5, and 6.

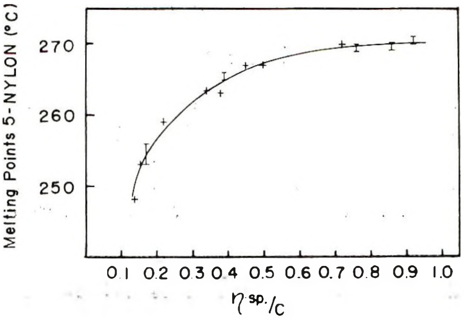

Fig. 10. Melting point versus reduced viscosity of nylon 5.

In contrast to nylon 6, nylons 4 and 5 showed undesirable thermal stability, and the temperature interval between melting point and degradation decreases in the following order: nylons 6 > 5 > 4. This may indicate the difficulty of treating nylons 4 and 5 in the melt state.

From the experimental results described above the melting points of polyamides are in the order of nylons 5 > 4 > 6; this thermal property may accord with the fact that the relationship between the melting point and the carbon number of polyamides shows a zigzag pattern,[12] and the groups in the polymer backbone may be considered an internal diluent, decreasing the amount of hydrogen bonding,[11] see Figure 11.

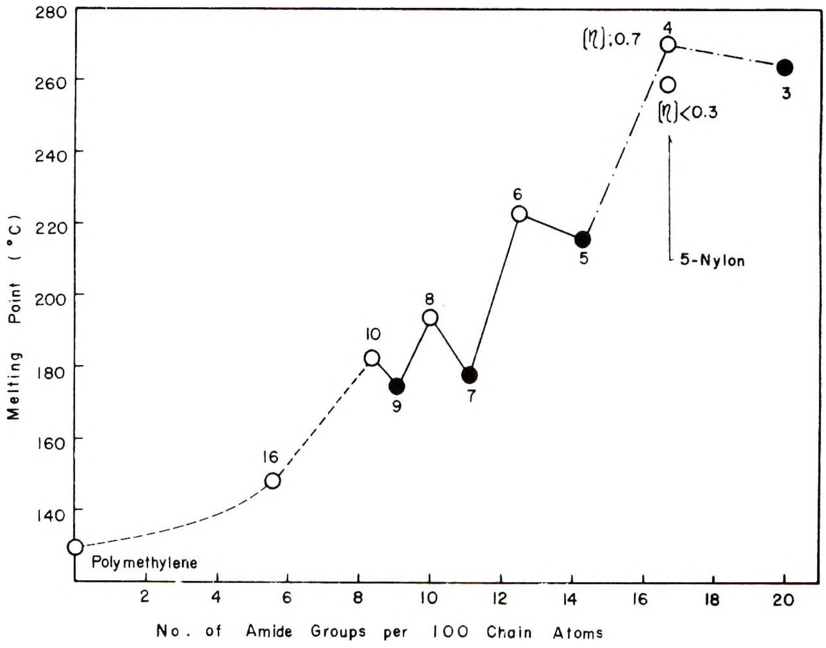

Fig. 11. Polyamides: (O) even number of CH_2 groups; (●) odd number of CH_2 groups.

The high molecular weight polymer of α-piperidone has a melting point of 270°C., which may be in accordance with that expected from the pattern described for the relation between melting points and number of CH_2 groups of amino acid polymers, which is 10–5.[12,13]

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Polymerization of α-Piperidone with M–$AlEt_3$, $MAlEt_4$, or $KAlEt_3$(Piperidone) as Catalysts and *N*-Acetyl-α-piperidone as Initiator*

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Synopsis

Low-temperature polymerization of α-piperidone was carried out by using $MAlEt_4$, $KAlEt_3$(piperidone), and M–$AlEt_3$ (where M is Li, Na, or K) as catalysts and *N*-acetyl-α-piperidone as initiator. The behavior in polymerization of these catalysts was superior to alkali metal or aluminum triethyl, and a polymer having an intrinsic viscosity of 0.8 dl./g. was obtained. Polymerization results and infrared analyses of the metal salts of lactams suggest that a complex, the structure of which was analogous to the one formed from M–$AlEt_3$, is formed in the case of the alkali metal piperidonate–ethyl aluminum dipiperidonate catalyst system and that it is changed to another complex having a different composition and lower catalytic activity by heat treatment The infrared absorption band of the metal salts of lactams and of $KAlEt_3$(piperidone) at 1570–1590 cm.$^{-1}$, which is attributable to the C=N group in enolate form, may be considered to be related to the catalytic activities of alkali metals and the polymerizabilities of lactams. Such special catalysts as $MAlEt_4$, alkali metal–$AlEt_3$, or $KAlEt_3$(piperidone) are supposed to suppress the consumption, by alkali metal, of *N*-acyl-α-piperidone group of growing polymer end. A prolonged polymerization required for obtaining a high molecular weight polymer, even when such catalysts are used, is ascribable to a greater difficulty in re-forming lactam anion from α-piperidone, the basicity of which is higher than that of the other lactams.

INTRODUCTION

In the course of an investigation of the polymerization of lactams we succeeded in obtaining high molecular weight polymer of α-piperidone by using $MAlEt_4$ or alkali metal–$AlEt_3$ catalyst system.[1]

In an earlier paper it was shown that an alkali metal catalyst, which possesses a superior property for the high polymerization of five- and seven-membered lactams, was unable to yield the high polymer of α-piperidone and that $MAlEt_4$, which gave the α-piperidone polymer with intrinsic viscosity of 0.8 dl./g. in low-temperature polymerization, exists as a certain type of complex salt and also participates in the stabilization of the

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alkali metal salt and in the protection of the initiator and the *N*-acyl lactam group of propagating polymer ends against an unfavorable side reaction.

The present investigation is concerned with the determination of the behavior of M–$AlEt_4$ in lactams at various temperatures and of the relation between the molar ratio of alkali metal, aluminum, and initiator. In addition, the polymerization of α-piperidone with the catalyst $KAlEt_3$-(piperidone), the structure of which is supposed to be equal to that of a solution of $KAlEt_4$ in monomer, was carried out at low temperature.

The polymerization results and the infrared spectral analyses of metal salts of lactams in lactam solution and of $KAlEt_3$(piperidone) the polymerizabilities of alkali metals and aluminum will be evaluated and discussed.

EXPERIMENTAL

Preparation of $MAlEt_4$

Alkali metal reacted with a concentrated toluene solution of triethylaluminum in a dry nitrogen atmosphere to give M–$AlEt_4$:

$$3\,M + 4\,AlEt_3 \rightarrow 3\,MAlEt_4 + Al$$

$LiAlEt_4$ and $NaAlEt_4$ were purified by repeated recrystallizations from toluene. $KAlEt_4$ was precipitated from its concentrated toluene solution by adding *n*-hexane, was washed repeatedly with *n*-hexane, and then was dissolved in tetrahydrofuran. The organo-aluminums were used in tetrahydrofuran solution.

The catalyst concentration was determined by alkalimetry, back-titration, and gasometry. The gaseous product evolved during the hydrolysis of the catalyst was proved to be ethane by gas chromatography (charcoal column: 2 m., 170°C.).

Preparation of the Complex $KAlEt_3$(Piperidone)

Potassium Piperidonate. To a solution of 20 ml. (about 0.220 mole) of α-piperidone in 20 ml. of dry toluene was added 4.29 g. (0.110 mole) of metallic potassium) under an atmosphere of dry nitrogen at temperatures from 30 to 50°C. The mixture was allowed to react with stirring. After completion of the reaction a white precipitate of potassium piperidonate was separated out by adding tetrahydrofuran. It was washed five times with dry tetrahydrofuran and was dried under reduced pressure at 120°C. Potassium piperidonate is hygroscopic, decomposes in air to form α-piperidone and potassium hydroxide, and is almost insoluble in benzene, *n*-hexane, and tetrahydrofuran.

$KAlEt_3$(Piperidone). Potassium piperidonate was heated to 120°C. under reduced pressure (0.1–0.4 mm. Hg) to remove a trace of solvent adhered to it. To a suspension of the salt in 40 ml. of dry *n*-hexane was added 10 ml. (0.0728 mole) of triethylaluminum, dropwise, with stirring, at room temperature. The salt changed gradually from a solid to a slightly yellow, highly viscous liquid. The viscous liquid phase was separated and washed five times with dry *n*-hexane, to remove unreacting triethylaluminum as completely as possible. It is very hygroscopic and unstable, decomposes violently in air, forming white, solid material, and reacts with alcohol or water under evolution of ethane gas, unlike potassium piperidonate. The isolation of this complex in crystalline form was unsuccessful.

Preparation of *N*-Acetyl-α-piperidone

N-Acetyl-α-piperidone was prepared in the same manner as described in the previous paper.[1]

Preparation of *O*-Ethyl Lactims

O-Ethyl-ε-caprolactim, *O*-ethyl-δ-valerolactim, and *O*-ethyl-γ-butyrolactim were prepared by the method described by Benson and Chairns[3] (b.p. 64°C. at 10 mm. Hg, 56°C. at 17 mm. Hg, 37°C. at 16 mm. Hg, respectively).

Polymerization of α-Piperidone

Preparation of Monomer Solution of Catalyst. Catalyst solution was prepared by using the monomer as a solvent. All procedures mentioned below were carried out in a dry nitrogen atmosphere. Monomer containing a given amount of potassium salt was prepared by adding a calculated amount of metallic potassium into monomer at a temperature below 80°C.

The monomer containing bis(2-oxopentamethyleneimine)ethylaluminum was prepared by dropwise addition of triethylaluminum to α-piperidone. In this reaction 2 moles of ethane were evolved for 1 mole of triethylaluminum.

The solution of $MAlEt_4$-piperidone catalyst was prepared to 40–50°C. by stirring a mixture of a catalytic amount of $MAlEt_4$ in tetrahydrofuran and α-piperidone; 1–2 moles of ethane per 1 mole of $MAlEt_4$ evolved.[1] Tetrahydrofuran was removed under reduced pressure as completely as possible by increasing the temperature to 60°C.

Solution of $KAlEt_3$(piperidone) in monomer was prepared as follows. A 1.3 ml. amount of a 2.09 mole-% solution of the complex in benzene was added slowly with stirring into 1.2 ml. (0.132 mole) of freshly distilled α-piperidone at 45–50°C. in a stream of nitrogen. Benzene was removed at 50–60°C. under reduced pressure as completely as possible.

Polymerization. The polymerization procedure was the same as that described in the previous paper. The polymerization was terminated by adding a mixture of methanol and 5 wt.-% aqueous solution (1:1 v/v). The reduced viscosity of the polymer solution was measured at a concentration of 0.5 g. of polymer per 100 ml. of *m*-cresol at 30°C.

RESULTS

Alkali Metal Catalyst

The alkali metal catalyst was unable to convert α-piperidone to a high molecular weight polymer having a reduced viscosity higher than 0.3. A trace of water contaminated in monomer acts as an initiator in the alkali-catalyzed polymerization of all of the five-, six-, and seven-membered lactams, although there is some difference in the degree of inhibition between these lactams. Therefore, inability to obtain a high molecular weight polymer only in the case of α-piperidone, even in a prolonged polymerization time, cannot be ascribed to the contamination of a trace of water. It is considered to be due to the depression of catalyst concentration resulting from the ease of consumption of *N*-acyl lactam group of the propagating polymer end. This consideration is supported by the fact that the molar ratio of catalyst to initiator affects the relationship between yield and reduced viscosity of the resulting polymer. In addition, an isolated potassium salt of α-piperidone gave an unsatisfactory result. The yield and the degree of polymerization of polymer have an optimum at about an equimolar ratio of catalyst to initiator, but even at this optimum ratio the increase in concentration of catalyst (and initiator) gave unsatisfactory results, as shown in Figure 1. The yield of polymer was a maximum at 7 mole-% of catalyst (and of initiator), but the reduced viscosity remained constant at 0.17–0.14 dl./g., regardless of catalyst concentration.

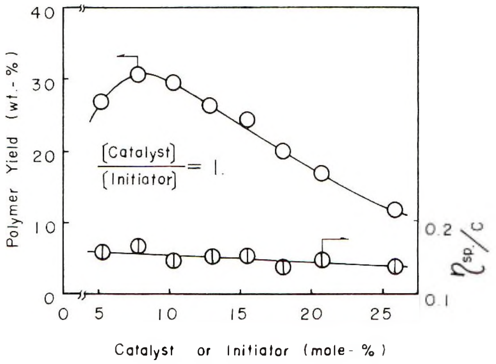


Fig. 1. Polymerization of α-piperidone at equimolar ratio of catalyst to initiator: catalyst, metallic potassium; initiator, *N*-acetyl-α-piperidone; polymerization temperature 40°C.; polymerization time 48 hr.

This result suggests that the initiator and the *N*-acyl lactam endgroup of propagating polymer are more rapidly consumed with increasing concentration of alkali metal salt in the polymerization of alkali metal salt in the system.

M–AlEt$_4$ Catalyst

In the previous paper[1] we assumed that in α-piperidone solution at room temperature MAlEt$_4$ (where M is Li, Na, or K) existed as a complex of the type

$$\mathrm{Li\underset{\smile}{N{-}C}{=}O \cdot AlEt(\underset{\smile}{N{-}C}{=}O)_2}, \qquad \mathrm{Na\underset{\smile}{N{-}C}{=}O \cdot AlEt_2\underset{\smile}{N{-}C}{=}O}, \qquad \mathrm{K\underset{\smile}{N{-}C}{=}O \cdot AlEt_3}$$

based on the experimental results of the number of ethyl groups in the MAlEt$_4$ molecule reactable at room temperature with lactam and on the decrease in catalytic activity for the polymerization of α-piperidone of KAlEt$_4$ by heat treatment of the catalyst in α-piperidone.

In the complexes the alkali metal salt of lactam (Lewis base) is neutralized and stabilized by $\mathrm{AlEt}_{3-n}(\mathrm{lac}_n)$, where n = 0, 1, or 2 (Lewis acid). To know the reaction occurring in the heat treatment process the amount of ethane evolved in the reaction of MAlEt$_4$ with α-piperidone was determined at various temperatures. The results shown in Tables I and II imply that the remaining ethyl groups in the complex further reacted

TABLE I
Determination of Ethane Gas Evolved in Reaction of Lactams with Sodium Tetraethylalanate at Various Temperatures[a]

Temp., °C.	α-Pyrrolidone	α-Piperidone	ε-Caprolactam
15–20[b]	1.4	1.4	0.74
50	1.67 (3.58)	2.78 (3.41)	—
80	2.12 (3.86)	3.22 (3.78)	3.24 (3.68)
120	3.47 (4.00)	3.54 (3.83)	3.54 (3.93)

[a] Values in the table are moles of ethane evolved per mole of NaAlEt$_4$ in the reaction with lactams; 0.20 ml. of a tetrahydrofuran solution of NaAlEt$_4$ (2.01 moles/l.) and 2.0 ml. of lactam were used. Values in parentheses are the moles of ethane evolved in the acid hydrolysis of the reaction products; 2.0 ml. of 5.0 wt.-% of aq. HCl solution was used.

[b] At this temperature 1.0 ml. of tetrahydrofuran was added to give a clear solution.

TABLE II
Determination of Ethane Gas Evolved in Reaction of KAlEt$_4$ with α-Piperidone at 50–230°C.[a]

Temp., °C.	Ethane/KAlEt$_4$, mole/mole	Temp., °C.	Ethane/KAlEt$_4$, mole/mole
50	0.71	145	3.61
70	0.91	180	3.75[b]
80	1.40	200	3.79[b]
90	2.36	230	3.91[b]
100	2.32		

[a] Here 0.20 ml. of a THF solution of KAlEt$_4$ (2.70 moles/l.) and 2.0 ml. of α-piperidone were used. The reaction times were 40 min. in the lower temperature range and 20 min. in the temperature range higher than 100°C.

[b] The color of the reaction mixture turned from faint yellow to pink.

to form lactamate. The decrease in polymerization activity is reasonably connected with the decrease in the electron affinity of the aluminum atom, and as a result the protecting effect of lactam for an active site is lowered.

Potassium Piperidonate–Ethylaluminum Dipiperidonate Catalyst System

As a support for the formation of the complexes mentioned above, the catalytic activities of the mixed catalyst systems containing various molar ratios of potassium piperidonate to ethylaluminum dipiperidonate were determined for the polymerization of α-piperidone.

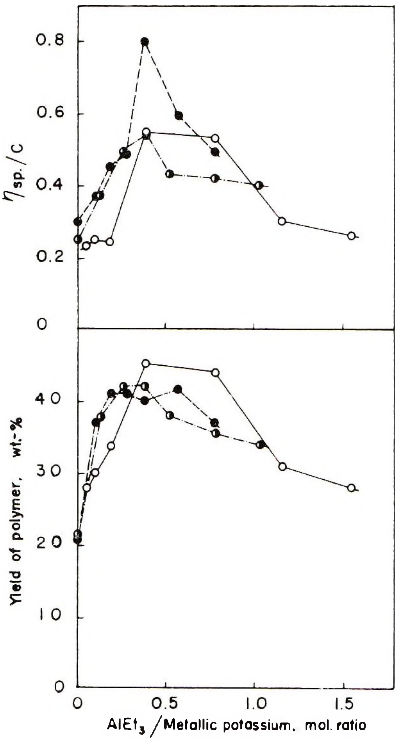
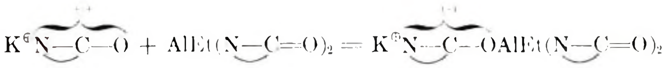


Fig. 2. Polymerization of α-piperidone with various molar ratios of triethylaluminum and metallic potassium catalyst system. Catalyst concentrations (mole-%): (◑) 3.85; (●) 5.16. Polymerization temperature 40°C.; polymerization time 240 hr.; N-benzoyl-α-piperidone, 2.0 mole-%.

An optimum condition for the formation of a very high molecular weight polymer is determined only by the relative amount of potassium to aluminum (Figure 2). This result together with the result of gasometry of the reaction of $AlEt_3$ and $MAlEt_4$ with α-piperidone (see Table I and p. 310 in the previous paper[1]) implies that also in this catalyst system a complex that is analogous to that derived from $MAlEt_4$ with α-piperidone is produced.



$$K^{\oplus}\overbrace{\underbrace{N-C}-O}^{(-)} + AlEt(\underbrace{N-C}=O)_2 \rightleftharpoons K^{\oplus}\overbrace{\underbrace{N-C}-O}^{(-)}AlEt(\underbrace{N-C}=O)_2$$

$KAlEt_3$(Piperidone) Catalyst

The complex $KAlEt_3$(piperidone) was prepared from potassium piperidonate and triethylaluminum and was used as a catalyst for the polymerization of α-piperidone (see Table III). In this case also the molecular weight of the polymer obtained was higher than that obtained by alkali metal salt catalyst.

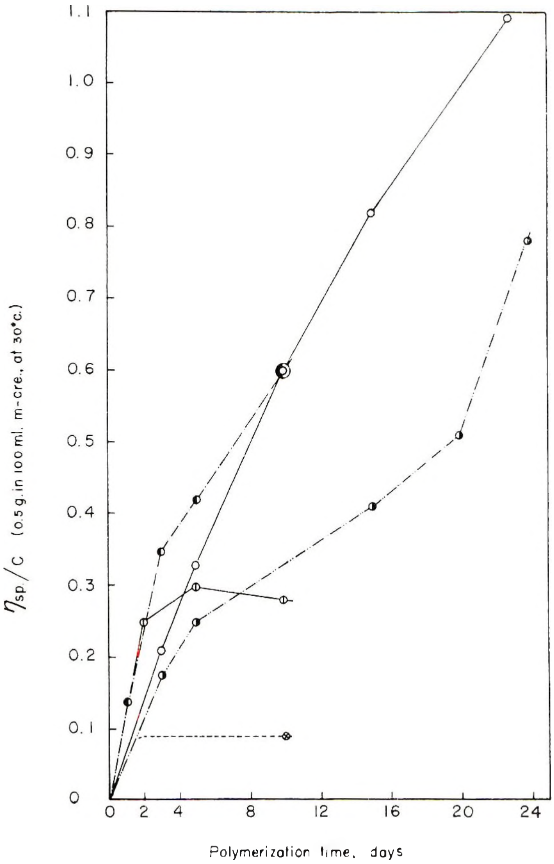


Fig. 3. Comparison of the reduced viscosities of the resulting polymers by using several catalyst systems. (○) $KAlEt_3$(piperidone), 2.0 mole-%; N-acetyl piperidone, 1.0 mole-%. (⦶) Metallic potassium, 2.58 mole-%; N-benzoyl piperidone, 2.0 mole-%. (◑) $KAlEt_4$, 2.58 mole-%; N-acetyl piperidone, 2.58 mole-%. (◐) Metallic potassium, 2.58 mole-%; $AlEt_3$/metallic potassium (mol. ratio) 2/3; N-acetyl piperidone, 2.58 mole-%. (⊗) $AlEt_3$, 3.0 mole-%; N-benzoyl piperidone, 2.0 mole-%.

TABLE III
Polymerization of α-Piperidone with Complex Derived from Isolated Potassium Salt and Triethylaluminum as Catalyst and N-Acetyl-α-piperidone as Initiator[a]

Polymn. time, days	Yield of polymer, wt.-%	η_{sp}/C	Melting point,[b] °C.
3	12.7	0.21	—
5	14.3	0.33	262
10	18.4	0.60	268
15	22.2	0.82	270
23	27.7	1.09	271

[a] Catalyst concentration 2.0 mole-%; initiator concentration 1.0 mole-%; polymerization temperature 45°C.

[b] Differential thermal analysis.

The reduced viscosity data of polymers obtained by various catalysts (see Fig. 3) show that $KAlEt_3$ (*in situ*), $KAlEt_4$, and $KAlEt_3$(piperidone) give far higher molecular weight polymer than triethylaluminum or potassium metal (in this group of catalysts the molecular weight of the polymer depends upon the presence of tetrahydrofuran or benzene; a trace of such solvents remaining in the polymerization system must be removed as completely as possible in order to obtain a high molecular weight polymer). A rather tough film can be obtained by casting the formic acid solution of nylon 5 prepared by the former group of catalysts.

The various properties of this polymer will be the subject of a succeeding paper.

Infrared Spectra of Metal Salts of Lactams

Infrared spectra of alkali metal salts and ethylaluminum salt of α-piperidone are shown in Figures 4, 5 and Table IV. The characteristic carbonyl stretching frequencies of lactams lie at 1680 for α-pyrrolidone (liq.), at 1664 for α-piperidone (liq.), and 1658 cm.$^{-1}$ for ε-caprolactam (KBr). The lactam solution of alkali metal salt of lactams had additional characteristic bands at 1640–1645 cm.$^{-1}$ and at 1570–1590 cm.$^{-1}$ The

TABLE IV
Infrared Spectra of Alkali Metal Salts of Five-, Six-, and Seven-Membered Lactams in Each Monomer[a]

Lactams	Salt of: Li	Na	K
α-Pyrrolidone	1586	1572	1564
α-Piperidone	1586	1583	1569
ε-Caprolactam	1585	1557	1553

[a] Alkali metal to monomer, mole/mole, 0.1. Monomer/solvent (toluene), vol./vol.: 0.20:0.10 for α-pyrrolidone and α-piperidone, 0.20:0.20 for ε-caprolactam. Values in the table indicate the characteristic absorption bands (cm.$^{-1}$).

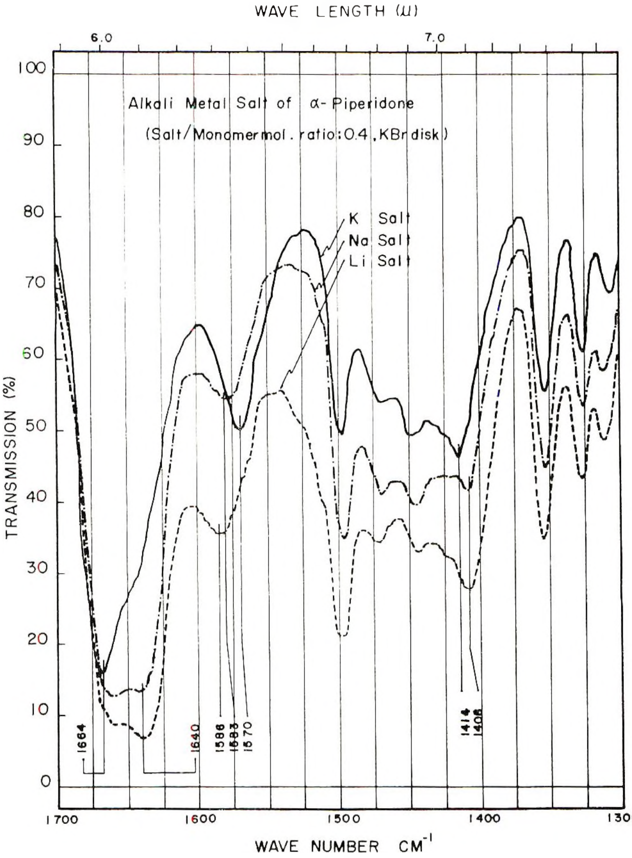


Fig. 4. Infrared spectra of alkali metal salts of α-piperidone: (——) potassium salt; (—·—) sodium salt; (- - -) lithium salt.

intensities of these bands increase with the increase in the concentration of the salt. The band at 1640–1645 cm.$^{-1}$ is difficult to evaluate because of separating it clearly from the very strong carbonyl bands at 1660–1680 cm.$^{-1}$. The frequency of the band at 1570–1590 cm.$^{-1}$ varies in this range, depending upon the nature of the metal and of the lactam (see Table IV). On the other hand, potassium salt of α-piperidone in the solid state had a characteristic band at 1569 cm.$^{-1}$. The difference observed in the solid and the solution state indicates that this compound exists in tautomeric forms in solution. The band at 1640–1645 cm.$^{-1}$ is assignable to the C=O group and that at 1570–1590 cm.$^{-1}$ to the N=C group. This interpretation is supported by two experimental results. First, it was found that *O*-ethyl-γ-butyrolactim, *O*-ethyl-δ-valerolactim, and *O*-ethyl-ε-caprolactim had the C=N band at 1632, 1637, and 1682 cm.$^{-1}$, respectively. Second, Chrzczonowicz et al.[3] have isolated alkali metal salts of ε-caprolactam and reported that the absorption band of the C=O group appeared at 1656 cm.$^{-1}$ for the sodium salt and at 1651 cm.$^{-1}$

for the potassium salt and that of the C=N group at 1594 and 1591 cm.$^{-1}$, respectively.

The absorption frequencies of the C=N vibration of alkali metal salts decrease in the order Li > Na > K; this is the reverse of the ionic character of the metal. Delocalization of electron charge of the oxygen atom in the enolate form is considered to be in the order K > Na > Li. The frequency of the C=N band was higher for the aluminum salt of α-piperidone than for lithium salt. This fact is ascribed to the covalent character of aluminum. The order of polymerization activity of metal salts, K > Na > Li > Al, parallels the order of frequency of the C=N band. This fact implies a close relation between the nature of the C=N band and the polymerization activity.

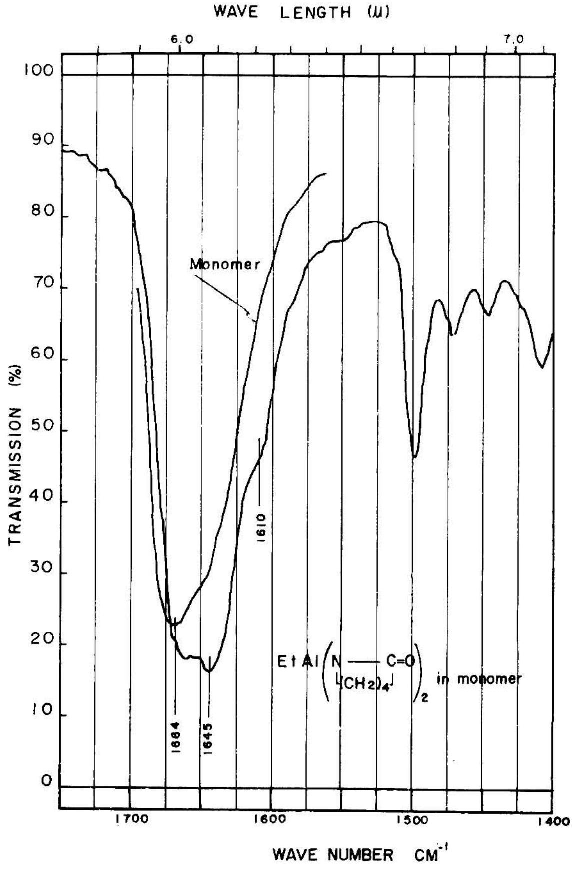


Fig. 5. Infrared spectrum of di-2-oxopentamethyleneimine ethylalanate.

A band at 1569 cm.$^{-1}$ of potassium piperidonate shifts to 1580 cm.$^{-1}$ by mixing with the α-piperidone solution of ethylaluminum dipiperidonate in a molar ratio of K to Al of 1:1. This band is ascribed to the C=N group in the complex formed *in situ* (see Fig. 6). The absorption frequency

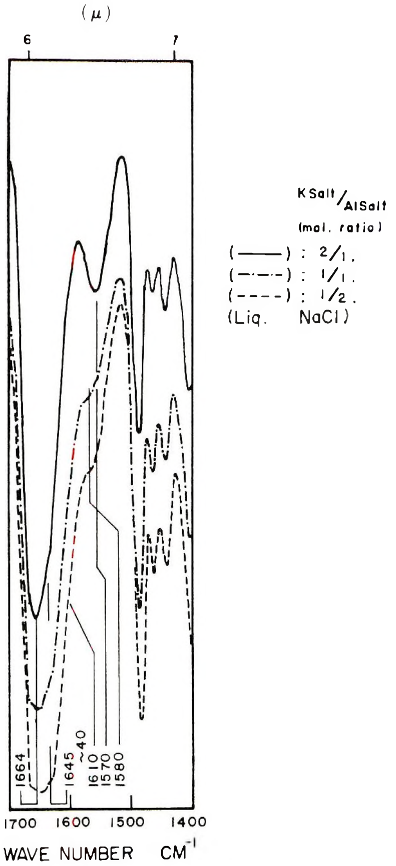


Fig. 6. Infrared spectra of mixtures of potassium salt and aluminum salt of α-piperidone; potassium salt, 20 mole-% of monomer. $[K_{salt}]/[Al_{salt}]$, moles (liq. NaCl): (——) 2:1; (-·-) 1:1; (- - -) 1:2.

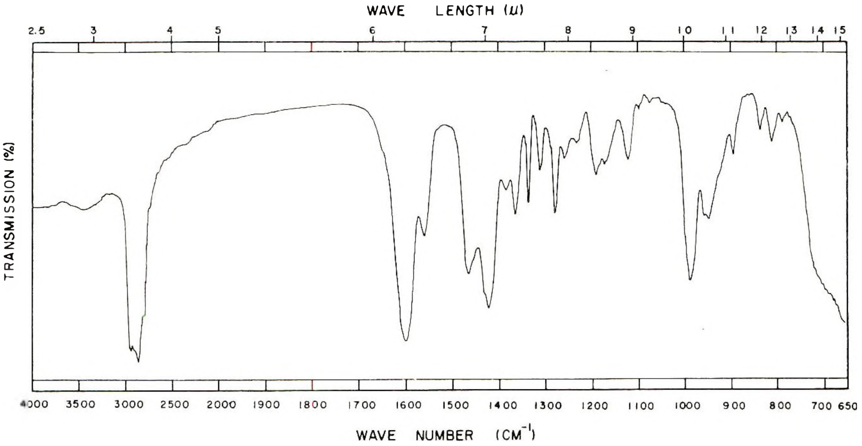


Fig. 7. Infrared spectrum of complex derived from an isolated potassium salt of α-piperidone and triethylaluminum (liq. state).

of the C=N band of the salt depends also on the ring size of the lactam and decreases in the order six > five > seven (see Table IV).

These results imply that the C=N absorption frequency, the bond character of metal-oxygen in enolate form, is related to the catalytic activity of catalyst and to the polymerizability of lactam.

Infrared Spectrum of Complex $KAlEt_3$(Piperidone)

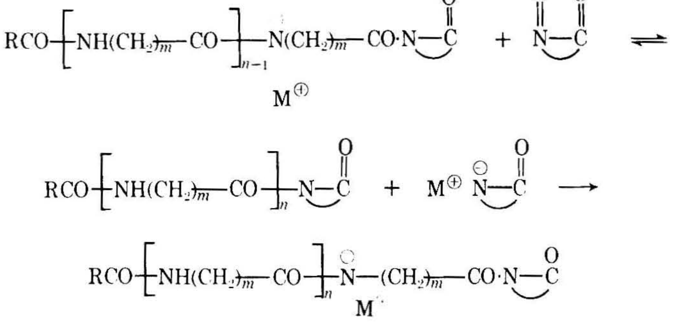
The infrared spectrum of $KAlEt_3$(piperidone), Figure 7, has a strong absorption band at 1600 cm.$^{-1}$, which is attributable to the —N=C(O$^-$)— group in a lactim form.

DISCUSSION

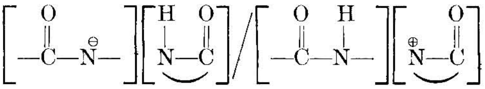
In the low-temperature polymerization of five-, six-, and seven-membered lactams the most peculiar behavior, observed only in the case of α-piperidone, is the fact that propagation reaction ceases soon after a relatively low molecular weight polymer forms.

The rise of the degree of polymerization with increase in the molar ratio of catalyst to initiator is not observed in the case of α-piperidone in the range of high molar ratios, in contrast to that of α-pyrrolidone and ϵ-caprolactam (see Fig. 8). This phenomenon suggests a remarkable consumption of *N*-acyl lactam at the growing polymer end. Moreover, even at a lower molar ratio of catalyst to initiator *N*-acyl lactam is presumed to be consumed at a higher catalyst concentration than 7 mole-% (see Fig. 1). The basicity of the polymerization system increases with increase of catalyst concentration. These results therefore indicate that the basicity of the polymerization system should be closely related to yield and molecular weight of polymer through consumption of the active polymer end and of initiator.

The following scheme is considered for propagation; it is the same as that proposed by Yoda and Miyake,[4] except that the reaction is reversible:



The equilibrium should be affected by the relative acidity of the amide group in lactam and in polymer, and therefore the equilibrium constant *K* derived from the following equation was evaluated for three different lactams:



$= K = K_{\text{lactam}}/K_{\text{polymer}}$

According to the basicity data of various amides reported by Huisgen, Walz, et al.[5] the pK_a of α-pyrrolidone, α-piperidone, and ε-caprolactam

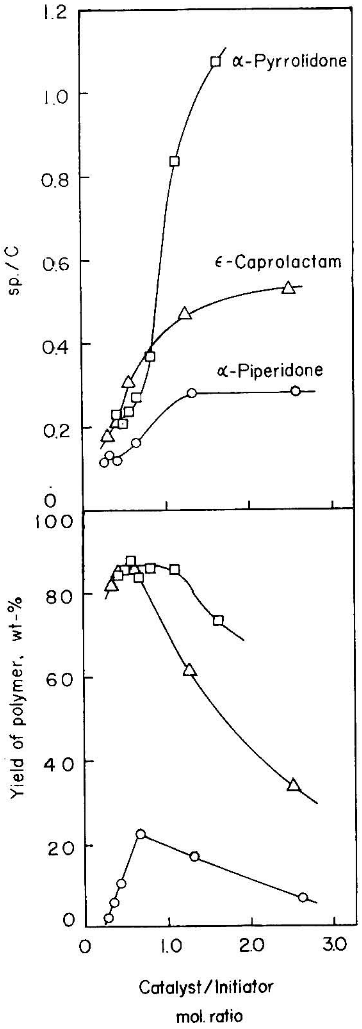


Fig. 8. Effect of the molar ratio of catalyst to initiator on yield and reduced viscosity of polymer. Catalyst (metallic potassium) concentration: 3.24 mole-% for α-pyrrolidone, 2.58 mole-% for α-piperidone, and 2.5 mole-% for ε-caprolactam. Initiators; corresponding N-acetyl compounds of polymerized lactams. Polymerization temperature; 40°C. for α-pyrrolidone, 45°C. for α-piperidone, 75°C. for ε-caprolactam, and 48 hr. for α-piperidone.

estimated by potentiometry are −0.03, 0.75, and 0.36, respectively. An average pK_a value (0.81) of *N*-methylbutylamide, *N*-methylacetamide, and *N*-butylacetamide is taken as a pK_a of the amide group in the polymer. The relative acidities of the amide groups of lactams and of polymer estimated by the ratio of K_L/K_P are 6.91 for α-pyrrolidone, 1.14 for α-piperidone, and 2.82 for ε-caprolactam, respectively.

The data referred to are consistent with the idea that the consumption of *N*-acyl lactam of propagating polymer ends is very predominant in the case of α-piperidone. An analogous suggestion has been made by Wichterle and Gregor[6] in the polymerization of caprolactam. The side reaction and the unfavorable reformation of lactam anion cooperate in the case of α-piperidone for the formation of low molecular weight polymer.

The results presented in this paper support the conclusion that triethylaluminum added forms a certain type of complex, the structure of which is analogous to one derived from $MAlEt_4$, and that it suppresses unfavorable side reactions by stabilizing the alkali metal salt as a complex.

A high molecular weight polymer of α-piperidone can thus be obtained by polymerizing it with $M–AlEt_3$ or $MAlEt_4$ as catalyst, although a prolonged polymerization time is required because of the characteristic property of this monomer.

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Polymerization of 2,5-Dimethyl-3,4-Dihydro-2*H*-Pyran-2-Carboxyaldehyde (Methacrolein Dimer). Part II

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Synopsis

2,5-Dimethyl-3,4-dihydro-2*H*-pyran-2-carboxyaldehyde (methacrolein dimer) gave a polymer consisting of only recurring bicyclic structure of 1,4-dimethyl-6,8-dioxa-bicyclo-[3,2,1]octane with the use of Lewis acid and protonic acid as catalyst at room temperature. On the other hand, the polymer obtained by using $BF_3 \cdot (C_2H_5)_2O$ under −78°C. was found to have the structures produced by the aldehyde group polymerization as well as the bicyclic ones. The polymer obtained at −40°C. had a low decomposition temperature (164°C.) owing to the presence of polyacetal group, whereas the fully saturated bicyclic polymer had a considerably high one (346°C.). The main factors affecting the polymerization were polymerization temperature and catalyst. Lowering temperature increased the polymerization of the aldehyde group. Anionic catalysts and weak cationic catalyst such as $Al(C_2H_5)_3$–H_2O, which were active catalysts for acrolein dimer, did not initiate the polymerization of methacrolein dimer. The fact that the relative viscosity of the polymer increased with polymerization time shows the polymerization of this monomer is a successive reaction.

INTRODUCTION

In the previous paper[1] it was shown that methacrolein dimer underwent an intraintermolecular polymerization to produce a soluble polymer having only recurring bicyclic structures of 1,4-dimethyl-6,8-dioxabicyclo[3,2,1]-octane in the presence of $BF_3 \cdot (C_2H_5)_2O$ as initiator at room temperature.

Methacrolein dimer, however, is expected to undergo four types of polymerization: of the cyclic vinyl ether group (I), of the aldehyde group (II), intraintermolecular (III), and dihydropyran ring-opening (IV).

The purpose of the present paper is to report on the microstructures of methacrolein dimer polymers obtained by using IR and NMR methods and on the relationships among polymerization conditions, polymer structures, and polymer character.

The characteristic of the methacrolein dimer polymerization will also be discussed.

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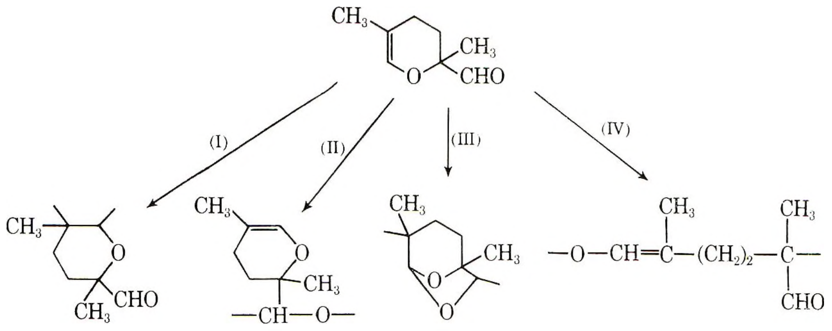


[I] [II] [III] [IV]

EXPERIMENTAL

Monomer and a Model Compound

Methacrolein dimer was prepared by thermal dimerization of anhydrous methacrolein in the presence of hydroquinone (1% by weight in methacrolein) in a stainless-steel autoclave at 160°C. for 3 hr. under nitrogen pressure; yield 30%.

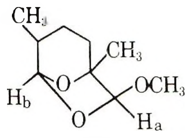
The main material fractionated at 68.1°C. at 24 mm. Hg was found to be 2,5-dimethyl-3,4-dihydro-2*H*-pyran-2-carboxyaldehyde.

The IR and NMR spectra of this compound have the following absorption bands and chemical shifts, which are assignable to the proposed structure: 1735 cm.$^{-1}$, 0.7 τ, due to —CHO, and 1150 cm.$^{-1}$, 3.82 τ, due to —$(CH_3)C{=}CH{-}O$—.

This monomer was redistilled over CaH_2 under reduced pressure prior to use in polymerization studies.

A model compound of 1,4-dimethyl-7-methoxy-6,8-dioxabicyclo[3,2,1]octane was synthesized by the Whetstone method.[2]

A colorless liquid distilling at 63–66°C. under 10 mm. Hg and containing 62.47% carbon and 9.64% hydrogen was obtained. Calcd. for $C_9H_{16}O_3$ (%): C, 62.75; H, 9.25. It was identified as having the apparent structure of 7-methoxy-1,4-dimethyl-6,8-dioxabicyclo[3,2,1]octane corresponding to structural formula [V], according to IR and NMR analyses.



[V]

The NMR spectrum of the model compound had neither peak with chemical shift due to a proton of the aldehyde group nor unsaturated ether group, but it had peaks with chemical shifts located at 5.50 τ, probably due to the acetal methinyl proton derived from the unsaturated ether group

(Hb in formula [V]), at 5.05 τ due to another proton from the aldehyde group (Ha in [V]), and at 6.60 τ due to protons of methoxy group.

The ratio of the integrated peak area of each hydrogen in this compound was 1:1:3:11 and exactly the same as the one calculated from the proposed structure [V].

Polymerization Procedures

The polymerization of methacrolein dimer was usually carried out by the following procedure. Methacrolein dimer and toluene were charged into an ampule under a nitrogen atmosphere, and then a catalyst was added to the system at polymerization temperature. After the polymerization the reaction mixture was diluted with toluene containing a little pyridine. The white, powdery polymer was precipitated from the solution by addition to ether or acetone.

It was washed with fresh acetone, dried by sucking, and finally dried in a vacuum oven at 35°C. for 24 hr.

Analysis of the Polymer Structures

IR and NMR analysis of the polymer structures were carried out by using Hitachi-EPI-2 and Varian A-60 apparatus. In the case of IR analysis the mole per cent of the residual cyclic unsaturated ether groups in a polymer were calculated from the ratio of the optical density of 1675 cm.$^{-1}$ to that of the monomeric methacrolein dimer in chloroform solution. The NMR method was also used for quantitative analysis of the polymer structures by evaluating ratios of peak areas of the chemical shifts assignable to unsaturated ether group protons or those of methinyl protons to the total area of all the protons in the polymers.

RESULTS

NMR Spectra of the Polymethacrolein Dimers

Figure 1 shows NMR spectra of the polymers obtained by using $BF_3 \cdot (C_2H_5)_2O$ as catalyst at −40 and −78°C. Chemical shifts of the polymers and their intensities are also summarized in Table I.

TABLE I

Chemical Shifts and Intensities of Polymethacrolein Dimer

Polymer No.[a]	4.1 (sharp), S_1	5.1–5.8, S_2, plus 5.6 (sharp), S_3	6.0–6.5 S_4	6.5 (sharp) S_5	Calcd. $S_2 + S_3$
(1)	1	15	1	13	15
(2)	1	5.67	0.9	3.67	5.8
(3)	1	2.14	0.74	0.24	1.98

[a] Polymers obtained with $BF_3(C_2H_5)_2O$ at (1) −20°C., (2) −40°C., and (3) −78°C.

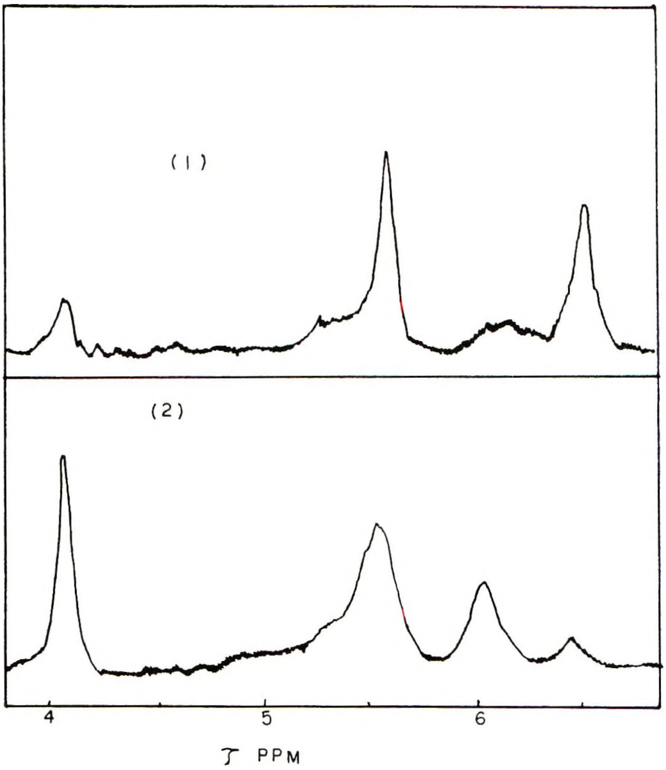


Fig. 1. NMR spectra of polymers measured at 40°C. by Varian A-60A working at 60 Mc./sec. in deuterated chloroform. Polymers obtained with $BF_3 \cdot (C_2H_5)_2O$ at: (*1*) −40°C.; (*2*) −78°C.

Those spectra have no chemical shift at 9.5 τ due to a proton of the aldehyde group. This means that the polymerizations of (I) and (IV) did not take place. They show, however, the same chemical shift at 4.1 τ as that present in the monomer, in addition to those at 6.5 and 5.6 τ due to the acetal methine protons of recurring bicyclic units [III].

Influence of Polymerization Conditions

The effects of polymerization temperature on the relative reaction rate of the functional group are shown in Table II.

By lowering the polymerization temperature the relative rate of the aldehyde-group polymerization increased. Table III shows the results of polymerization of methacrolein dimer with the use of various catalysts.

At room temperature both anionic catalysts such as butyllithium and active catalysts for acrolein dimer, $Al(C_2H_5)_2Cl$ or $Al(C_2H_5)_3$–H_2O, did not initiate any polymerization of this monomer, whereas Lewis acids such as $SnCl_4$, $BF_3(C_2H_5)_2O$, and I_2 and protonic acids such as H_2SO_4 produced a polymer containing recurring bicyclic units.

TABLE II
Effects of Polymerization Temperature on Reactivity of Methacrolein Dimers and Their Polymer Structures[a]

Temp., °C.	Yield, g.	Structure, %		
		(II)	(III)	η_{sp}/C[b]
50[c]	0.270	0	100	
15	0.540	0	100	0.45
0	0.763	2	98	0.86
−20	0.659	7	93	0.61
−40	0.407	18	82	0.29
−78[d]	0.180	49	51	

[a] Polymerization conditions: methacrolein dimer 1 cm.³, toluene, 9 cm.³, $BF_3(C_2H_5)_2O$ 1.0 mole-% of monomer, time 60 min.

[b] Measured in 1% chloroform solution at 35°C.

[c] $BF_3(C_2H_5)_2O$ 0.05 mole-% of monomer.

[d] Monomer 2 cm.³, toluene 8 cm.³, $BF_3(C_2H_5)_2O$ 2.0 mole-% of monomer, time 24 hr.

TABLE III
Polymerizations of Methacrolein Dimer with the Use of Various Catalysts[a]

Catalyst	Temp., °C.	Polymn. time	Yield, g.	Reaction soln.[b]
Butyl Li	10	48 hr.	0	none
$Al(C_2H_5)_3$	"	"	0	"
$Al(C_2H_5)_2Cl$	"	"	0	"
$Al(C_2H_5)Cl_2$	"	"	0	"
$BF_3(C_2H_5)_2O$	"	15 min.	0.43	opaque gel
I_2	"	24 hr.	0.26	visc. liq.
$SnCl_4$	0	90 min.	0.64	transpar. gel
H_2SO_4	10	24 hr.	0.63	"
$FeCl_3$	0	90 min.	0.81	"
$Al(C_2H_5)_2Cl$	−78	48 hr.	0	none
$Al(C_2H_5)_3$	"	"	0	visc. liq.
C_2H_5MgBr	"	"	0.03	transpar. gel
$BF_3(C_2H_5)_2O$	"	24 hr.	0.18	visc. liq.

[a] Polymerization conditions: monomer 15 cm.³, catalyst concentration 1 mole-% of monomer.

[b] At polymerization temperature.

TABLE IV
Effect of Polymerization Time on Polymerization of Methacrolein Dimer with $BF_3(C_2H_5)_2O$ at 0°C. for 15 min.[a]

Polymn. time	Yield, g.	η_{sp}/C, dl./g.
15 min.	0.0	—
80 min.	0.17	0.12
120 min.	0.36	0.18
21 hr.	0.61	0.32

[a] Polymerization conditions: catalyst concentration 0.05 mole-% of monomer, monomer 1 cm.³, toluene 15 cm.³.

At the low temperature of −78°C. the reaction solution with $Al(C_2H_5)_3$ or C_2H_5MgBr changed into a transparent, viscous gel in 2 or 3 hr. but did not give any precipitate when poured into acetone.

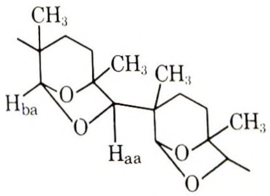
Table IV shows the dependence of time on the polymerization of methacrolein dimer.

The relative viscosity (η_{sp}/C) of the polymer increased with polymerization time, and yields of the polymer also increased in 3 or 4 hr.

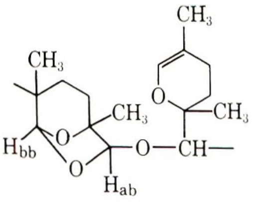
DISCUSSION

Polymer Structures

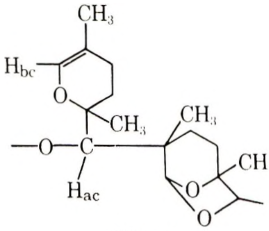
Experimental results show the existence of two kinds of polymerization, (II) and (III). Therefore, there are supposed to be four combinations of addition reactions, as shown below:



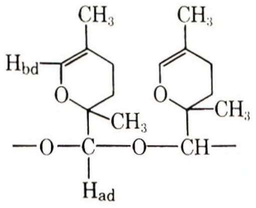
(III) (III)
A



(III) (II)
B



(II) (III)
C



(II) (II)
D

The ratios of these four addition structures in the polymer were determined by the following procedure (assumption, calculation, and verification) with the use of NMR results.

In the NMR spectrum of a polymer having structure A the chemical shifts due to Haa, the methinyl proton of the ether group, and Hba, the acetal proton, appear at 6.5 and 5.6 τ, respectively, as observed in the completely bicyclic polymer reported in the previous paper.[1] Protons Hbb and Hab in structure B coincide with the Hb and Ha of structure [V] for a model compound, respectively, so that the chemical shift due to Hbb probably appears at 5.5 τ and that due to Hab at 5.1 τ, which is easily understood from the fact that Hbb has nearly the same environment of Hba, whose chemical shift appears at 5.6 τ.

On the other hand, in the NMR spectra of structures C and D the protons Hbc and Hbd are easily understood to have the same τ value, 4.1, as that of the methinyl proton of the unsaturated ether group in this monomer, whereas Hac is supposed to give a chemical shift greater than Haa, coming out at 6.0–6.4 τ, and Had would be expected to have 5–5.5 τ as acetal protons in polyacetaldehyde.[3] The intensities of the peaks in the NMR spectra are designated $S_1, S_2, \ldots, S_5$, as shown in Table I.

S_1 is considered to be due to protons Hbc and Hbd, S_4 of the broad peak at 6.0–6.5 τ is expected to be assignable to Hac, and S_5 of a sharp peak at 6.5 τ, to Haa. Consequently, the ratios of structure [II], A, and B in polymers of the methacrolein dimer are determined according to the following equations:

$$\text{[II] structure \% in the polymer} = S_1/\tfrac{1}{2}S \times 100 \qquad (1)$$

$$\text{A \%} \quad S_4/\tfrac{1}{2}S \times 100 \qquad (2)$$

$$\text{C \%} \quad S_5/\tfrac{1}{2}S \times 100 \qquad (3)$$

where $S_1 = S + S_2 + S_3 + S_4 + S_5$. In the three kinds of polymer shown in Table I the experimental values of S_2 plus S_3 agreed with those values calculated by using ratios of A and C derived from S_1, S_4, and S_5.

Therefore these results give further evidence of the correctness of the peak assignments in the NMR spectra of the polymers. Table V summarizes the results on the polymer structures, which were also confirmed by IR analysis.

TABLE V

Polymer Structure of Polymethacrolein Dimer

Polymer No.	Structure, % (II)	(III)	A	B	C	D
(1)	6.5	93.5	87	6.5	6.5	0
(2)	18	82	66	16	16	2
(3)	49.5	50.5	12	38	37	13

Even polymer (3) having the same quantity of [II] as [III] contains A and D units, so that it is shown not to be a completely alternating copolymer of [II] with [III].

Although the fully saturated bicyclic polymer had a considerably high decomposition point, 346°C., the polymer obtained at −40°C. was very thermally unstable and had a low decomposition point, 164°C. This is explained by the presence of the acetal unit D in the polymer.

Polymerization Reactivity of Methacrolein Dimer

The main factors affecting the reactivity of methacrolein dimer are the polymerization temperature and initiators, as shown in Tables II and III.

This monomer did not give any polymer at room temperature with catalyst $Al(C_2H_5)_2Cl$, which did initiate polymerization of acrolein dimer.

Only a strong acid, such as Lewis or protonic acid, initiated the polymerization of methacrolein dimer and gave a bicyclic polymer at room temperature; see Table III.

These findings seem to be explained as follows. The cyclic unsaturated ether group of methacrolein dimer has a more cationic character but a lower reactivity, owing to steric hindrance of its methyl group, than that of acrolein dimer. Though the unsaturated ether group is more cationically reactive than the aldehyde group, a carbonium cation derived from the unsaturated ether group seems to be added rather more easily to the aldehyde group in the same monomer than to a functional group in another monomer because of the steric hindrance of each methyl group.

With anionic catalysts, such as ethylmagnesium bromide, methacrolein dimer gave a viscous liquid at −78°C., but no polymer was found at room temperature.

It is postulated, from above facts, that anionic catalyst initiates polymerization (II) to give a polymer having polyacetal structure D, which is too unstable to give a polymer at room temperature.

In other words, there seems to be a ceiling temperature in polymerization (II) with anionic catalyst, as in the case of acetaldehyde,[4] and that of methacrolein dimer is expected to be lower than that of acetaldehyde.

The relationship between the relative viscosity of the polymer and polymerization time seems to show that the polymerization of this monomer is a successive reaction.

The author is grateful to T. Takizawa of Tokyo University and to H. Ohama and H. Kobayashi of Technical Research Laboratory, Asahi Chemical Industry Co., Ltd., for helpful discussions. He also wishes to thank Suzuki, director of our laboratory, for permission to publish this research.

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Polymers from 1,3-Dipole Addition Reactions: The Nitrilimine Dipole from Acid Hydrazide Chlorides*

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Synopsis

An investigation of the suitability of the 1,3-dipole addition reaction of bisnitrilimines, generated from the corresponding acid hydrazide chlorides, with diyne and dinitrile dipolarophiles was carried out. The reactions of iso- and terephthaloylphenylhydrazide chlorides and 4,4'-oxydibenzoylphenylhydrazide chloride with the dipolarophiles *m*- and *p*-diethynylbenzene, *m*-divinylbenzene, and perfluoroglutaronitrile in the presence of triethylamine gave moderate molecular weight polymers containing pyrazole or triazole units along the polymer backbone. The polymers were soluble in such polar solvents as hexamethylphosphoramide and acids but had inherent viscosities only as high as 0.32. The thermogravimetric analyses of the finely powdered polypyrazoles showed breaks near 500°C. in air and in nitrogen atmospheres.

INTRODUCTION

The cycloaddition reaction may be employed in theory as a mode of propagation in the synthesis of macromolecules; the 1,2-, 1,3-, and 1,4-cycloadditions are well-known organic reactions. Diels-Alder additions have been investigated as polymerization reactions[1] and have been used for preparing a variety of polymers containing rings in the backbone. The 1,2-addition reactions do not appear to be particularly attractive propagation reactions, since the yields are usually too low to be effective propagation modes, and either the additions must be photocatalyzed[2] or, if the addition is thermally induced,[3] the olefins must be substituted with groups that would require a very difficult monomer synthesis. Furthermore, the strain in a cyclobutane ring provides a measure of instability in polymer degradation; the reverse cycloaddition takes place readily at elevated temperatures.

Many of the 1,3-dipolar addition reactions[4] are suitable, however, for use as polymer-forming reactions, since the difunctional monomers are synthesized readily, and many of the dipolar additions are nearly quantitative. We have previously reported[5] a polymerization that utilizes the 1,3-dipolar addition reaction of benzalazine for propagation. Especially suited to the production of a stable polymer is the fact that certain prod-

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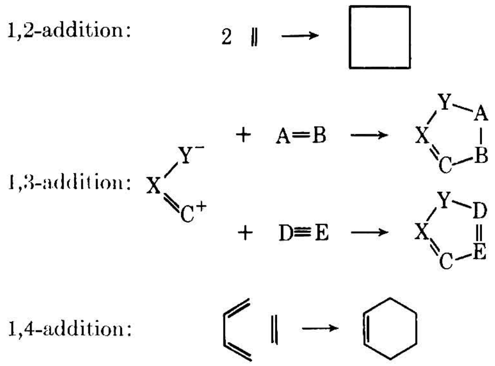
* Presented as a part of a talk, "1,3-Dipole Addition Polymers," at the IUPAC Symposium on Macromolecular Chemistry at Brussels-Louvain, 12–16 June 1967.



ucts of the 1,3-dipolar addition are five-membered aromatic heterocycles. Thus, when the dipolarophile is a triple-bonded species, such as an acetylene or a nitrile, and the dipole contains an atom Y, which retains a lone pair of electrons in the product, the ring contains the requisite six π electrons.

Three types of 1,3-dipoles—the sydnones, the nitrilimines, and the nitrile oxides—seemed especially suited in this respect. In fact, the polymerization reactions of the bisnitrile oxide[6–8] and bisnitrone[9] dipoles have been already investigated.

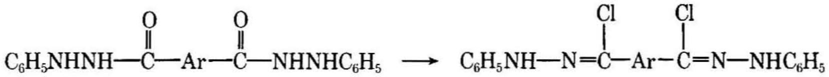
One of the objects of this study was to obtain thermally stable polymers containing pyrazole or triazole units. Therefore, the monomers that were synthesized contained the dipole and dipolarophile portions connected by structures that are in their own right thermally stable and relatively insensitive to oxidative attack. Preliminary reports of polymerization reactions of bissydnone dipoles[10] and bisnitrilimine dipoles[11,12] with diacetylenes, giving polypyrazoles, have revealed that these reactions may be useful for the formation of thermally stable polymers. Olefin dipolarophiles also undergo this type of polymerization reaction with bisnitrilimine dipoles.[13] In this paper we report the polymerization reactions of double dipolarophiles with bisnitrilimines generated from bis(acid hydrazide chlorides). In the paper that follows[14] the polymerization reactions of double dipolarophiles with bissydnones are described.

DISCUSSION

Nitrilimines may be generated by the action of base on acid hydrazide chlorides or by the thermal decomposition of tetrazoles.[15–20] Nitrilimines react rapidly with alkynes and alkenes to form pyrazoles and pyrazolines, respectively.[16] Although the dipolarophile activity of the nitrile group is less, triazoles are formed when the nitrilimine dipole is generated in the presence of nitriles.[18] Further, only one pyrazole or triazole isomer has been reported when two are possible, and the yield of pyrazole or triazole is increased by the presence of electron-withdrawing groups attached to the dipolarophile.

Monomers

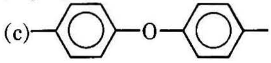
The acid hydrazide chlorides isophthaloylphenylhydrazide chloride (Ia), terephthaloylphenylhydrazide chloride (Ib), and 4,4-oxdibenzoylphenylhydrazide chloride (Ic) were prepared by the reaction of phosphorus pentachloride on the respective dihydrazides:



$$C_6H_5NHNH{-}\overset{O}{\overset{\|}{C}}{-}Ar{-}\overset{O}{\overset{\|}{C}}{-}NHNHC_6H_5 \longrightarrow C_6H_5NH{-}N{=}\overset{Cl}{\overset{|}{C}}{-}Ar{-}\overset{Cl}{\overset{|}{C}}{=}N{-}NHC_6H_5$$

(I)

Ar = (a) m-C_6H_4
(b) p-C_6H_4
(c)



These acid hydrazide chlorides eliminate hydrogen chloride on treatment with base to afford the intermediate nitrilimine dipole:

$$(I) \xrightarrow{(C_2H_5)_3N} C_6H_5{-}\overset{-}{N}{-}N{=}\overset{+}{C}{-}Ar{-}\overset{+}{C}{=}N{-}\overset{-}{N}{-}C_6H_5$$

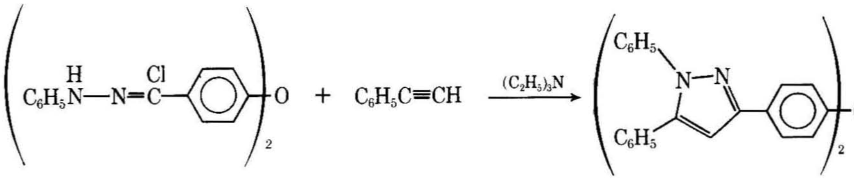
The diacetylenes m- and p-diethynylbenzene (IIa,b)[21] and the dinitrile, perfluoroglutaronitrile (III)[22] were synthesized for use as double dipolarophile monomers:

$HC{\equiv}C{-}C_6H_4{-}C{\equiv}CH$
(II)
(a) m-C_6H_4
(b) p-C_6H

$N{\equiv}C{-}(CF_2)_3{-}C{\equiv}N$
(III)

Model Compounds

The reactions of the acid hydrazide chlorides (Ia,b) with phenylacetylene and the reactions of m- and p-diethynylbenzene (IIa,b) with benzoylphenylhydrazide chloride in the presence of base have been reported.[23] These reactions afford 1,1′,5,5′-tetraphenyl-3,3′-m- and p-phenylenedipyrazole and 1,1′,3,3′-tetraphenyl-5,5′-m- and p-phenylenedipyrazole, respectively. In addition, the analogous reactions of (Ic) with phenylacetylene and benzoylphenylhydrazide chloride with (III) and m-divinylbenzene were carried out to afford a series of model compounds (Table I):



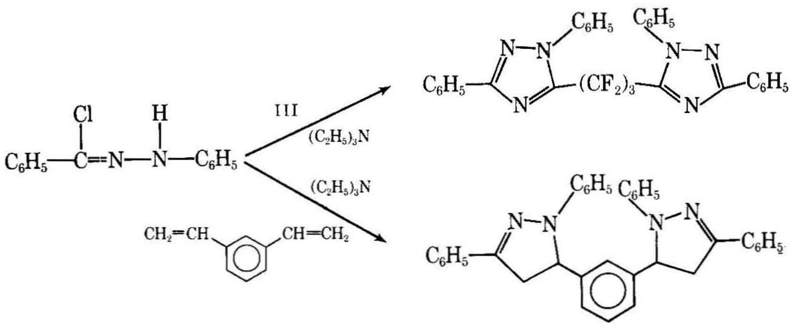
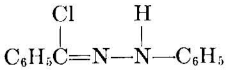
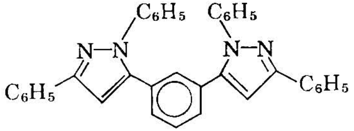
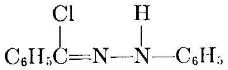
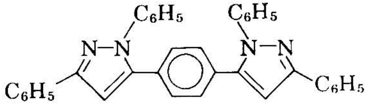
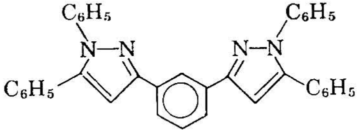


TABLE I
Model Compounds

Acid hydrazide chloride	Dipolarophile	Model compound	M.p., ° C.	Analysis, %					
				Calcd.			Found		
				C.	H	N	C	H	N
 $C_6H_5\overset{Cl}{\overset{\vert}{C}}{=}N{-}\overset{H}{\overset{\vert}{N}}{-}C_6H_5$	(IIa)		236–238	84.01	5.09	10.89	83.73	5.26	10.82
 $C_6H_5\overset{Cl}{\overset{\vert}{C}}{=}N{-}\overset{H}{\overset{\vert}{N}}{-}C_6H_5$	(IIb)		247–248	84.01	5.09	10.89	84.34	5.01	10.66
(Ia)	$C_6H_5C{\equiv}C{-}H$		210–211	84.01	5.09	10.89	83.98	5.25	10.87

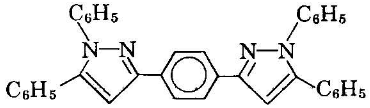
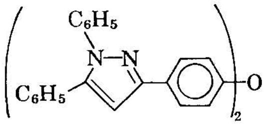
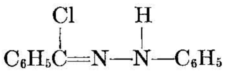
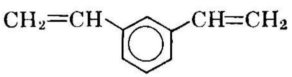
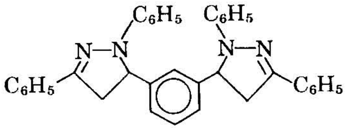
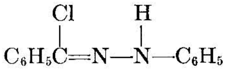
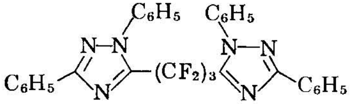
(Ib)	$C_6H_5C{\equiv}C{-}H$		269–271	84.01	5.09	10.89	84.12	5.27	10.71
(Ic)	$C_6H_5C \div C{-}H$		212–214	83.14	4.94	9.23	82.76	5.02	9.18
 $C_6H_5C(Cl){=}N{-}N(H){-}C_6H_5$			211–213	83.37	5.83	10.80	83.37	5.99	10.71
 $C_6H_5C(Cl){=}N{-}N(H){-}C_6H_5$	(III)		197–198	63.05	3.41	14.23	62.75	3.10	13.93

TABLE II
Polymers

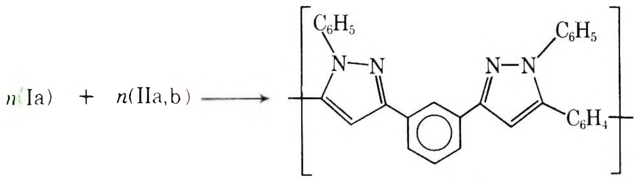
Polym. No.	Convsn., %	TGA (air)[a]		Analysis, %					
				Calcd.			Found		
		[η]	°C.	C	H	N	C	H	N
(IVa)	85	0.11	500	82.55	4.62	12.83	80.85	4.37	13.04
(IVb)	80	0.10	500	82.55	4.62	12.83	80.46	4.50	14.55
(Va)	82	0.14	500	82.55	4.62	12.83	80.95	4.38	12.33
(Vb)	89	0.32	500	82.55	4.62	12.83	81.00	4.79	10.54
(VI)	78	0.15	460	81.80	4.58	10.60	80.45	5.13	9.98
(VII)	91	0.28	360[b]	81.79	5.49	12.72	81.00	5.54	12.63
(VIII)	75	0.13	350	58.60	2.75	16.40	59.70	3.53	15.86
(IX)	77	0.10	275	65.26	3.65	14.50	66.34	3.99	13.98
(Xa)	91	0.08	300	77.40	4.55	18.05	75.17	5.21	16.09
(Xb)	94	0.26	310	77.40	4.55	18.05	74.40	6.38	16.63

[a] Inherent viscosities were obtained in 98% formic acid at 25°C. and at a polymer concentration of 0.25 g. per 100 ml. The polymers exhibited no significantly different thermal stability in nitrogen atmospheres.

[b] See Figure 1.

Polymers

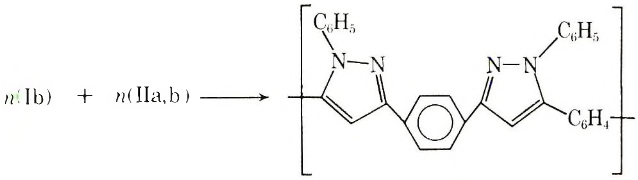
The reactions of the acid hydrazide chloride monomers (Ia–c) with the diynes (IIa,b) in refluxing anhydrous tetrahydrofuran in the presence of triethylamine afforded the polypyrazoles (IV), (V), and (VI) in high conversions (Table II):



(IV)

(a)m-C_6H_4

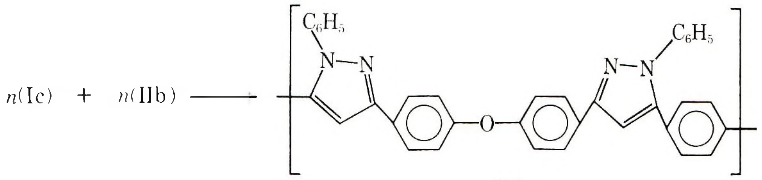
(b)p-C_6H_4



(V)

(a)m-C_6H_4

(b)p-C_6H_4



(VI)

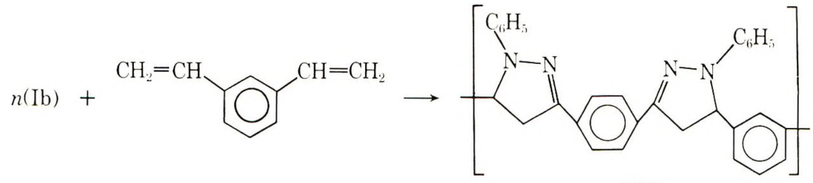
Similarly, the polypyrazoline (VII) was obtained when an olefin dipolarophile, m-divinylbenzene, was employed in the polymerization reaction with terephthaloylphenylhydrazide chloride (Ib).

The polymerization of (Ib) with perfluoroglutaronitrile (III) in a sealed tube in anhydrous tetrahydrofuran and in the presence of triethylamine afforded the polytriazole (VIII) containing perfluoromethylene units in the chain. Although the reactions of acid hydrazide chlorides with alkyl nitriles in the presence of triethylamine generally do not give high yields of triazoles, electron-withdrawing groups attached to the cyano function have been shown to increase the yield dramatically.[18]

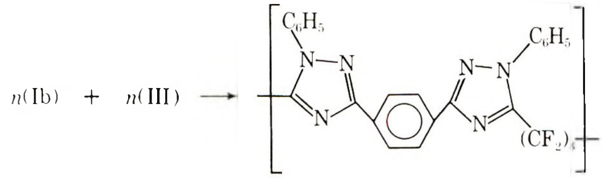
Since carbon disulfide has been reported to undergo cycloaddition reactions with 1,3-dipoles,[24] a polymerization employing this dipolarophile was carried out. The reaction of (Ib) with carbon disulfide in tetrahydrofuran in the presence of triethylamine gave the polymer (IX) containing spirobisthiadiazoline units.

The infrared spectrum of each polymer sample showed maxima characteristic of the particular heterocyclic structure that it possessed and could be compared directly with the spectrum of the corresponding model compound.

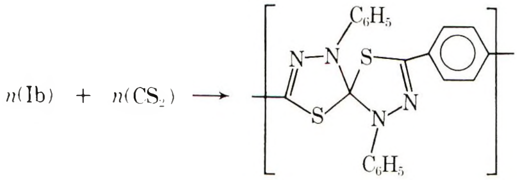
Nitrilimines are known to undergo head-to-tail self-dimerization reactions in the absence of a good dipolarophile.[25] In fact, dihydrotetrazine polymers (Xa,b) can be obtained from the reactions of iso- and terephthaloylhydrazide chloride with triethylamine in refluxing tetrahydrofuran. This reaction could, in fact, account for the rather low molecular weights (inherent viscosities, Table II) of the polymers obtained in the cycloaddition reaction of the nitrilimines. Thus a disruption of monomer balance through the self-dimerization would afford low molecular weight polymers with acetylene ends. This dimerization could also explain the difficulty encountered in obtaining good elemental analyses of the polymer samples (Table II). Altering the initial monomer balance over a range of



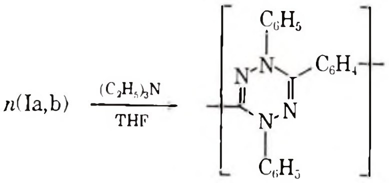
(VII)



(VIII)



(IX)



(X)

(a) m-C_6H_4

(b) p-C_6H_4

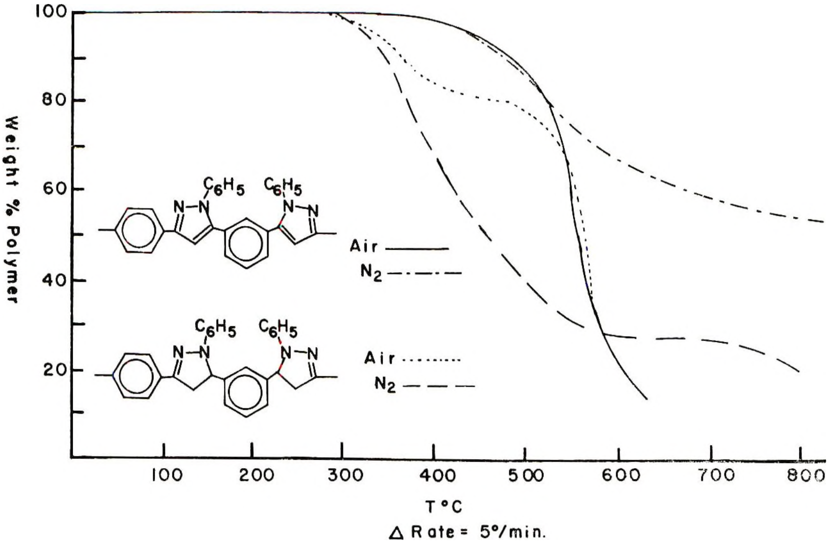
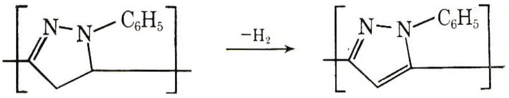


Fig. 1. Thermogravimetric analyses of polypyrazole (Va) and polypyrazoline (VII).

larger molar ratios of acid hydrazide chloride to dipolarophile, however, did not increase the molecular weight. All polymers were obtained in high yields.

All of the polypyrazoles were completely soluble in 98% formic acid. The solubility of (IVa), for example, which contains all *m*-phenylene links along the chain, is much greater in polar organic solvents (hexamethylphosphoramide) than (Vb), which contains all *p*-phenylene links.

The high thermal stabilities of the polypyrazoles in both air and nitrogen atmospheres are comparable to those of other polymers containing heterocyclic aromatic rings in the backbone. A comparison of the thermogravimetric analysis of the polypyrazoline (VII) with the polypyrazoles (IV), (V), and (VI) is particularly interesting. An initial break in the curve in air (Fig. 1) is obtained at 360°C., and after approximately a 15% weight loss the remainder of the curve follows that of the polypyrazoles and shows a break at 520°C. In nitrogen the thermogravimetric analysis of the polypyrazoline shows a break followed by complete decomposition at 360°C. This greater ultimate stability in air rather than nitrogen can be explained on the basis of the oxidation or dehydrogenation of the pyrazoline moieties to pyrazole units.[26] The 15% weight loss is, of course, greater



than that calculated for the loss of hydrogen only; so, evidently, some pyrazoline groups are degrading before their oxidation takes place. The infrared spectrum indicates that this preliminary degradation proceeds

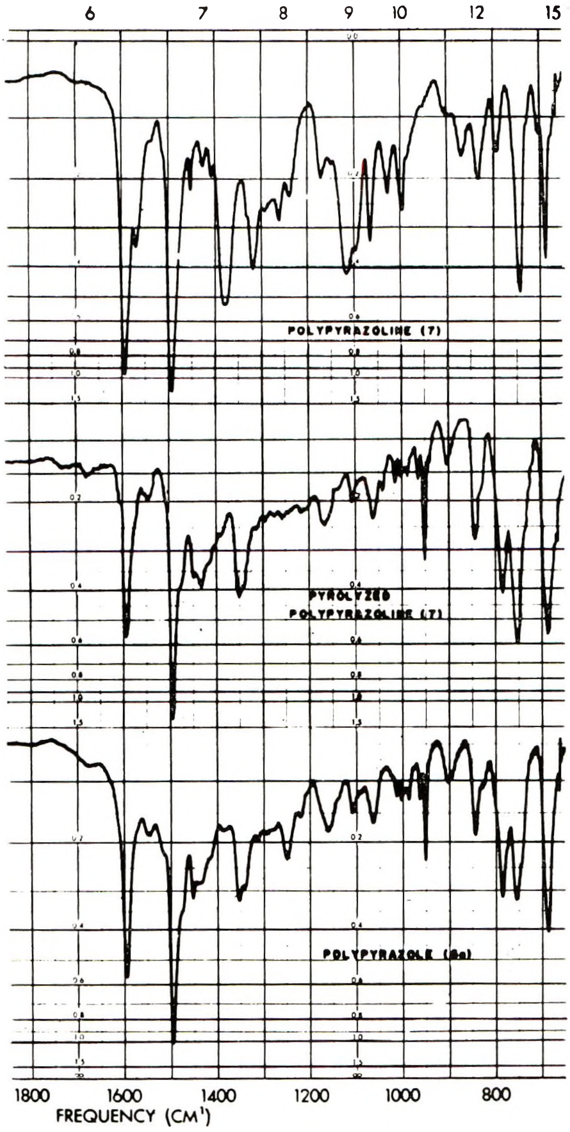


Fig. 2. Infrared spectra of pyrazole and pyrazoline polymers.

with the incorporation of nitrile groups (2220 cm.$^{-1}$) into the polymer backbone. This conversion of pyrazoline to pyrazole was supported by comparing the infrared spectrum of the polymer taken just after the 360°C. break, but before the 520°C. break, to the spectra of the untreated polypyrazoline and corresponding polypyrazole (Fig. 2).

EXPERIMENTAL

Monomers

Isophthaloylphenylhydrazide Chloride (Ia). Treatment of isophthaloylphenylhydrazide with phosphorus pentachloride as described[23] afforded isophthaloylphenylhydrazide chloride. Recrystallization from benzene afforded white needles; m.p. 170–171°C. (lit.[23] 165–166°C.).

Terephthaloylphenylhydrazide Chloride (Ib). The preparation of terephthaloylphenylhydrazide chloride was carried out as described[23] for the *m*-isomer. Recrystallization from benzene afforded yellow crystals; m.p. 210–211°C. (lit.[23] 205–206°C.).

4,4′-Oxydibenzoylphenylhydrazide Chloride (Ic). A mixture of 4.38 g. (0.010 mole) of 4,4′-oxydibenzoylphenylhydrazide and 5.0 g. (0.024 mole) of phosphorus pentachloride in 25 ml. of anhydrous ether was heated under reflux for 24 hr. To the mixture was added 10 g. of phenol in 15 ml. of ether, followed by the slow addition of 20 ml. of methanol. The solution was allowed to cool, and the dark-grey precipitate was filtered. Recrystallization from benzene afforded 2.74 g. (57.7%) of white product; m.p. 197–198°C.

ANAL. Calcd. for $C_{26}H_{20}N_4Cl_2O$ (%): C 65.97, H 4.25, N 11.84. Found (%): C 65.54, H 3.99, N 11.66.

***m*-Divinylbenzene.** Pure *m*-divinylbenzene was obtained from Labofina, 98–100 Chaussée de Vilvorde, Bruxelles 12, Belgium, and distilled under reduced pressure prior to use.

***m*-Diethynylbenzene (IIa).** The bromination of pure *m*-divinylbenzene and the subsequent dehydrobromination of the tetrabromo intermediate according to the known procedure[21] afforded product; b.p. 76–78°C. at 14 mm. (lit.[21] 78°C. at 14 mm.).

***p*-Diethynylbenzene (IIb).** *p*-Diethnylbenzene was prepared as described[21] from a commercial divinylbenzene mixture. Sublimation of the crude product afforded colorless crystals; m.p. 95–96°C. (lit.[21] 96.5°C.).

Perfluoroglutaronitrile (III). The dehydration of perfluoroglutaramide with benzotrichloride as described[22] provided the dinitrile; b.p. 38–39°C. (lit.[22] 38°C.).

Model Compounds

Four dipyrazole model compounds (1,1′,3,3′-tetraphenyl-5,5′-*m*- and -*p*-phenylenedipyrazole and 1,1′,5,5′-tetraphenyl-3,3′-*m*- and -*p*-phenylenedipyrazole) were prepared as previously described.[23] Yields of the crude reaction products of the following model compounds were higher than those reported for the materials that had been recrystallized several times and were analytically pure.

1,1′,5,5′-Tetraphenyl-3,3′-(oxydi-*p*-phenylene)dipyrazole. To a solution of 0.447 g. (0.0009 mole) of 4,4′-oxydibenzoylphenylhydrazide chloride (Ic) in 10 ml. of phenylacetylene was added 3 ml. of triethylamine. After the addition was complete, the mixture was heated at 80–90°C. for 18 hr. The solution was then evaporated to low volume and allowed to cool. The dark-brown precipitate that formed was filtered, washed with ethanol to remove triethylamine hydrochloride, and recrystallized from pyridine–water, yielding 0.300 g. (52.4%) of light-yellow product; m.p. 212–214°C.

1,1′,3,3′-Tetraphenyl-5,5′-*m*-phenylenedi-2-pyrazoline. To a mixture of 0.490 g. (0.003 mole) of *m*-divinylbenzene and 1.380 g. (0.006 mole) of benzoylphenylhydrazide chloride in 12 ml. of benzene at the reflux temperature was added 4 ml. of triethylamine. After the addition was complete, the mixture was heated under reflux for 3 hr. The triethylamine hydrochloride that formed was filtered, and the solution was evaporated to a low volume. The dark-yellow precipitate that formed was recrystallized from pyridine–water, yielding 0.769 g. (66.4%) of light-yellow product; m.p. 211–213°C.

1,1′3,3′-Tetraphenyl-5,5′-perfluoropropyldi-1,2,4-triazole. A mixture of 1.154 g. (0.005 mole) of benzoylphenylhydrazide chloride, 0.507 g. (0.0025 mole) of perfluoroglutaronitrile (III), and 3 ml. triethylamine in 10 ml. of anhydrous tetrahydrofuran was sealed in a glass tube. The tube was placed in a Parr bomb and heated to 65°C. for 24 hr. The reaction mixture was filtered, to remove triethylamine hydrochloride, and the filtrate was slowly added to methanol. The precipitate that formed was recrystallized from acetone–water, yielding 0.768 g. (52%) of white needles; m.p. 197–198°C.

2,2′-Spirobis-[3,5-diphenyl-2,3-dihydro-1,3,4-thiadiazole]. The synthesis of this compound was carried out according to the known procedure,[24] yielding product; m.p. 147–149°C. (lit.[24] 148.5–149.5°C.).

Polymers

The polypyrazoles (IVa,b), (Va,b), and (VI) were prepared by the same general procedure. A typical polymerization yielding poly[1,1′-diphenyl-3,3′-*p*-phenylene-5,5′-*m*-phenylenedipyrazole], (Va), follows. To a mixture of 1.5331 g. (0.004 mole) of terephthaloylphenylhydrazide chloride (Ib) and 0.5046 g. (0.004 mole) of *m*-diethynylbenzene (IIa) in 15 ml. of anhydrous tetrahydrofuran at the reflux temperature was slowly added 4 ml. of triethylamine. After the addition was complete, the mixture was heated under reflux for 24 hr. The solution was then filtered, to remove triethylamine hydrochloride, evaporated to low volume, and slowly added to methanol. The dark-yellow precipitate that formed was filtered and reprecipitated from tetrahydrofuran, yielding 1.436 g. (82.2%) of yellow polymer, which did not melt at 400°C.

Poly[1,1′-diphenyl-3,3′-*p*-phenylene-5,5′-*m*-phenylenedi-2-pyrazoline] (VII). To a mixture of 0.651 g. (0.005 mole) of *m*-divinylbenzene and 1.916 g. (0.005 mole) of terephthaloylphenylhydrazide chloride (Ib) in 15 ml. of anhydrous tetrahydrofuran at the reflux temperature was added 4 ml. of triethylamine. After the addition was complete, the mixture was heated under reflux for 12 hr. The solution was then filtered, evaporated to low volume, and slowly added to 50 ml. of methanol. The dark-yellow precipitate that formed was filtered and reprecipitated from pyridine, yielding 2.02 g. (91.3%) of light-yellow polymer.

Poly[1,1′-diphenyl-3,3′-*p*-phenylene-5,5′-perfluoropropyldi-1,2,4-triazole] (VIII). A mixture of 0.3775 g. (0.0018 mole) of perfluoroglutaronitrile (III), 0.7160 g. (0.0018 mole) of terephthaloylphenylhydrazide chloride (Ia), and 3 ml. of triethylamine in 15 ml. of anhydrous tetrahydrofuran was sealed in a glass tube. The tube was placed in a Parr bomb and heated to 65°C. for 24 hr. The reaction mixture was filtered, to remove triethylamine hydrochloride, and the filtrate was slowly added to methanol. The brown precipitate that formed was filtered and reprecipitated from tetrahydrofuran, yielding 0.719 g. (75.4%) of dark-brown polymer, which did not melt at 300°C.

Poly[5,5′-*p*-phenylene)-2,2′-spirobis-(3-phenyl-2,3-dihydro-1,3,4-thiadiazole)] (IX). A mixture of 1.1498 g. (0.003 mole) of terephthaloylphenylhydrazide chloride (Ib), 0.2284 g. (0.003 mole) of carbon disulfide, and 3 ml. of triethylamine in 20 ml. of anhydrous tetrahydrofuran was sealed in a glass tube and allowed to stand overnight at room temperature. The tube was then placed in a Parr bomb and heated to 80°C. for 12 hr. The reaction mixture was filtered, to remove triethylamine hydrochloride, evaporated to low volume, and slowly added to methanol. The dark-yellow precipitate that formed was filtered and reprecipitated from tetrahydrofuran, yielding 0.896 g. (77.3%) of yellow polymer.

Poly[1,4-diphenyl-3,6-*m*-phenylene-1,4-dihydro-1,2,4,5-tetrazine] (Xa). To a solution of 0.7664 g. (0.002 mole) of isophthaloylphenylhydrazide chloride (Ia) in 10 ml. of anhydrous tetrahydrofuran at the reflux temperature was added 3 ml. of triethylamine. After the addition was complete, the mixture was heated under reflux for 24 hr. The solution was then evaporated to low volume and slowly added to 50 ml. of methanol. The dark-brown precipitate that formed was filtered and reprecipitated from pyridine, yielding 0.567 g. (91.3%) of light-brown polymer.

Poly[1,4-diphenyl-3,6-*p*-phenylene-1,4-dihydro-1,2,4,5-tetrazine] (Xb). The polymerization of terephthaloylphenylhydrazide chloride (Ib) was carried out as described for the *m* isomer to afford 0.586 g. (94.4%) of dark-brown polymer.

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Polymers from 1,3-Dipole Addition Reactions: The Sydnone Dipole*

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Synopsis

An investigation of the suitability of certain 1,3 dipole addition reactions as polymerization reactions was carried out. Reaction of *p*-phenylene-3,3′-disydnone and *N*,*N*′-hexamethylenedisydnone with the dipolarophiles *m*- and *p*-diethynylbenzene, *m*-divinylbenzene, and *p*-benzoquinone gave moderate molecular weight polymers containing pyrazole or pyrazoline units along the polymer backbone. The polymers are crystalline and have inherent viscosities of 0.4–0.6. The thermogravimetric analyses of the finely powdered polypyrazoles showed breaks near 420°C. in air and 500°C. in nitrogen atmospheres.

INTRODUCTION

In a preceding paper[1] the suitability of cyclo-addition reactions, particularly the 1,3-dipolar cyclo-addition, as a mode of polymerization was discussed, and the results of the investigation of the nitrilimine dipole addition polymerization was reported. Many of the dipole additions gave high yields,[2,3] and the necessary difunctional monomers can be prepared.

The object of this investigation was to study the dipole addition polymerization of sydnone monomers and obtain thermally stable polymers containing pyrazole units as a result of the addition of the sydnone dipoles to acetylene dipolarophiles.

DISCUSSION

Sydnones are generally prepared by the dehydration of *N*-nitroso-α-amino acids.[4,5] The addition of acetylenes to sydnones produces pyrazoles, and the reaction is facilitated by the presence of polar groups attached to the acetylene.[6,7] The reaction presumably goes through an intermediate Diels-Alder type of adduct with a subsequent loss of carbon dioxide. The cycloadditions afford predominantly one isomer when the possibility of several isomers exist, and the direction of addition usually can be predicted from a consideration of sites in both the dipole and dipolarophile.

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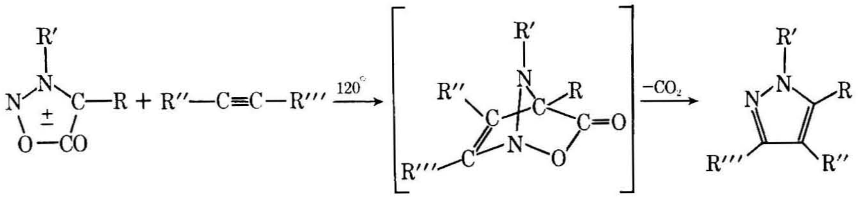
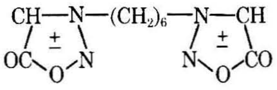
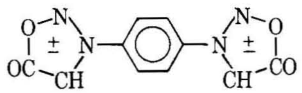


Monomers and Model Compounds

Several bissydnones have been synthesized. Both monomers (1a)[8] and (1b)[9] have been synthesized from hexamethylenediamine and *p*-phenylenediamine as starting materials, respectively, by conventional amino acid syntheses followed by the sydnone-forming reactions.



(1a)

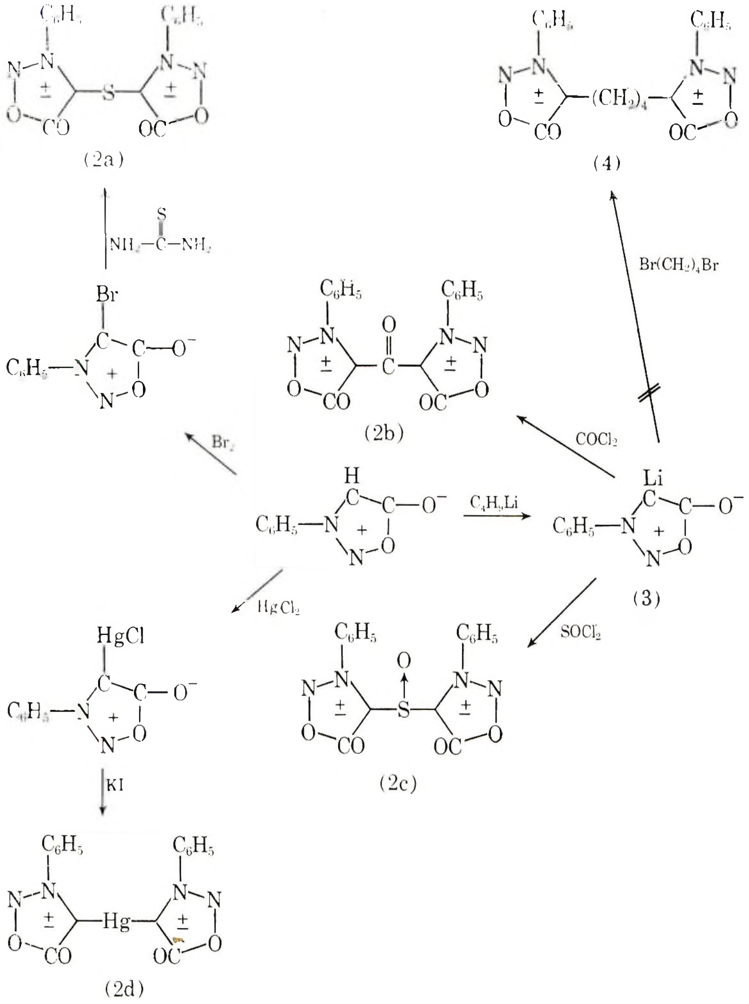


(1b)

The bromination of 3-phenylsydnone to 4-bromo-3-phenylsydnone and the treatment of this intermediate with several reagents, giving bissydnone products, have been reported.[10] The reaction of the brominated sydnone with thiourea afforded the di-4-(3-phenylsydnone)sulfide (2a);[10] while reaction with butyllithium to give the 4-lithio derivative (3) or the direct formation of (3) by reaction of butyllithium with phenylsydnone,[11] followed by a reaction with phosgene, yielded the di-4-(3-phenylsydnone)ketone (2b).[12] The disydnone 4,4′-bis(3-phenylsydnonyl)sulfoxide (2c) was also prepared from the lithium salt. The preparation of the disydnone 4,4′-mercuri-bis-3-phenylsydnone (2d) was carried out according to the described method.[13]

Since it was possible that electron-withdrawing groups, such as the carbonyl groups on the sydnone ring, might affect the 1,3-dipolar addition, an attempt was made to prepare a similar bissydnone without these groups. Unfortunately, the reaction of the lithium salt of 3-phenylsydnone with 1,4-dibromobutane did not give the expected product (4).

The synthesis of 3-phenylsydnone-4-carboxylic acid (5) was effected by the direct lithiation of 3-phenylsydnone and the subsequent carbonation of this intermediate according to the known procedure.[11] This acid was converted to 3-phenylsydnone-4-carbonyl chloride (6) as described.[14] From this derivative a series of bissydnones was prepared through the reactions of the acid chloride with diamines and diols. Reaction of the acid chloride (6) with 1,6-hexanediamine, *m*-phenylenediamine, *p,p*′-methylenedianiline, and hydroquinone gave the following respective bissydnones: *N,N*′-hexamethylene-bis(3-phenylsydnone-4-carboxamide) (2e), *N,N*′-*m*-phenylene-bis(3-phenylsydnone-4-carboxamide) (2f), *N,N*′-*p*-diphenylenemethane-bis(3-phenylsydnone-4-carboxamide) (2g), and *p*-phenylene-bis-(3-phenylsydnone-4-carboxalate) (2h).

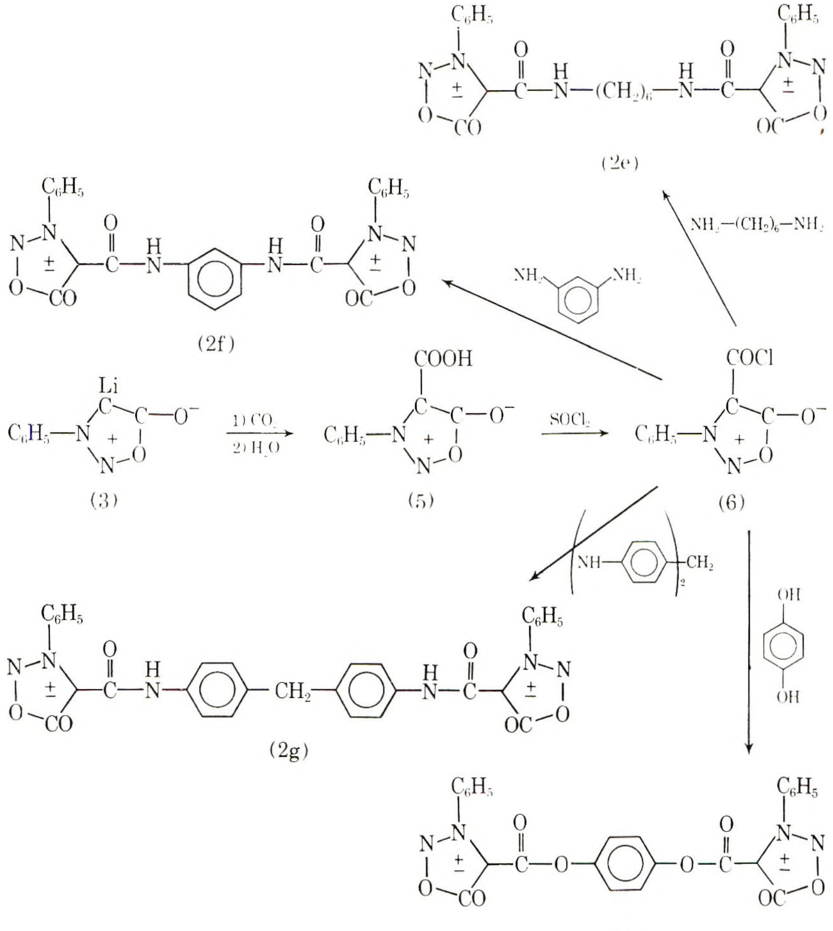


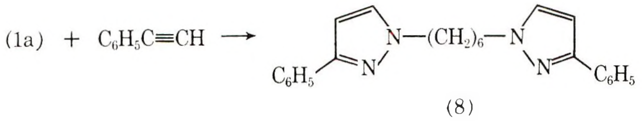
Two bisdipolarophiles, *m*- and *p*-diethynylbenzene, were synthesized by bromination of *m*- and *p*-divinylbenzene followed by the elimination reactions of the respective tetrabromides.[15] The monomer *p*-diethynylbenzene (7b) was prepared from a commercial mixture of *m*- and *p*-divinylbenzene, and *m*-diethynylbenzene (7a) was prepared from pure *m*-divinylbenzene.

$$HC{\equiv}C{-}C_6H_4{-}C{\equiv}CH \qquad \begin{array}{ll} \text{a.} & m\text{-}C_6H_4 \\ \text{b.} & p\text{-}C_6H_4 \end{array}$$

(7)

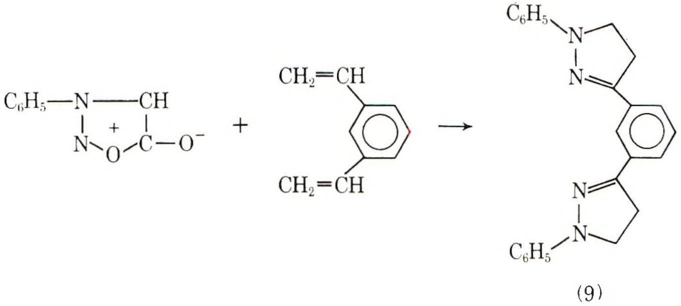
The reactions of (1b) and 3-phenylsydnone[16] with phenylacetylene and *m*- or *p*-diethynylbenzene, respectively, giving the phenyl-substituted pyrazoles, were studied to determine the optimum reaction conditions and have been reported elsewhere.[17] In addition, the analogous reaction of (1a) with phenylacetylene was carried out to afford another pyrazole model compound in a low yield (37%).





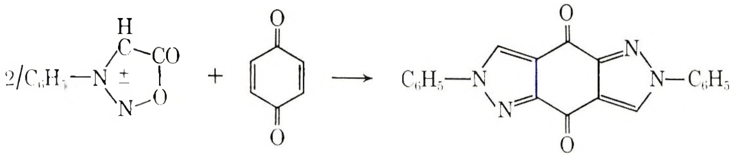
(8)

The reaction of *m*-divinylbenzene with 3-phenylsydnone in refluxing xylene afforded a 95% yield of 1,1′-diphenyl-3,3′-*m*-phenylene-Δ^2-pyrazoline (9).



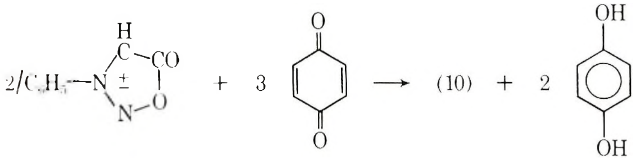
(9)

The compound 2,4,6,8-tetrahydro-4,8-dioxo-2,6-diphenylpyrazolo-[3,4-f]indazole (10) was prepared by the reaction of 3-phenylsydnone with *p*-benzoquinone. A much higher yield than that reported[18] was obtained by the use of nitrobenzene as the reaction solvent. An oxidation takes place; the loss of four atoms of hydrogen is required, and nitrobenzene or quinone may serve as the oxidizing agent. If nitrobenzene is used, then the stoichiometry of the reaction is a simple 2:1 molar balance, as illustrated:



(10)

However, when nitrobenzene is not present, then the stoichiometry of the reaction is a 2:3 ratio as shown:



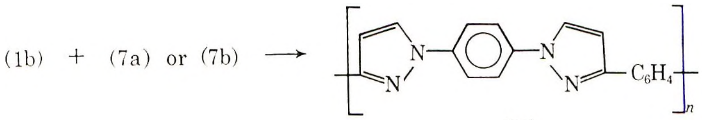
If the reaction is run in air, then air oxidation could take place, reoxidizing the hydroquinone back to quinone, and the statements above might not be entirely valid. Nevertheless, since most polymerizations are run in an inert atmosphere such as nitrogen, a polymerization of this type could not take place unless the monomer balance illustrated above followed.

Reactions of the sydnones (2a) to (2h) with phenylacetylene were investigated. Although the same conditions were employed as those used in the reactions of 3-phenylsydnone and *p*-phenylene-3,3′-disydnone with phenylacetylene [with an exception of (2d), which produced free mercury], only starting compound was recovered, and no evolution of carbon dioxide was noticed. It appears that the electronic effect of the different groups such as carbonyl, sulfur, or amido might have hindered the 1,3-dipolar addition. With the mercury compound it is quite probable that decomposition of the bissydnone took place before the reaction.

Polymers

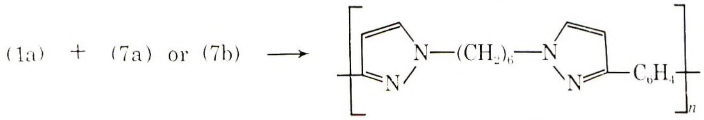
The polymerization reactions of the sydnones with the diacetylenes afforded polypyrazoles in variable conversions. The reactions with *p*-phenylene-3,3′-disydnone (1b) and the diacetylenes gave nearly quantitative yields of polypyrazoles. However, the reactions with *N*,*N*′-hexamethylene-disydnone and the diacetylenes afforded the polymers in low yields. This is not unexpected, considering the low yield of (8) obtained from the reaction of (1a) with phenylacetylene. Polymers (11a) and

(11b), whose spectra were nearly superimposable on those of the corresponding model compounds, were obtained when the reactions were carried out in nitrobenzene at 190°C. Polymers (12a) and (12b), whose spectra were also very similar to those of the corresponding model compound, were prepared in tetralin at 175°C.



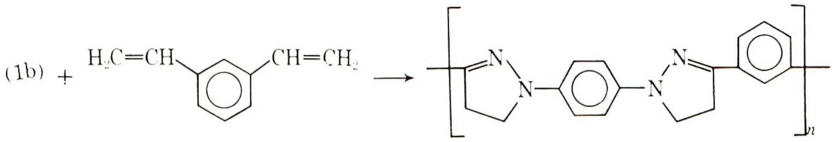
(11)

a. m-C_6H_4
b. p-C_6H_4

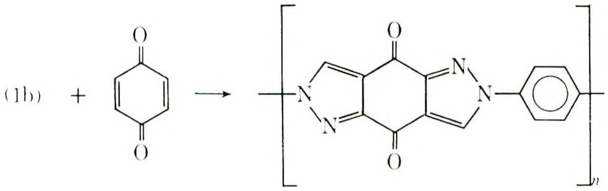


(12)

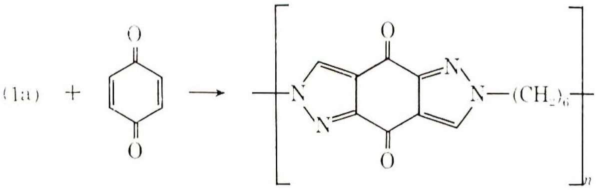
a. m-C_6H_4
b. p-C_6H_4



(13)



(14)



(15)

These polymers were only slightly soluble in such polar solvents as dimethylformamide, dimethylacetamide, and hexamethylphosphoramide. Inherent viscosities only as high as 0.6 could be obtained (Table I). The low molecular weights could be a consequence of the precipitation of the polymer before it reached a higher molecular weight, but when the reaction was

TABLE I
Polymerization of Bissydnones

Polymer No.	Convsn., %	$[\eta]$[a]	TGA temp.,[b] °C. Air	N_2
(11a)	90	0.35	430	520
(11b)	90	0.40	400	510
(12a)	30	0.10	350	420
(12b)	45	0.40	390	410
(13)	50	0.11	410	485
(14)	63	0.60	410	500
(15)	50	0.12	300	400

[a] Inherent viscosities were determined in hexamethylphosphoramide at concentrations of 0.2 g. per 100 ml. at 25°C.

[b] The temperature at which the polymer began to decompose rapidly (break in curve). Thermogravimetric analyses were carried out at a heating rate of 5°/min. on a du Pont 950 TGA.

carried out in a sealed tube at 250°C. under such conditions that the polymer did not precipitate, no increase in molecular weight was noticed.

The polymerization of (1b) with *m*-divinylbenzene in nitrobenzene gave polymer (13), containing the pyrazoline unit. The spectra of the model compound (9) and the polymer were nearly superimposable.

The polymerization of (1b) with *p*-benzoquinone in nitrobenzene at 190°C. gave a 63% yield of poly[2,4,6,8-tetrahydro-4,8-dioxo-2,6-*p*-phenylpyrazolo(3,4-f) indazole] (14). Unlike the polymers (11a) and (11b), polymer (14) remained in solution. An inherent viscosity of 0.6 was obtained for this polymer (Table I). The polymerization of *N*,*N'*-

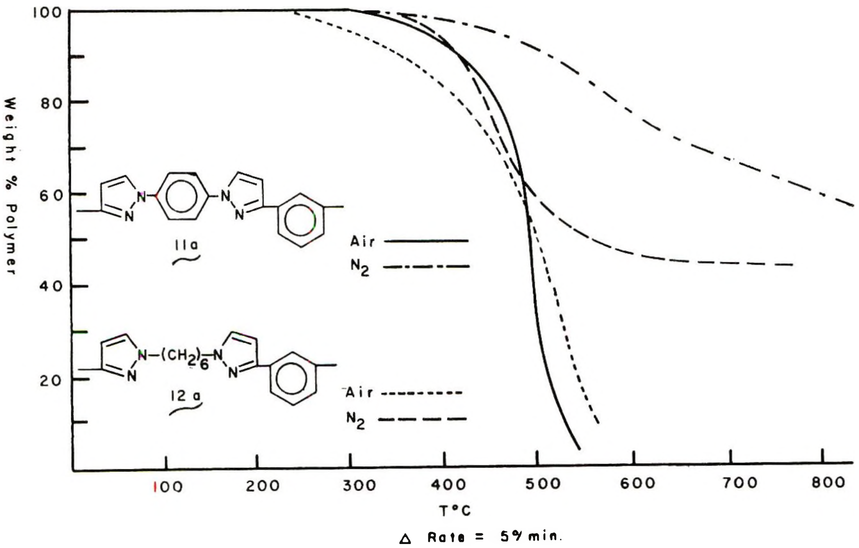


Fig. 1. Thermal gravimetric analyses of polypyrazoles.

hexamethylene-bissyndone and *p*-benzoquinone was carried out to yield poly[2,4,6,8-tetrahydro-4,8-dioxo-2,6-hexamethylenepyrazolo(3,4-f)indazole] (15) in a 40% yield. An inherent viscosity of 0.12 was obtained (Table I). The infrared spectra of polymers (14) and (15) showed the characteristic maxima displayed by the corresponding model compound (10).

Thermogravimetric analyses (Table I, Fig. 1) of polymers (11a), (11b), (13), and (14) showed breaks near 420°C. in air and 500°C. in nitrogen. Polymers (12a), (12b) and (15) showed breaks near 400°C. in air and 420°C. in nitrogen.

X-ray powder patterns showed the polypyrazoles (11a), (11b), and (12b) to be highly crystalline; however, polymer (12a) showed very little crystallinity. Differential thermal analyses of the polymers shows (12b) as having a crystalline transition temperature at 155°C. Polymers (11a), (11b), and (12a) show no crystalline transition; presumably these lie above the decomposition temperature. Second-order transition temperatures were found for (11a) at 75 and 80°C. (11b) at 75 and 100°C., (12a) at 70°C., and (12b) at 55 and 80°C. Polymers containing the CH_2 link show slightly lower second-order transition temperatures; polymers containing the *p*-phenylene link display two second-order transitions.

EXPERIMENTAL

Monomers

***N,N′*-Hexamethylenebissydnone** (1a). This compound was prepared according to the known procedure[8] yielding product; m.p. 115°C. (lit.[8] 114–116°C.

***p*-Phenylene-3,3′-disydnone** (1b). This monomer was prepared by the dehydration of *N,N′*-dinitroso-*p*-phenylenediglycine[9] and was recrystallized from water; m.p. 255–256°C.

4,4′-Bis(3-phenylsydnonyl)sulfide (2a). The reaction of thiourea with either 3-phenyl-4-bromosydnone or 3-phenyl-4-iodosydnone gave (2a),[10] which was recrystallized from acetone and ethanol; m.p. 164–165°C. (lit.[10] 165°).

4,4′-Bis(3-phenylsydnonyl)ketone (2b). This reaction was carried out as described[12] for yielding product; m.p. 229–230°C. (lit.[12] 230°).

4,4′-Bis(3-phenylsydnonyl)sulfoxide (2c). A solution of 22.7 ml. of *n*-butyllithium (22.2% in hexane) was added dropwise to a suspension of 3-phenylsydnone (6.72 g., 0.0415 mole) in 150 ml. of ether at −20°C. in a nitrogen atmosphere. After a 1 hr. stirring, 2.52 g. (0.02 mole) of thionyl chloride in 15 ml. of benzene was added dropwise to the solution at 0°C.

Finally the mixture was poured into cold water, and the product was filtered and recrystallized from tetrahydrofuran to give light-yellow crystals; m.p. 155–156°C.

ANAL. Calcd. for $C_{16}H_{10}N_4O_5S$ (%): C 51.89, H 2.72, N 15.12. Found (%): C 52.16, H 2.77, N 15.50.

4,4′-Mercuribis-3-phenylsydnone (2d). This compound was prepared as described for giving a product; m.p. 279–280°C. (lit.:[13] 280°C.)

***N,N′*-Hexamethylenebis(3-phenylsydnone-4-carboxamide)** (2e). To a solution of 1.12 g. (0.005 mole) of 3-phenylsydnone-4-carbonyl chloride in 20 ml. of benzene at the reflux temperature was added 0.290 g. (0.0025 mole) of 1,6-hexanediamine and 1 ml. of triethylamine dissolved in 20 ml. of benzene. After the addition was complete, the mixture was heated under reflux for 1 hr. The white precipitate was filtered, washed well with water, and then recrystallized from alcohol to afford 0.861 g. (70%) of white product; m.p. 209–210°C.

ANAL. Calcd. for $C_{24}H_{24}N_6O_6$ (%): C 58.53, H 4.91, N 17.06. Found (%): C 58.77, H 4.91, N 17.14.

***N,N′*-*m*-Phenylenebis(3-phenylsydnone-4-carboxamide)** (2f). The reaction was carried out exactly as described for (2e), except that *m*-phenylenediamine was substituted for 1,6-hexanediamine. The yellow precipitate was recrystallized from 2-methoxyethanol to give 0.79 g. (65%) of yellow product; m.p. 295–296°C.

ANAL. Calcd. for $C_{24}H_{16}N_6O_6$ (%): C 59.51, H 3.33, N 17.34. Found (%): C 59.85, H 3.45, N 17.07.

***N,N′*-*p*-Diphenylenemethanebis(3-phenylsydnone-4-carboxamide)** (2g). The reaction was carried out exactly as described for (2e), except that *p,p′*-methylenedianiline was substituted for 1,6-hexanediamine. The yellow product was filtered and recrystallized from 2-methoxyethanol to give 1.05 g. (73%) of light-yellow product; m.p. 256–257°C.

ANAL. Calcd. for $C_{31}H_{22}N_6O_6$ (%): C 64.81, H 3.86, N 14.62. Found (%): C 64.87, H 3.98, N 14.69.

***p*-Phenylenebis(3-phenylsydnone-4-carboxalate)** (2h). To a solution of 0.44 g. (0.004 mole) of hydroquinone in 15 ml. of pyridine at 0°C. was added 2.24 g. (0.010 mole) of 3-phenylsydnone-4-carbonyl chloride in small portions over a period of 1 hr. After the addition was complete, the mixture was heated to the reflux temperature for 1 hr. The white precipitate was filtered and recrystallized from ethanol to yield 1.24 g. (64%) of white product; m.p. 119–120°C.

ANAL. Calcd. for $C_{24}H_{14}N_4O_8$ (%): C 59.27, H 2.90, N 11.51. Found (%): C 59.16, H 2.84, N 11.46.

3-Phenyl-4-lithiosydnone (3). 3-Phenylsydnone was directly converted into 3-phenyl-4-lithiosydnone according to the described procedure,[11] and was assayed as the carboxylic acid.

Reaction of Lithium Salt of 3-Phenylsydnone with 1,4-Dibromobutane. A solution of 22.7 ml. of *n*-butyllithium (22.2% in hexane) was added dropwise to a suspension of 3-phenylsydnone 6.72 g. (0.0415 mole) in 150 ml. of ether at −20°C. in a nitrogen atmosphere. After a 1 hr. stirring 4.57 g. (0.0207 mole) of 1,4-dibromobutane was added dropwise to the solution at 0°C. The mixture was then poured into cold water; the only product isolated was 3-phenylsydnone.

3-Phenylsydnone-4-carboxylic acid (5). The synthesis of this compound was effected via the direct lithiation of 3-phenylsydnone and the subsequent carbonation of this intermediate;[11] m.p. 192°C. (lit.:[11] 190–191°C.).

3-Phenylsydnone-4-carbonyl chloride (6). This compound was prepared as described;[14] m.p. 133°C. (lit.:[14] 133–134°C.).

m-**Diethynlbenzene** (7a). This compound was prepared by the bromination of pure *m*-divinylbenzene and the subsequent dehydrobromination of this intermediate according to the known procedure[15] (pure *m*-divinylbenzene was obtained from Labofina, Bruxelles 12, Belgium). The monomer was freshly distilled prior to use.

p-**Diethynylbenzene** (7b). This compound was prepared[15] from a divinylbenzene mixture.

Model Compounds

3,3′-Diphenyl-1,1′-hexamethylenedipyrazole (8). To a solution of 0.508 g. (0.002 mole) of *N*,*N*′-hexamethylene-bissydnone (1a) in 25 ml. of xylene was added 5 ml. of phenylacetylene. The mixture was heated at 130°C. for 20 hr. and allowed to cool. The yellow crystals that formed were removed and recrystallized from acetone, giving 0.244 g. (33%) of yellow product; m.p. 148 to 149°C.

ANAL. Calcd. for $C_{24}H_{26}N_4$ (%): C 76.23, H 7.08, N 15.12. Found (%): C 76.01, H 6.82, N 15.36.

1,1′-Diphenyl-3,3′-m-phenylene-Δ^2-pyrazoline (9). To a solution of 1.62 g. (0.010 mole) of 3-phenylsydnone in 10 ml. of *o*-xylene was added 0.65 g. (0.005 mole) of *m*-divinylbenzene. The mixture was heated at the reflux temperature for 12 hr. After it was cooled, yellow crystals formed, which were removed and recrystallized from pyridine. There was obtained 1.75 g. (95%) of bright-yellow product; m.p. 208–209°C.

ANAL. Calcd. for $C_{24}H_{22}N_4$ (%): C 78.66, H 6.05, N 15.29. Found (%): C 78.69, H 5.89, N 15.56.

2,4,6,8-Tetrahydro-4,8-dioxo-2,6-diphenylpyrazolo[3,4-f] indazole[18] (10). To a solution of 0.81 g. (0.005 mole) of 3-phenylsydnone in 25 ml. of nitrobenzene was added 0.270 g. (0.0025 mole) of *p*-benzoquinone. The mixture was heated at 150°C. for 24 hr. The solvent was evaporated to a low volume and the mixture allowed to cool. The light-brown precipitate that formed was filtered and recrystallized from pyridine, giving 0.230g. (27%) of pure product; m.p. 335°C.

ANAL. Calcd. for $C_{20}H_{12}N_4O_2$ (%): C 70.58, H 3.55, N 16.46. Found (%): C 70.60, H 3.81, N 16.28.

Polymers

Poly[1,1′-*p*-phenylene-3,3′-*m*-phenylenedipyrazole] (11a). To a solution of 1.95 g. (0.0079 mole) of *p*-phenylene-3,3′-disydnone (16) in 50 ml. of nitrobenzene was added 1.0 g. (0.0079 mole) of *m*-diethynylbenzene (7a). The mixture was heated at 190°C. for 24 hr. The solvent was evaporated to a low volume, and the mixture was poured into 200 ml. of methanol. The yellow precipitate was filtered, extracted with benzene for 20 hr., and dried, giving 0.94 g. (90%) of product.

Anal. Calcd. for $(C_{18}H_{12}N_4)_n$ (%): C 76.04, H 4.25, N 19.71. Found (%): C 74.12, H 4.34, N 19.14.

Poly[1,1′-*p*-phenylene-3,3′-*p*-phenylenedipyrazole] (11b). The polymerization was carried out exactly as described for (11a), except that *p*-diethynylbenzene (7b) was substituted for the *m* isomer. The product polymer was extracted with benzene for 10 hr., and dried, giving 0.94 g. (90%) of yellow product.

Anal. Calcd. for $(C_{18}H_{12}N_4)_n$ (%): C 76.04, H 4.25, N 19.71. Found (%): C 75.97, H 4.33, N 17.99.

Poly[1,1′-hexamethylene-3,3′-*m*-phenylenedipyrazole] (12a). A solution of 1.016 g. (0.004 mole) of *N*,*N*′-hexamethylene-bissydnone and 0.504 g. (0.004 mole) of *m*-diethynylbenzene in 5 ml. of tetralin was sealed in a glass polymerization tube under reduced pressure in the absence of oxygen by subjecting the monomers and solvent to several freeze–thaw–evacuate cycles at liquid-nitrogen temperatures. The tube was placed in a Parr bomb, which also contained tetralin, to equalize external and internal pressures, and heated to 175°C. for 24 hr. The tube was opened, and the solid polymer was removed by filtration and extracted with benzene. The filtrate, which was evaporated to a low volume and poured into methanol, did not give any more product. The light-brown polymer weighed 0.35 g. (30%).

Anal. Calcd. for $(C_{18}H_{20}N_4)_n$ (%): C 73.95, H 6.90, N 19.16. Found (%): C 74.05, H 6.60, N 18.96.

Poly[1,1′-hexamethylene-3,3′-*p*-phenylenedipyrazole] (12b). A solution of 1.016 g. (0.004 mole) of *N*,*N*′-hexamethylene-bissydnone and 0.504 g. (0.004 mole) of *p*-diethynylbenzene in 5 ml. of tetralin was sealed in a polymerization tube and polymerized as described for the preparation of (12a). The light-brown precipitate was filtered, extracted with benzene for 20 hr., and dried, giving 0.53 g. (45%) of product.

Anal. Calcd. for $(C_{18}H_{20}N_4)_n$ (%): C 73.95, H 6.90, N 19.16. Found (%): C 73.50, H 6.42, N 18.82.

Poly[1,1′-*p*-phenylene-3,3′-*m*-phenylenedi-Δ^2-pyrazoline] (13). To a solution of 0.492 g. (0.002 mole) of *p*-phenylene-3,3′-disydnone in 25 ml. nitrobenzene was added 0.260 g. (0.002 mole) of *m*-divinylbenzene. The mixture was heated at 180°C. for 24 hr. The solvent was evaporated to a low volume, and the mixture was poured into 200 ml. of methanol. The light-brown solid was filtered, extracted with benzene for 10 hr., and dried, giving 0.28 g. (50%) of light-brown product.

Anal. Calcd. for $(C_{18}H_{16}N_4)_n$ (%): C 74.97, H 5.59, N 19.43. Found (%): C 75.21, H 4.96, N 18.60.

Poly[2,4,6,8-tetrahydro-4,8-dioxo-2,6-*p*-phenylene-pyrazolo[3,4-f]indazole] (14). To a solution of 0.47 g. (0.0019 mole) of *p*-phenylene-3,3′-disydnone in 25 ml. of nitrobenzene was added 0.205 g. (0.0019 mole) of *p*-benzoquinone. The mixture was heated at 190°C. for 24 hr. The solvent was evaporated to a low volume, and the mixture was poured into 200 ml. of methanol. The dark-brown precipitate was filtered, extracted with benzene for 20 hr. and dried to afford 0.29 g. (63.2%) of product.

ANAL. Calcd. for $(C_{14}H_6N_4O_2)_n$ (%): C 64.12, H 2.29. Found (%): C 62.54, H 1.83.

Poly[2,4,6,8-tetrahydro-4,8-dioxo-2,6-hexamethylenepyrazolo-[3,4-f)indazole] (15). A solution of 0.508 g. (0.002 mole) of *N,N'*-hexamethylenebissydnone and 0.216 g. (0.002 mole) of *p*-benzoquinone in 15 ml. of nitrobenzene was sealed in a polymerization tube and polymerized as described for the preparation of (12a). The tube was opened, the solvent was evaporated to a low volume, and the mixture was poured into 100 ml. of methanol. The dark-brown precipitate was filtered, extracted with benzene for 15 hr., and dried, giving 0.246 g. (50%) of product.

ANAL. Calcd. for $(C_{14}H_{14}N_4O_2)_n$ (%): C 62.22, H 5.22. Found (%): C 63.63, H 4.93.

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Polycondensation Equilibrium and the Kinetics of the Catalyzed Transesterification in the Formation of Polyethylene Terephthalate

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Synopsis

The polycondensation equilibrium constant for bis(β-hydroxyethyl) terephthalate was found to be 0.50. By means of this value for determining the relative reactivity of two kinds of hydroxyl groups, the kinetic data were found to fit a third-order reaction for the transesterification: one order each with respect to hydroxyl group, methoxy group, and catalyst. An order with respect to hydroxyl group, which had previously been in doubt, was proved in a series of experiments in which the concentration of ethylene glycol was varied. Third-order rate constants were determined for the reactions catalyzed by lead, zinc, and calcium salts, and the activation energies were found to be 12.5, 15.0, and 14.5 kcal./mole, respectively. The results are consistent with the author's theory of aromatic transition states and are difficult to explain on the basis of ionic theories of reaction mechanism.

INTRODUCTION

In the classical two-step method of preparing polyethylene terephthalate (PET) both steps involve a transesterification reaction. The kinetics of the catalytic transesterification has received the attention of several investigators, but little agreement has been reached even as to the order of the reaction. Skwarski[1] first reported on the polycondensation kinetics and found the catalyzed reaction to be third-order, Griehl and Schnock[2] investigated the kinetics of both steps, the "precondensation" and polycondensation, and reported each reaction to be first-order (with respect to ester group alone), although they showed also that the rate of reaction was proportional to catalyst concentration. Peebles and Wagner[3] in a kinetic investigation of the transesterification of dimethyl terephthalate (DMT) by ethylene glycol could not decide on the basis of their data whether the reaction was first-order or second-order (disregarding the order with respect to catalyst concentration).

The interpretation of the kinetics of the first-stage transesterification process is complicated by the multiplicity of reactions occurring simultaneously and the uncertainties in the relative reactivities of similar groups

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on different, small molecules. For example, Peebles and Wagner[3] in their interpretation of this process as two consecutive second-order reactions assumed equal hydroxyl group reactivity for the hydroxyl group on ethylene glycol and on half-esterified glycol and were thereby led to the rather implausible deduction that the methoxy group on half-transesterified DMT is about three times as reactive as a methoxy group on DMT. Challa[14] has shown by equilibrium measurements that the two methoxy groups in question are equally reactive, as one would expect. Since the relative reactivity of a hydroxyl group on free glycol and half-esterified glycol is related to the general polycondensation constant of the system, the present work included an investigation of the polycondensation equilibrium besides the kinetic investigation of the transesterification reactions.

When one examines the literature on the value of the polycondensation constant for the PET system there is found again a considerable amount of confusion. Griehl and Forster[5] first reported a fairly constant average value of 4.9 at 280°C. in systems with average degrees of polymerization of 28–107. Koepp and Werner[6] gave the average value 0.75 at 223°C. and found it to be fairly constant over the $\bar{P}_n$ range of 1.8–15.6. Challa[7] gave the average value 0.49 as insensitive to temperature in the temperature range 195–282°C. and at low degrees of polymerization but claimed a marked increase to about 1.2 with increasing degree of polymerization. On the basis of these data Challa challenged the applicability of the Flory principle of equal reactivity in the PET system. By strict application of the principle of equal reactivity (extended to monomer and condensate) the equilibrium constant should, of course, be unity, as has been reported for the polycondensation equilibrium in the related system polyethylene isophthalate.[8]

The present experimental work was carried out as part of a program of studied for obtaining basic information on the equilibrium and kinetics of the reactions involved in the formation of PET and to elucidate the manner in which various catalysts operate. The present results explain many of the discrepancies in the literature. It is believed, further, that significant new concepts have been derived concerning the mechanism of these reactions.

THE POLYCONDENSATION EQUILIBRIUM

The equilibrium studies were made during the earlier kinetic runs after completion of the first stage but are here considered first because of the need of the relative reactivities for the interpretation of the kinetic data. The results of these studies are presented in Table I.

Early in the experimental work it was found that PET systems catalyzed by zinc salts did not reach a stable glycol equilibrium at the end of the first stage but continued to condense slowly with the evolution of water and acetaldehyde. When lead oxide was used as a catalyst (runs 11, 14, 15, and 16), a stable glycol equilibrium was attained, and it was found that the

TABLE I

Glycol Equilibrium Data

Run No.	t, °C.	p, mm.	Glycol removed,[a] at 0°C.	g	p/p_g	K[b]	K[c]
9	230.9	760	2.2		0.391		0.50
10	222.4	602	2.4		0.387		0.50
11	179.2	162	1.9	0.383	0.373	0.46	0.43
		0	11.9				
14	199.2	308	4.0	0.374	0.383	0.52	0.56
		0	12.7				
15	199.2	315	2.9	0.407	0.392	0.61	0.54
		300	4.7	0.359	0.373		
		180	8.5	0.229	0.224		
		0	12.8	0.000			
16	228.2	764	1.5		0.419		0.59
	249.0	764	11.8		0.254		0.47
	278.5	764	18.7		0.136		0.42

[a] Volume corrected as described under "Experimental."

[b] K determined from measured glycol in experiments in which the lead oxide catalyst was poisoned.

[c] K determined by applying Raoult's law.

equilibrium could be frozen by deactivating the catalyst by reaction with hydrogen sulfide. Subsequently the free glycol could be quantitatively removed and determined, as was done in runs 11, 14, and 15. The removal in run 15 was carried out in stages so as to make feasible a determination of the conformity to Raoult's law. The equilibrium glycol pressure could also be determined in the zinc-catalyzed systems, if carried out soon after termination of the first stage (runs 9 and 10).

The first-column K values in Table I were determined, from the amount of glycol removed after poisoning the catalyst, by making use of the equation

$$K = g[1 - r(1 - g)]/r(1 - g)^2 \tag{1}$$

where g is the mole fraction of glycol in the melt, and r is related to the overall composition of the system by $r = G/T - 1$, G being the total moles of glycol or glycol residue, and T being the moles of terephthalic acid residue Equation (1) is based on the principle of equal reactivity and can be readily identified with similar equations previously defined by Challa[7] (eq. 12, p. 113) and Koepp and Werner[6] (first eq., p. 86).

A comparison of values of g and p/p_g in Table I shows that glycol follows Raoult's law to within the experimental error of the results. The last column of K values were then calculated from mole fractions of glycol based on Raoult's law. Vapor pressures of pure glycol, p_g, were taken from the older literature, and the more recent values of Griehl and Forster[5] at higher and lower temperature all fitted approximately by an equation of the Juliusberger type:

$$\log_{10} p_g \text{ (mm.)} = 21.610 - 3729/T - 4.042 \log_{10} T \tag{2}$$

The average value of K was very nearly 0.50, and this was interpreted to mean that the hydroxyl group reactivity for each of the hydroxyl groups on free glycol is 2 times the hydroxyl group reactivity of the half-esterified glycol. This ratio of relative reactivities of hydroxyl group was used in the subsequent kinetic correlations.

THE TREATMENT FOR THE FIRST-STAGE KINETICS

All previous investigators agree that the ester interchange reaction has an order of unity with respect to ester group and that, in addition, the rate of reaction is proportional to catalyst concentration, as was confirmed roughly in preliminary experiments in the present work. Because of the relatively large volume changes in the PET system it was not only appropriate but also necessary to take into account the changing catalyst concentration, i.e., to treat the catalyst component as an ordinary reagent. The principal remaining question was then concerned with whether or not there existed an additional order with respect to hydroxyl group, i.e., whether the overall reaction was second-order or third-order. As will be seen in sequel, the reaction proved to be third-order, and the main treatment is that appropriate for a third-order reaction in a system of changing volume.

In the original kinetic interpretation of the results of this work it was assumed that the reactivity of all methyl ester groups was the same. This assumption was subsequently validated by the work of Challa. Thus, the ester interchange process of the first step was treated as two consecutive third-order reactions, as follows (where the order with respect to catalyst is absorbed in the k's):

$$R_m + g \xrightarrow{k_1} R_g + m \tag{3}$$

$$R_g + R_m \xrightarrow{k_2} R_gR + m \tag{4}$$

where g is moles of glycol, m is moles of methanol, and the quantities R_m, R_g and R_gR are equivalents of methyl ester, half-esterified glycol, and fully esterified glycol, respectively. The rate of formation of R_g is given by

$$dR_g/dt = k_1R_mg - k_2R_mR_g \tag{5}$$

and the rate of disappearance of g is given by

$$-dg/dt = k_1R_mg \tag{6}$$

Dividing eq. (5) by eq. (6) gives the differential equation

$$-dR_g/dg + (k_2/k_1)(R_g/g) = 1 \tag{7}$$

whose solution is

$$R_g = (g^{k_2/k_1}\,g_0^{1-k_2/k_1} - g)/(1 - k_2/k_1) \tag{8}$$

where g_0 is the moles of glycol initially present. Another relationship derivable from stoichiometry is

$$m_t = 2(g_0 - g) - R_g \tag{9}$$

where m_t = total moles of methanol formed. From the equilibrium measurements it was deduced that glycol —OH was twice as reactive as polymer —OH. This means that $k_2/k_1 = 0.25$, since 2 equivalents of glycol —OH are involved in reaction (3). Equation (8) then becomes

$$R_g = (g_0^{0.75}g^{0.25} - g)/0.75 \tag{10}$$

The general hydroxyl group reactivity for the system was defined by

$$[\mathrm{ROH}] = 2g + 1/2R_g \tag{11}$$

Thus, for the three experimental values of g_0, (0.75, 1.00, and 1.50) the three equations (9), (10), and (11) were used for calculating [ROH] as a function of m_t.

To obtain the total quantity m_t of methanol formed from the experimentally observed quantity m_r two corrections were applied, one for the amount of methanol remaining in solution and another for the small amount of glycol taken overhead with the methanol. The first correction was based on the assumption that both methanol and glycol formed perfect solutions in the melt. The result of the first correction gave m_s, where

$$m_s = m_r + NP/p_m - g(P_g/p_m) \tag{12}$$

N being the total moles in the melt, P being the total pressure, and p_m being the vapor pressure of pure methanol (in millimeters) derived from data in the International Critical Tables.[9] Approximate values of N and g were used in the correction terms. The approximate value of N was defined by

$$N = g_0 + [\mathrm{DMT}]_0 - m_r \tag{13}$$

and the approximate g was defined by eqs. (9) and (10), where m_r was substituted for m_t in eq. (9).

The second correction was usually quite small and was based on the assumption of uniform composition in the overhead methanol stream. The stoichiometric endpoint of the reaction was determined by plotting the experimental rate near the end of the reaction against m_s and extrapolating to zero rate to determine m_e; then m_t was determined by

$$m_t = 2[\mathrm{DMT}]_0 m_s/m_e \tag{14}$$

The quantity m_t as a function of time being obtained, plots were made of m_t versus time, and rates were determined by the slopes at suitable intervals. The third-order rate constants were obtained from

$$k_{\mathrm{III}} = (dm_t/dt)V^2/R_m[\mathrm{ROH}]C \tag{15}$$

where dm_t/dt is the rate of methanol generation in moles per second, V is the volume of the melt in liters, and C is the catalyst amount in moles.

The units for k are thus the standard units [g equivalents per square liter]$^{-2}$ [sec.]$^{-1}$, based on unit reactivity for the single glycol hydroxyl group and the catalyst considered monofunctional.

Second-order rate constants were calculated from

$$k_{\mathrm{II}} = (dm_t/dt)V/R_mC \tag{16}$$

where the units are [g equivalents per liter]$^{-1}$ per second.

THE EXPERIMENTAL DETERMINATION OF THE ORDER OF REACTION

The order of the transesterification reaction was first determined in runs in which a constant temperature was maintained over as long a portion of the run as practicable and the methanol was driven out by a progressive reduction in pressure. Both second-order and third-order rate constants were calculated, and the results of a typical run are shown in Table II. As may be seen from this table, the second-order rate constants show much more drift than the third-order ones. Similar drifts were shown in the second-order constants in two additional runs with the same composition but at different temperatures, and the third-order constants were 0.091 ± 0.004 for run 8 at 177.7°C. and 0.0339 ± 0.0013 for run 9 at 172.7°C.

TABLE II

Sample Kinetic Run with a Constant-Temperature Portion,
Run 10:97.1 g. of DMT, 62.1 g. of Glycol, and 0.0199 g. of $Zn(OAc)_2 \cdot 2H_2O$

Time, min.	t, °C.	P, mm.	CH_3OH, ml. at 0°C.	m_t, moles	Rate ($\times 10^2$) moles/min.	k_{II}	k_{III}
0	158.2	738	0	0.035	—	—	—
5	180.2	738	5.7	0.172	2.70	0.95	0.086
10	179.2	700	11.0	0.296	2.36	0.94	0.091
15	182.1	620	16.5	0.426	1.90	0.89	0.093
20	179.2	504	20.0	0.504	1.55	0.81	0.090
28	181.2	379	25.0	0.620	1.06	0.70	0.084
35	180.2	310	27.5	0.677	0.82	0.69	0.078
43	174.2	240	29.5	0.721	0.66	0.57	0.074
50	179.2	240	31.0	0.762	0.55	0.55	0.074
60	187.1	240	33.0	0.813	0.48	0.60	0.085
90	218.6	602	39.0	0.955	0.36	Av.:	.084
100	220.5	605	39.9	0.978	0.16		
115	222.4	603	40.6	0.994	0.04		

The third-order nature of the reaction was demonstrated more convincingly in a series of runs with constant amounts of DMT and lead oxide catalyst and a varying amount of glycol. The results of a typical run are presented in Table III, and the second-order and third-order rate constants are shown in Figures 1 and 2, respectively. In these runs both rate constants were found to drop appreciably toward the end of the run, and this

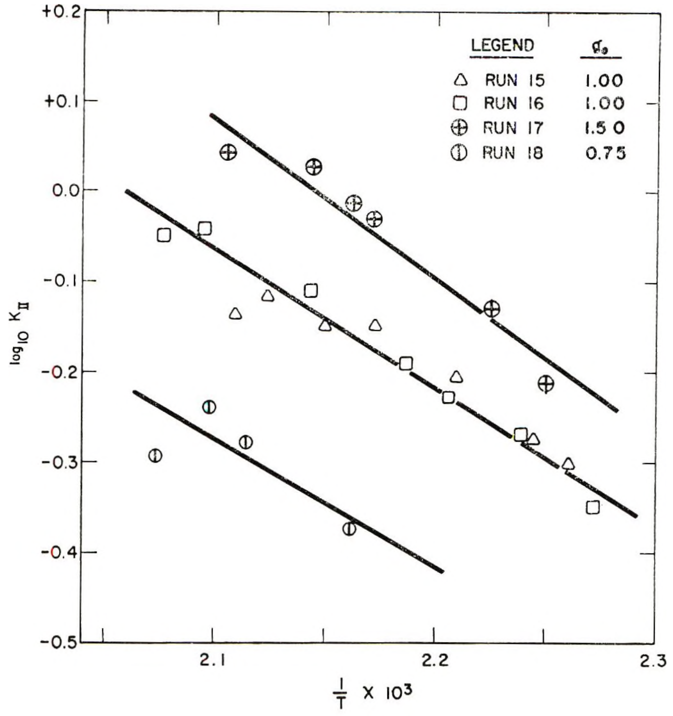


Fig. 1. Second-order rate constants with lead oxide catalyst.

drop was associated with the appearance of cloudiness in the melt (due to partial reduction of lead salts to metallic lead at high temperature). For this reason only those rate constants from data obtained before the appearance of cloudiness were considered. The results in Figure 1 clearly show a wide divergence in the second-order rate constants with changing glycol/DMT ratio, while the third-order rate constants for all the runs

TABLE III
Kinetics of a Typical Run with Lead Oxide Catalyst at Varying Temperatures: Run 16, 97.1 g. of DMT, 62.1 g. of glycol, and 0.0518 g. of PbO; P = 764 mm.

Time, min.	Temp., °C.	CH_3OH, ml. at 0°C.	m_t (corr.), moles	Rate, moles/min.	k_{II}, [eq./liter]$^{-1}$ sec.$^{-1}$	k_{III}, [eq./liter]$^{-2}$ sec.$^{-1}$
0	152.2	0	0.058	—	—	—
5	167.2	6.7	0.197	3.2	0.44	0.040
10	173.2	13.0	0.365	3.2	0.54	0.055
15	180.1	20.0	0.515	2.8	0.59	0.065
20	184.1	25.0	0.636	2.4	0.65	0.080
25	193.0	29.8	0.755	2.0	0.78	0.108
30	204	34.0	0.857	1.40	0.91	0.140
35	207.9	36.0	0.906	0.90	0.88	0.143
65	228.2	39.9	0.999	—	—	—

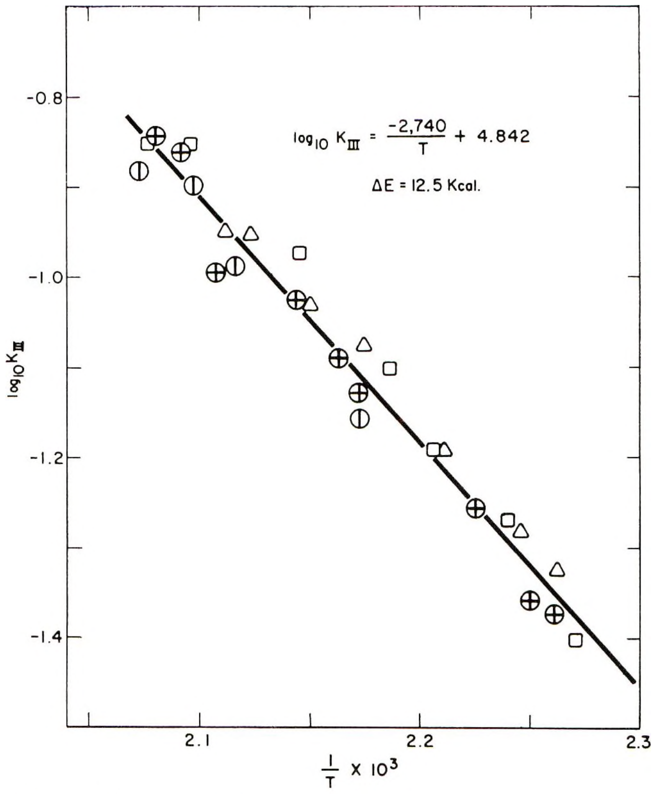


Fig. 2. Third-order rate constants with lead oxide catalysts.

superimpose to within experimental error, as seen in Figure 2. These data clearly show the reaction to be third-order. The third-order rate constants for lead oxide are given by the equation

$$\log_{10} k_{III} = -2740/T + 4.482 \tag{17}$$

and the activation energy was about 12.5 kcal./mole.

CATALYSIS BY ZINC, CALCIUM AND ANTIMONY SALTS

When the order of the tranesterification reaction and the techniques for determining rate constants were established, it was possible to examine the behavior of various catalyst systems. Although lead oxide as a catalyst was found to behave in a normal way and to yield consistent results with a reasonable activation energy (except at higher temperatures), it was anticipated that other catalyst systems might not be so well behaved. As will be seen in the sequel, they were not.

The experiments with zinc catalysts gave third-order rate constants that were not always consistent between different runs or even within the same run. In some runs a considerable drop in catalyst activity was noted near the end of ester interchange, even though no cloudiness developed. In

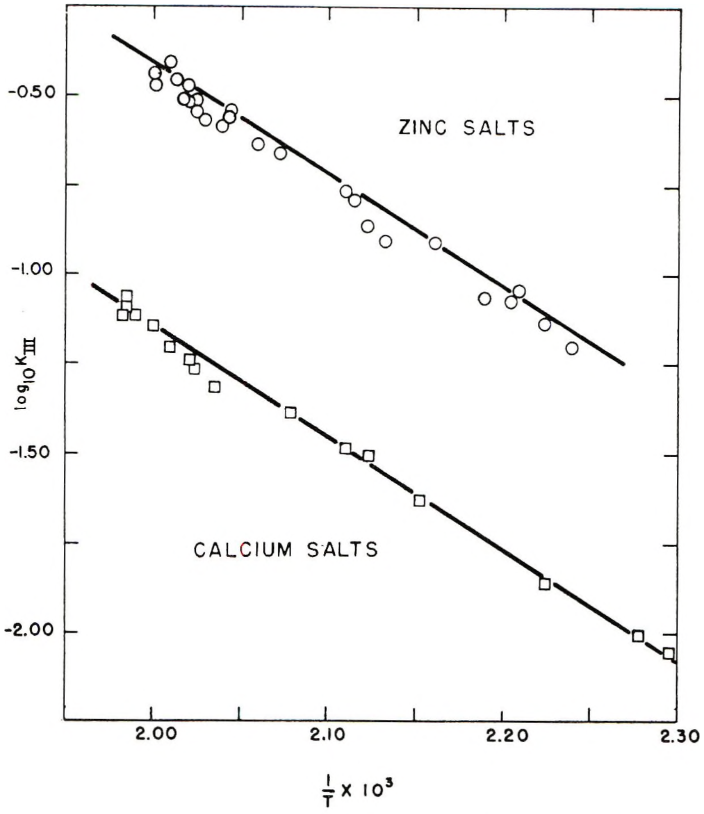


Fig. 3. Third-order rate constants for zinc and calcium salts.

most runs there was evidence of an induction period. In one run only about half of the expected catalyst activity ever developed, and in another run at low catalyst concentration the catalyst became essentially inactive after about 67% conversion. Runs with zinc chloride showed activity only at high temperatures, the activity rising sharply and not very reproducibly and tending to approach that of zinc acetate catalysts toward the end of ester interchange. In one run with excess zinc acetate, methyl acetate was identified in the condensation product. Five runs, however, did yield a fairly consistent set of third-order constants over most of the range of reaction, as seen in Figure 3, and these were at top levels of activity. The rate constants are given by the equation

$$\log_{10} k_{III} = -3290/T + 6.15 \tag{18}$$

and the activation energy was 15.0 kcal./mole. The results were interpreted on the basis that the active form of the catalyst was the alcoholate (polymer glycolate) rather than the acid salt and that the fully active form was the dialcoholate, $Zn(OR)_2$. On this basis the catalyst could become inactive with development of acid groups due to side reaction, especially near the end of ester interchange. The relatively high concentration of points near the half-activity level, the half-activity of the constant temperature portion of one run, and the hesitation near the half-activity level in another (conversion range of about 25–60%) was taken as evidence of the presence and activity of the half-alcoholate Zn(OR)(OAc).

The runs with calcium-containing catalysts were much more difficult to activate fully, as might have been expected from the less amphoteric character of calcium salts than of zinc and lead. By means of a relatively high concentration of calcium acetate [0.100 g. of $Ca(OAc)_2 \cdot H_2O$] in combination with antimony trioxide (0.030 g. Sb_2O_3) consistently high activities were developed after a brief induction period. The significant data, also shown in Figure 3, yielded third-order constants given by

$$\log_{10} k_{III} = -3170/T + 5.19 \tag{19}$$

and an activation energy of 14.5 kcal./mole.

The key role of antimony compounds as catalyst component for obtaining high molecular weight PET is well recognized in the patent literature.[10] Antimony compounds are said to function mainly as polymerization catalysts with little or no effect on ester interchange (cf. U.S. Pat. 2,739,957). In the present work antimony trioxide alone was shown to have negligible ester interchange activity, and later experiments, starting with pure bis[β-hydroxyethyl) terephthalate, likewise showed antimony trioxide alone to have negligible polycondensation activity. The enhancement of catalytic activity of other compounds by antimony compounds is believed to be due to its effectiveness in scavenging acid ends, so that the catalyst (other than the antimony compound) is maintained in the active alcoholate form. The antimony compounds may thus have catalytic activity toward the direct esterification reaction.

DISCUSSION

The Polycondensation Equilibrium

The high value, 4.9, for the equilibrium constant obtained by Griehl and Forster was apparently due to an error in the interpretation and application of the polycondensation equation [eq. (18), p. 133] previously derived by Schulz.[11] The error appeared to be the substitution of mole fraction of glycol in the melt for moles of condensate per "Grundmol," as required in the Schulz equation. When the experimental results of Griehl and Forster are substituted in eq. (1) above, expressed in the equivalent form,

$$K = g(\overline{\mathrm{DP}} - 1), \tag{20}$$

the K values are found to vary from 0.19 to 0.04 as the degree of polymerization increases from 28 to 107, as seen in Table IV. These low and decreasing values of K suggest that under the experimental conditions used Griehl and Forster not all ends were glycol ends but that some were acid or other kinds of ends.

TABLE IV
Reinterpretation of Polycondensation Data of Griehl and Forster[5]

$\overline{\mathrm{DP}}$	g ($\times 10^4$), mole fraction	K	α	$1/\alpha - 1$	$g^{1/2}$ ($\times 10^2$)
107	3.81	0.041	0.714	0.401	1.95
107	3.81	0.041	0.714	0.401	1.95
104	4.16	0.043	0.706	0.416	2.04
94	5.37	0.050	0.684	0.462	2.32
91	6.23	0.056	0.664	0.506	2.49
84	7.27	0.060	0.653	0.531	2.69
83	9.70	0.080	0.602	0.661	3.11
75	9.52	0.069	0.628	0.592	3.08
59	17.3	0.100	0.552	0.812	4.16
57	21.1	0.118	0.514	0.946	4.59
40	43.3	0.169	0.418	1.392	6.58
29	69.3	0.194	0.377	1.653	8.32
28	69.3	0.187	0.387	1.584	8.32

In the presence of acid ends of mole fraction α the expression for the glycol equilibrium becomes

$$K = g(\overline{\mathrm{DP}} - 1)/(1 - \alpha)^2 \tag{21}$$

By assuming K to be constant and to have a value 0.50, as found in this work, values of α can be calculated, as shown in Table IV. These results can be explained on the basis of a relatively rapid and reversible dissociation of PET to form acid ends and vinyl ester ends, both ends then reacting irreversibly with hydroxyl ends to yield water and acetaldehyde, respectively. These reactions may be represented by:

$$2\mathrm{E} \underset{k_1}{\overset{k_0}{\rightleftharpoons}} \mathrm{Z} + \mathrm{g} \tag{22}$$

$$\mathrm{Z} \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \mathrm{A} + \mathrm{V} \tag{23}$$

$$\mathrm{V} + \mathrm{E} \xrightarrow{k_4} Z + \mathrm{CH_3CHO} \tag{24}$$

$$\mathrm{A} + \mathrm{E} \xrightarrow{k_5} \mathrm{Z} + \mathrm{H_2O} \tag{25}$$

where E is glycol end, Z is internal ethylene ester, G is glycol, A is acid end, and V is vinyl ester end. The steady-state solution is

$$(1/\alpha - 1)^2 = 4k_1k_3k_4g/k_0k_2k_5(1 + k_4/k_5)^2$$

where
$$\alpha = (a + \mathrm{V})/(\mathrm{E} + \mathrm{A} + \mathrm{V}) \tag{26}$$

As may be seen in Figure 4, a plot of $(1/\alpha - 1)$ versus $g^{1/2}$ gives a good straight line through the origin.

The assumption of the occurrence of the reversible reaction (23) is not a novel postulate. In the thermal decomposition of ester oils the analogous reaction has been previously proposed to explain the relative instability of ester oils containing hydrogen on the beta carbon of the alcohol portion.[12]

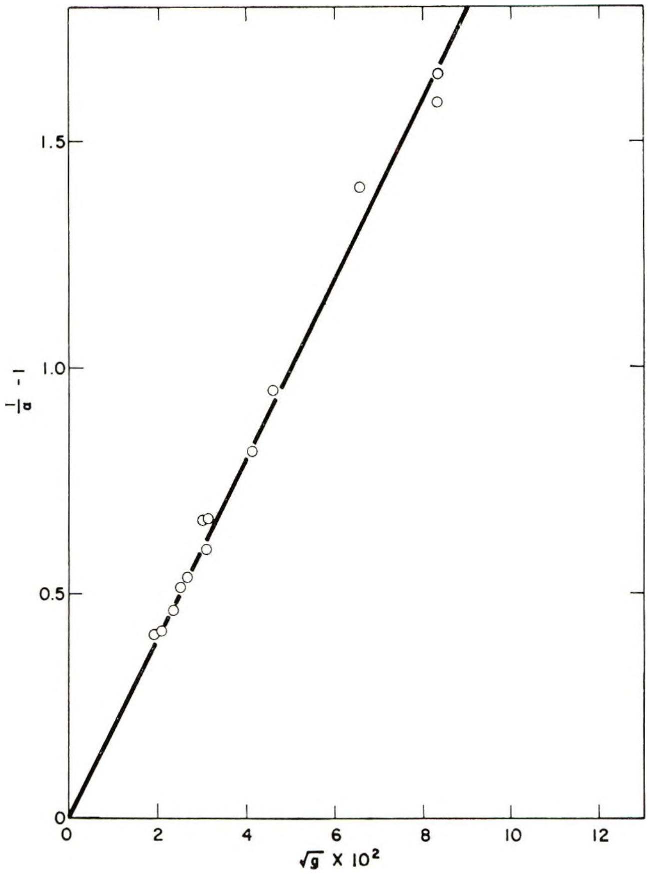


Fig. 4. Correlation of data of Griehl and Forster.[5]

The present determination of the polycondensation equilibrium constant is in excellent agreement with the values of Challa at low degree of polycondensation and in fair agreement with those of Koepp and Werner. The increase in K with degree of polymerization, claimed by Challa,[7] however, was not confirmed; nor does the evidence of such increase appear to be con-

TABLE V
Reinterpretation of Data of Challa[7]

Sample no.	p_e, equilibrium extent of reaction			
	From $K = 0.50$	From G_e/U_0 data	From $E_e/2U_0$	From monomer data
1	0.429	(0.42)	—	0.443
2	0.653	0.67	—	0.650
3	0.709	0.74	0.722	0.676
4	0.823	0.84	0.854	0.816

clusive or even convincing. It can be noted that the determination of K from Challa's equation 12 becomes very sensitive to p_c, the equilibrium extent of reaction, especially at higher DP levels.[7] By assuming a normal Flory-Schulz distribution various values of p_c can be calculated for the four samples of Challa, as seen in Table V, where the different values were calculated; (*1*) from the assumption $K = 0.50$, (*2*) from the glycol equilibrium data, (*3*) from endgroup data, and (*4*) from monomer concentration data. Of the three independent experimental determinations only the last was relatively independent of acid endgroups, since the distilled monomer would have normally contained also the mono glycol ester. Thus, it is indicated that p_c, determined either from endgroup analysis or glycol determination, was too high because of the presence of appreciable amounts of acid ends in the equilibrium product. It had already been previously established that acid ends develop in PET with thermal treatment,[13] and the same effect was apparently present, as already seen in the results of Griehl and Forster.

The conclusion to be drawn from this discussion of the present results and the previous literature results is that the value of the polycondensation constant is close to 0.50 and sensibly independent of temperature or degree of polycondensation and that the normal Flory-Schultz distribution does hold in the PET system.

Kinetics of Ester Interchange

Although detailed comparisons of kinetic data are difficult, the present results substantiate in a general way the conclusions first reached by Skwarski, that the reaction is third-order, and they disagree with the conclusion of Griehl and Schnock, that the reaction is second-order (including catalyst), both conclusions having been drawn from polycondensation rates. The present results of the ester interchange reaction (first stage) are more directly comparable to those of Peebles and Wagner.[3]

The kinetic analysis of Peebles and Wagner[3] may be criticized for the simplifying assumption that the reactions of all higher species can be neglected, for this is untenable except very near the beginning of the process, as can be verified by simple calculation. This objection can be removed if one includes (in their equation 35) all reactions of DMT with hydroxyl-bearing species and includes (in their reaction 36) all reactions of hydroxyl-bearing species with half-transesterified DMT, whether in the monomer or polymer form. However, this is tantamount to assuming the equivalence of all hydroxyl groups, an assumption inconsistent with the value 0.50 for the polycondensation constant. Furthermore, a best fit of the experimental data then requires a definite value of about 3 for the one adjustable parameter, $K = k_2/k_1$, a value inconsistent with the equilibrium measurements of Challa. In the present treatment both inconsistencies were removed, as described, by using the appropriate classification of all the reactions.

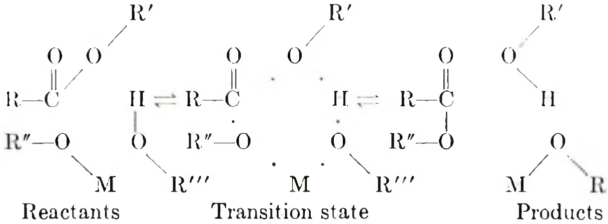
The averaged rate data of Peebles and Wagner (as read graphically) were recalculated according to the present method, and the results are given in Table VI. The third-order rate costants show no drift and are in good agreement with those of other zinc salts at the half-activity level.

TABLE VI
Averaged Data of Peebles and Wagner[3] Recalculated

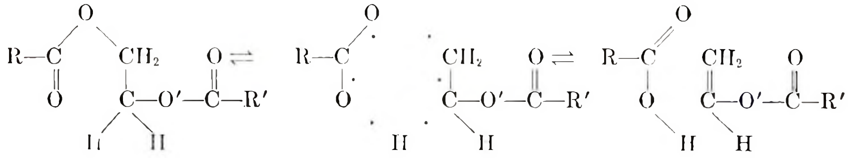
Time, min.	m_t	g_0	g	R_g	OR[H]	R_m	V, liters	Rate, m./min.	k_{III}
0	0	3.58	3.58	0.00	7.16	1.91	0.419	—	—
20	0.76	3.52	2.79	0.70	5.93	1.15	0.380	0.033	0.034
40	1.26	3.48	2.29	1.12	5.14	0.65	0.355	0.019	0.035
60	1.55	3.45	2.00	1.35	4.68	0.36	0.340	0.010	0.034
80	1.67	3.44	1.89	1.43	4.49	0.23	0.333	0.006	0.031
100	1.73	3.43	1.83	1.47	4.39	0.17	0.330	—	—

Reaction Mechanism

As seen from present kinetic evidence, the reactions involved in the formation of PET definitely appear to be third-order and are characterized by a relatively low energy of activation and a relatively high entropy of activation. These characteristics are indicative of a true termolecular reaction in homogeneous liquid phase. Furthermore, in these systems the ester and hydroxyl groups involved are almost certainly not ionic to any appreciable extent, and if, as indicated, the catalytic reagent is the metal alcoholate, this probably is essentially non-ionic too. In addition, it appears difficult to explain these reactions in terms of ionic intermediates by any reasonable mechanism. A mechanism of the general ester interchange reaction that accounts for the kinetics and also satisfies the theory of aromatic transition states[14] may be depicted as follows:



where the R's represent portions of long or short polymer chains, including simple organic radicals, and M represents the catalytic metal atom. The thermal decomposition reaction [eq. (21)] may be represented by a first-order reaction also involving an aromatic transition state as follows:



The theory of aromatic transition states is believed to be applicable not only to the above reactions but also to many other types, including ionic and non-ionic, homogeneous and heterogeneous, and liquid and gas phase reactions of first, second, or third order. As examples of the diversity of application may be mentioned cationic[14] and anionic[15] polymerization of olefins, pyrolytic *cis* elimination reactions,[16] and the Diels-Alder reaction. However, further discussion of this interesting theory of reaction mechanisms is beyond the scope of this paper.

EXPERIMENTAL

The apparatus used for both the equilibrium and rate studies consisted of a stirred reactor and a standard 1-liter three-necked flask equipped with a thermowell, stirrer, and takeoff column. The reactor was immersed to the bottom of the ground-glass joints in a silicone (D.C. 550) oil bath equipped with heaters, a thermostat, stirrer, and thermometer. The column (about 20 theoretical plates) was a concentric tube about 15 in. long with a thermowell down the center and was equipped with a heating coil and air cooler. Reflux was controlled by the countercurrent air stream in the surrounding jacket. The liquid takeoff system was designed to minimize holdup, with a miniature water-cooled condenser and direct delivery to the calibrated receiver. A liquid-nitrogen trap followed the liquid receiver. The system was also provided with a small McCleod gage, a full-range pressure manometer, and means of evacuating or supplying nitrogen. The stirrer was of the standard lubricated ground-glass type with air-cooled sleeve and grease cup at the top. It was driven by a 0.25 h.p. electric drill motor. Silicone stopcock grease was used as the stirrer lubricant.

Considerable difficulty was experienced initially with leaks and product contamination when silicone grease was used on the reactor ground-glass joints. This difficulty was eliminated by using Lexan (a G.E. polycarbonate polymer). A dope of Lexan in methylene chloride was painted on the male part of the joint, and closure was affected by uniform heat-sealing under vacuum.

Internal reactor temperatures and bath temperatures were read on thermometers carefully calibrated by comparison with a standard thermometer previously calibrated at the Bureau of Standards. The column temperatures were read on an Alnorco direct-reading (voltmeter) thermometer with an iron–constantan thermocouple, which could be moved to explore column temperatures.

The receivers were carefully calibrated and read at 0°C. These included a 50 ml. receiver for the methanol and a special glycol receiver consisting of a standard 20 ml. bottom part, superimposed by a slender 10 ml. top portion, to increase accuracy in volume measurements in the later stages of condensation.

For the glycol equilibrium measurements it was necessary to apply corrections for the amount of glycol taken over with the methanol, the amount in the reactor vapor, the column holdup, and the amount held up in the collection system. The column holdup was found to vary linearly with boilup rate as measured by temperature difference between reactor and bath. The correction for column holdup was Δ ml. = $0.5 + 0.15\Delta t$°C. The correction for delivery system holdup was Δ ml. = $0.1 + 0.1R$, where R was the delivery rate in milliliters per 10 min. It was not necessary to apply corrections for holdup in the rate measurements.

The standard charge of material was 0.5 mole of DMT, Hercules polymer grade, and 1 mole of glycol (except in those runs in which the amount of glycol was varied).

The raw data for the kinetic study consisted of a set of determinations taken at frequent intervals during the first stage. These included time, reaction temperature, bath temperature, volume of methanol collected at 0°C., pressure, and a column temperature reading usually about half-way up the column. The reaction was carried out under conditions designed for rapid removal of methanol in order to minimize the effect of the reverse reaction. This was accomplished by maintaining a constant and fairly rapid boilup and reflux rate, controlled by means of the bath temperature and the cooling air flow. Generally, the reactor temperature was raised rapidly enough to maintain a temperature of 100–120°C. at the middle of the column, and the reflux cooling was controlled to give about a 10°C. differential between bath and reactor. When a run at constant temperature was wanted, the pressure was reduced to maintain approximately the same column conditions.

The molar volumes of the melt components were assumed to be additive, and the total melt volume was calculated from the following molar volumes for the components at reaction temperature t°C.: $V_t(\text{DMT}) = 191.5[1 + 0.0014(t - 140)]$, $V_t(\text{CH}_3\text{OH}) = 43.9[1 + 0.0014(t - 140)]$, and $V_t(\text{glycol}) = 60.6[1 + 0.0014(t - 140)]$.

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Polymérisation "Basse Pression" de l'Ethylène en Présence de Noir de Carbone

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Synopsis

The polymerization of ethylene with Ziegler-Natta catalysts in the presence of carbon black has shown three characteristic features both with a heterogeneous catalyst, $AlBu_3$–$TiCl_4$, and with a soluble catalyst, $Cl_2Ti(C_5H_5)_2$–$AlEt_2Cl$. They are, in order of increasing importance: reactivity of the organoaluminum derivatives with surface chemical groups of the carbon black, adsorption of a certain amount of organoaluminum compounds on the carbon black surface, and influence of the specific surface of carbon black, which controls the dispersion degree of the catalytic system. Furthermore, it was possible to obtain polyethylene by this procedure, containing different amounts and different types of carbon black.

Un certain nombre de brevets récents[1] mentionnent la possibilité de polymériser l'éthylène par des catalyseurs du type Ziegler-Natta en présence de charges actives et notamment de divers types de noirs de carbone. En effet, si la résistance du polymère au vieillissement par oxydation thermique ou photochimique peut être sensiblement améliorée par l'incorporation d'une charge, elle dépend beaucoup d'une répartition uniforme de celle-ci, difficilement réalisable par incorporation directe du noir de carbone au polymère préformé; la dispersion est excellente, par contre, même pour des teneurs élevées en noir de carbone, si la charge est présente dans le milieu réactionnel dès le début de la polymérisation.

Il est ainsi possible de préparer deux catégories du substances: si la charge est prédominante, on obtient des solides qui sont en fait des charges possédant des propriétés nouvelles; si le polymère est prépondérant, on obtient des matières plastiques renforcées et à propriétés différentes du simple mélange charge-polymère.

La présente étude concerne la polymérisation de l'éthylène en présence de noirs de carbone.

POLYMERISATION PAR UN CATALYSEUR DU TYPE HETEROGENE

Partie Experimentale

Le système catalytique choisi résulte d'une réaction d'oxydo-réduction entre l'aluminium triisobutyle et le tétrachlorure de titane en solution

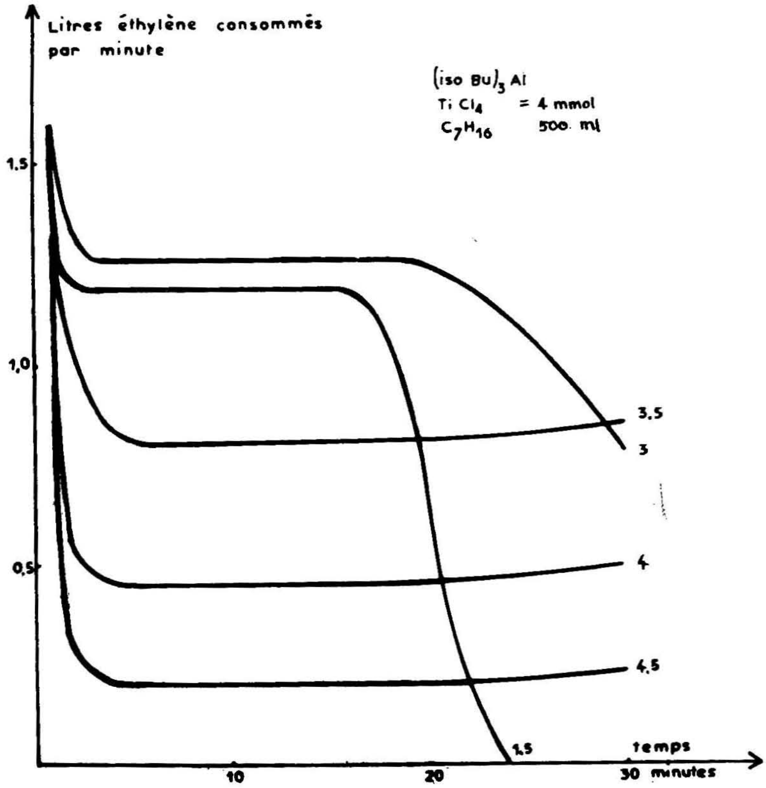


Fig. 1. Courbes type, évolution de la vitesse de réaction en cours de polymérisation pour divers rapports Al/Ti.

dans l'heptane. Cette réaction peut s'écrire schématiquement:

$$Al(Bu)_3 + TiCl_4 \rightarrow Al(Bu)_2Cl + TiCl_3Bu$$

$$TiCl_3Bu \rightarrow TiCl_3 \downarrow + Bu^*$$

Bu étant un reste butyle. La mise en oeuvre de ce système catalytique exige des conditions opératoires extrêmement strictes en ce qui concerne l'élimination des traces d'humidité, d'oxygène, de gaz carbonique et celle des dérivés soufrés des réactifs. La purification soignée des réactifs est indispensable pour obtenir une bonne reproductibilité des essais.

L'heptane utilisé a été purifié par distillation sur sodium en atmosphère inerte et par passage sur du tamis moléculaire 13×. L'éthylène et l'azote R sont débarrassés des dernières traces d'oxygène, d'humidité et de CO_2 par passage sur du catalyseur BTS (BASF) et sur du tamis moléculaire 5 A.[2]

Les polymérisations sont effectuées dans un autoclave muni d'une agitation magnétique efficace (2,000 tours/min.) et dont le réacteur thermostaté en verre Pyrex permet une observation directe en cours de réaction.

L'ordre d'introduction des éléments du système catalytique est le suivant: heptane, $Al(Bu)_3$ puis $TiCl_4$. Dans le cas où nous opérons en présence de

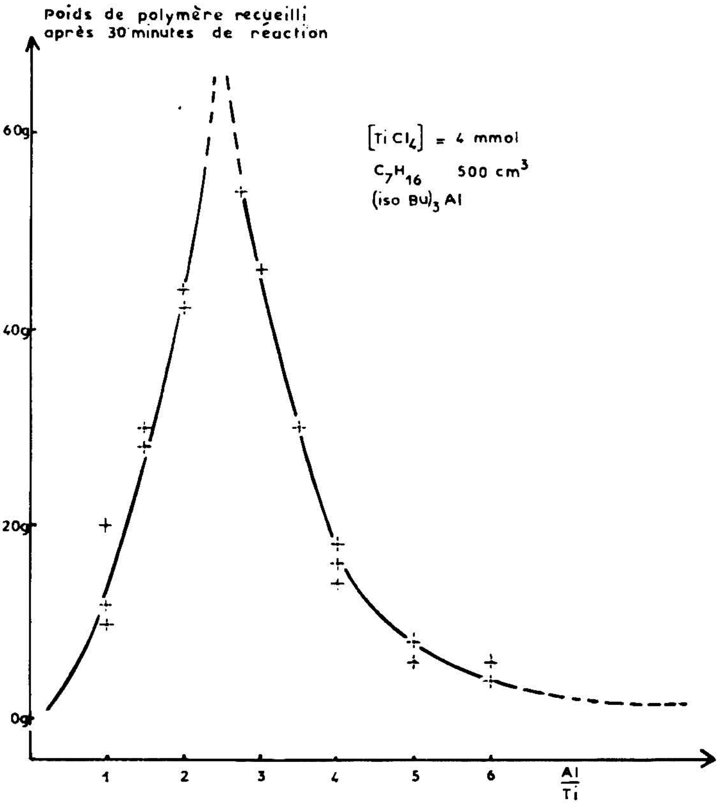


Fig. 2. Activité du système catalytique hétérogène en fonction de sa composition; t = 59 ± 2,5°C.

noir de carbone, nous introduisons d'abord le noir préalablement dispersé dans l'heptane, puis $Al(Bu)_3$ enfin $TiCl_4$.

Le système catalytique est formé à 50°C, mais lors de l'introduction de l'éthylène, nous assistons à une réaction exothermique de sorte que la température réactionnelle se stabilise vers 60°C.

Résultats de l'Étude Cinétique

Polymérisation de l'Éthylène en Absence de Noir de Carbone. L'activité catalytique d'un système peut être définie par la vitesse de polymérisation en fonction de la durée de réaction (Fig. 1), mais également par le poids de polymère formé pendant un certain temps de réaction (Fig. 2). La Figure 2, qui décrit la variation de l'activité (moyenne de 3 essais) en fonction du rapport molaire Al/Ti du système catalytique, fait apparaître un maximum d'activité pour un rapport Al/Ti de l'ordre de 2,5.

Une courbe analogue a déjà été signalée par Ludlum et coll.[3] et à titre de comparaison, nous avons reproduit sur la Figure 3 les résultats de ces auteurs. Il semble qu'on puisse attribuer ce maximum à la superposition de plusieurs réactions et notamment à l'adsorption de monomère à la surface du catalyseur.

En Presence de Noir de Carbone. Nous avons étudié le comportement du système catalytique en présence d'un noir "au four," le Vulcan 3, dont la surface spécifique est voisine de 75 m.^{2}/g.

Les composants du mélange réactionnel sont introduits dans l'ordre suivant: heptane, 0,5 litre; noir de carbone Vulcan 3, 0–15 g.; iso-Bu$_3$Al, 16 mmoles; TiCl$_4$, 4 mmoles.

Etant donné qu'une partie du dérivé organoaluminique peut être adsorbée à la surface du noir et que d'autre part il peut y avoir consommation de AlR$_3$ par réaction avec les fonctions superficielles de la charge, notamment les groupements —OH et —COOH, nous avons choisi un rapport molaire de départ assez élevé, soit Al/Ti = 4.

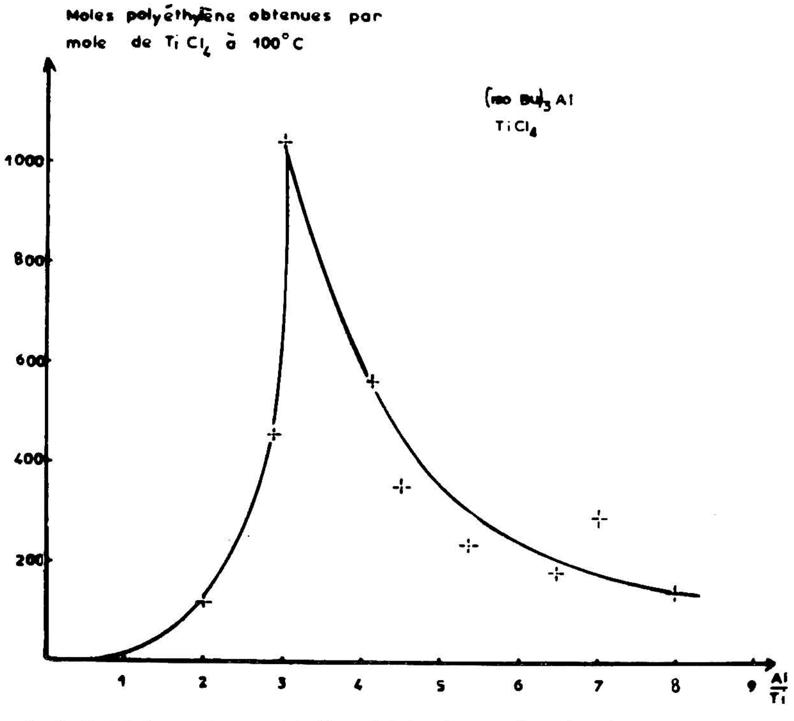


Fig. 3. Activité du système catalytique hétérogène en fonction de sa composition, selon Ludlum et al.[3]

Nous estimons que, compte tenu de l'ordre d'introduction des réactifs, TiCl$_4$ ne peut réagir avec le noir: d'une part, du fait que l'organoaluminique a déjà réagi avec l'ensemble des groupes superficiels de la charge, d'autre part, parce que TiCl$_4$, au moment où on l'introduit dans la suspension, se trouve en présence d'un large excès de Al(Bu)$_3$ avec lequel il réagit instantanément. Pour une quantité de charge variable, la concentration en TiCl$_4$ actif, contrairement à celle de Al(Bu)$_3$, est donc à priori une constante.

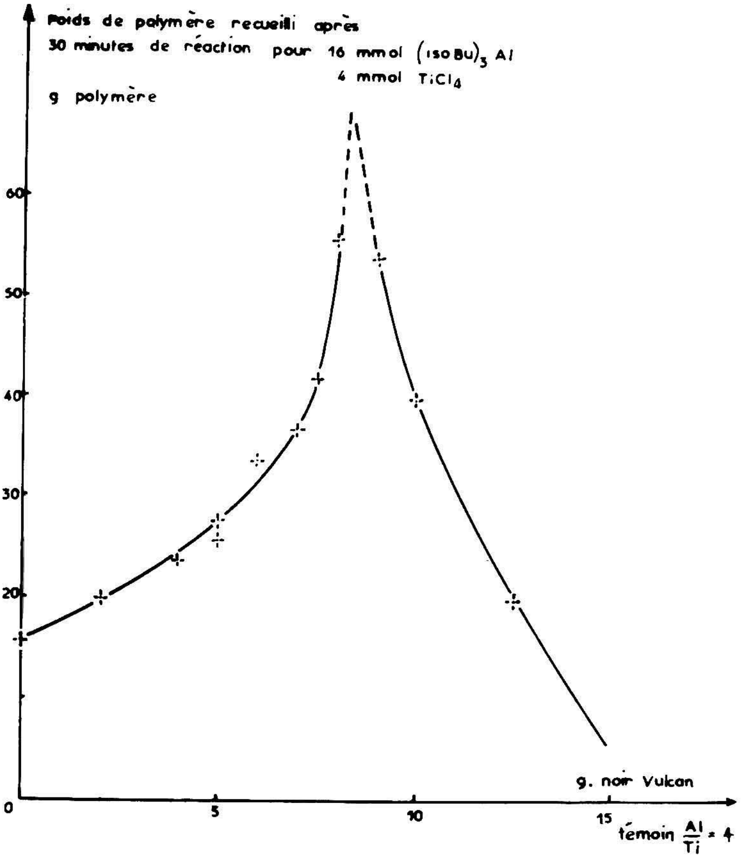


Fig. 4. Variation de l'activité du système catalytique hétérogène pour une composition donnée en fonction de la quantité de charge introduite.

Sur la Figure 4, où nous avons porté le poids de polymère recueilli après 30 min. de réaction en fonction de la quantité de noir engagé, on constate un maximum d'activité, comparable à celui trouvé précédemment en absence de noir, mais avec des rapports Al/Ti variables (Fig. 2).

A première vue, tout se passe comme si une partie de l'organoaluminique était désactivée par le noir de carbone, soit par adsorption, soit par réaction chimique. Comme par ailleurs la quantité de $TiCl_4$ reste constante, le rapport Al/Ti subirait une diminution et entraînerait ainsi une augmentation de la vitesse réactionnelle (Fig. 2).

Par comparison des courbes données par les Figures 2 et 4, il est possible de déterminer la quantité de $Al(Bu)_3$ théoriquement désactivée par le noir de carbone. La Figure 5 représente cette quantité de $Al(Bu)_3$ en fonction de la concentration en noir.

Deux autres hypothèses peuvent également être avancées pour expliquer ce fait: d'une part, une adsorption préférentielle du polymère formé sur le noir, libérant ainsi les sites actifs du catalyseur, d'autre part,

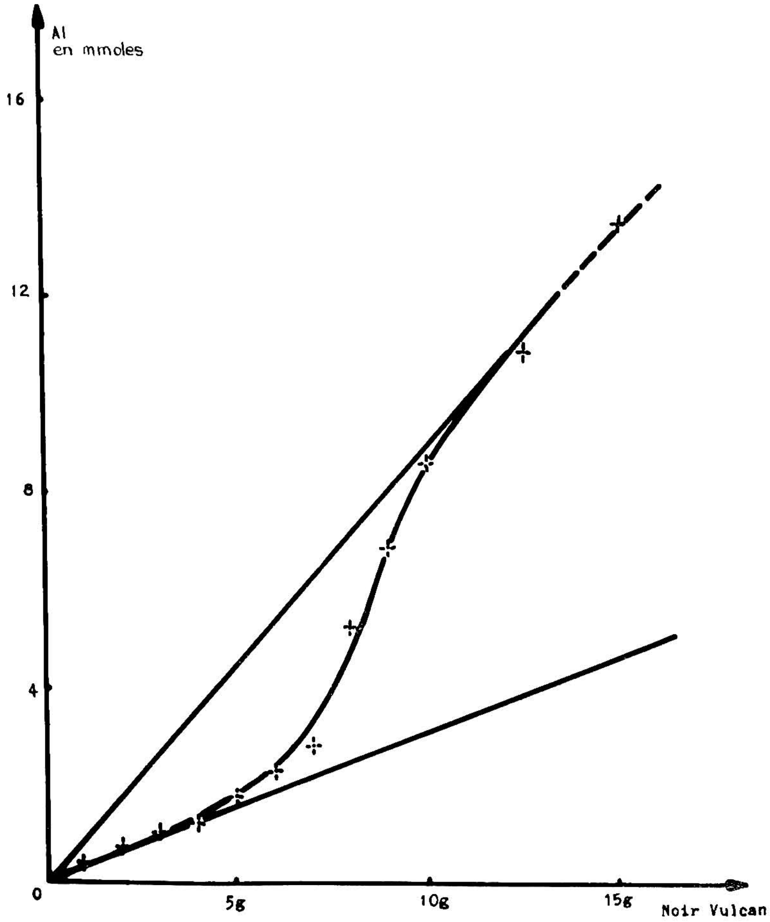


Fig. 5. AlBu$_3$ désactivé en fonction de la quantité de noir de carbone; $t = 59 \pm 2{,}5$°C.

une interaction entre le catalyseur Ziegler et le noir de carbone susceptible de provoquer une baisse d'activité du système. Ces deux phénomènes concurrents pourraient donc expliquer l'existence d'un maximum d'activité. Pour vérifier ces hypothèses, nous avons étudié l'interaction noir–Al(Bu)$_3$ et le comportement d'un catalyseur Ziegler préformé en présence de noir de carbone.

Interaction Noir de Carbone–Al(Bu)$_3$

En ce qui concerne l'interaction noir–Al(Bu)$_3$, il faut distinguer entre une adsorption purement physique à la surface de la charge et les réactions chimiques possibles avec les groupements fonctionnels présents à la surface du noir.

Détermination de la Quantité Totale de Al(Bu)$_3$ Bloqué par la Charge. Dans une première série d'essais, le noir est dispersé en quantités croissantes dans l'heptane et traité par 16 mmoles de Al(Bu)$_3$ à 30°C. pendant 30 min.

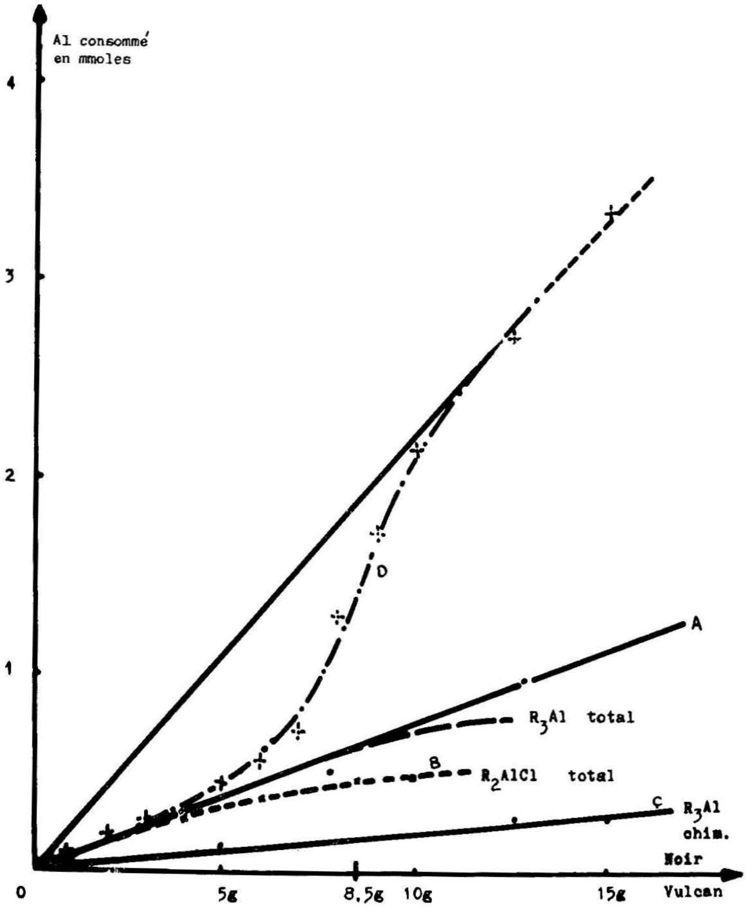


Fig. 6. Étude de la réaction noir–organoaluminique.

On prélève la solution surnageante, dont on détermine la concentration en aluminium et par différence, il est donc possible de connaître la quantité de $Al(Bu)_3$ retenue par le noir.

Sur la Figure 6, qui reprend la courbe donnée par la Figure 5, nous avons porté la quantité de $Al(Bu)_3$ consommée en fonction de la quantité de noir engagée (courbe OA).

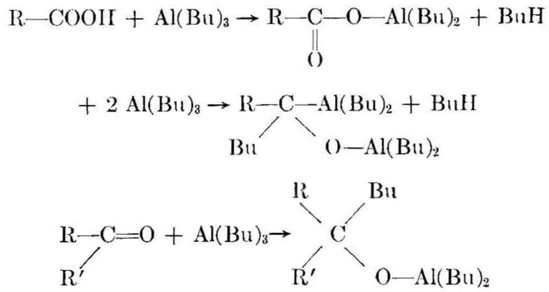
Il est donc possible de constater que la diminution de l'activité du système catalytique, donnée par la courbe D, n'est pas due uniquement à une consommation de $Al(Bu)_3$ ou d'un autre dérivé organoaluminique par le noir, essentiellement aux concentrations élevées de ce dernier.

Il était également nécessaire d'étudier le comportement de $Al(Bu)_2Cl$ formé par interaction entre $TiCl_4$ et $Al(Bu)_3$ et dont on sait qu'il s'adsorbe préférentiellement sur le catalyseur Ziegler précipité. La courbe OB (Fig. 6) montre que $Al(Bu)_2Cl$ se comporte de façon analogue à $Al(Bu)_3$.

Détermination de la Quantité de $Al(Bu)_3$ Bloqué par Voie Chimique. Dans une seconde série d'essais, les noirs ayant subi les traitements précédents sont prélevés, puis filtrés et lavés à l'heptane jusqu' à ce que le filtrat ne contienne plus d'aluminium discernable. Le noir résiduel est ensuite traité par HCl *N* dans le but d'hydrolyser l'aluminium chimiquement fixé en surface et de le doser dans le filtrat acide.

Etant donné que le noir Vulcan contient en surface: 0,018 mmoles de groupes quinoniques par gramme de noir, 0,0125–0,020 mmoles de groupes hydroxyles et 0,020 mmoles de groupes carboxyles, les réactions avec Al(Bu)$_3$ peuvent s'écrire:

$$\mathrm{R{-}OH + Al(Bu)_3 \rightarrow RO{-}Al(Bu)_2 + BuH}$$



$$\mathrm{R{-}COOH + Al(Bu)_3 \rightarrow R{-}\underset{\underset{O}{\|}}{C}{-}O{-}Al(Bu)_2 + BuH}$$

$$\mathrm{+\ 2\ Al(Bu)_3 \rightarrow R{-}\underset{Bu\quad O{-}Al(Bu)_2}{C}{-}Al(Bu)_2 + BuH}$$

$$\mathrm{\underset{R'}{R{-}C{=}O} + Al(Bu)_3 \rightarrow \overset{R\quad Bu}{\underset{R'\quad O{-}Al(Bu)_2}{C}}}$$

Par traitement du noir par Al(Bu)$_3$, on observe une fixation chimique de 0,08 mmoles d'aluminium par gramme de noir (courbe OC, Fig. 6), ce qui correspond bien à la somme des groupements fonctionnels et en admettant ce schéma réactionnel.

Il faut néanmoins signaler que, par dosage Zeisel après hydrolyse du noir ainsi traité, il est possible de mettre en évidence 0,016 mmoles de groupe éther par gramme de noir, soit une valeur qui correspond au taux de groupes hydroxyles initialement présents sur le noir. A l'heure actuelle, il n'est pas possible de préciser si cette alcoylation se fait par réaction directe entre le groupe OH et Al(Bu)$_3$ ou uniquement lors de la réaction d'hydrolyse.

Polymérisation sur Système Catalytique Préformé.

Comme l'adsorption de Al(Bu)$_3$ sur le noir n'explique pas complètement le comportement de la polymérisation Ziegler en présence de noir, nous avons également effectué quelques essais en vue de préciser l'interaction entre la charge et un catalyseur Ziegler préformé.

Dans le réacteur porté à 30°C. et contenant 500 cm.^{3} d'heptane, on injecte 16 moles Al(Bu)$_3$. Après 30 min., on ajoute 4,0 mmoles de TiCl$_4$ et on porte progressivement la température à 50°C.

Après 60 min., le noir est ajouté quelques instants avant le début de la polymérisation. A part le mode d'introduction du noir, la catalyse est donc opérée selon la méthode décrite précédemment.

Sur la Figure 7 où nous avons porté le poids de polymère recueilli après 30 min. en fonction de la concentration en noir, on constate une diminution nette du rendement en polymère lorsqu'on opère avec des taux de charge croissants.

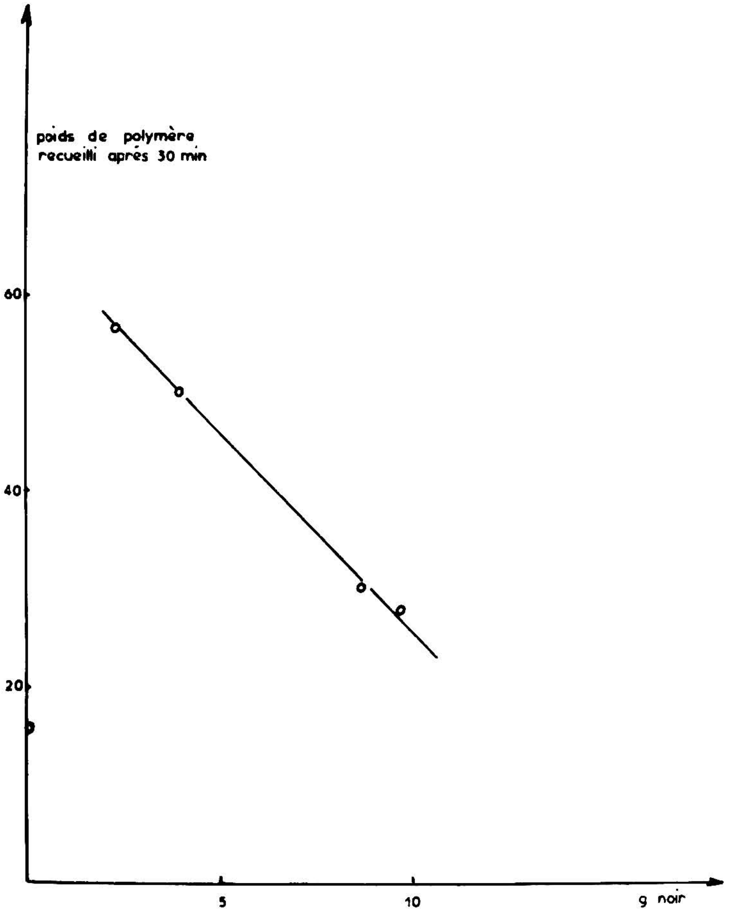


Fig. 7. Système catalytique hétérogène préformé.

Il semble donc que la cinétique de la catalyse Ziegler en présence de noir puisse s'expliquer par la superposition de deux phénomènes au moins, à savoir l'interaction entre noir et $Al(Bu)_3$ d'une part et celle entre noir et catalyseur Ziegler d l'autre.

Comportement du Système Catalytique en Présence d'un Noir Graphité

Il peut être intéressant d'étudier le comportement du système catalytique $Al(Bu)_3$–$TiCl_4$ en présence d'un noir différent du Vulcan 3. A cet effet, nous avons choisi un noir graphité à 2.700°C., le Graphon, dont la surface est légèrement supérieure à celle du noir précédent. L'absence totale de groupes chimiques superficiels, ses propriétés électriques et sa structure interne le différencient nettement du noir précédemment engagé.

En opérant dans le mêmes conditions que celles décrites précédemment, on obtient une activité catalytique qui est représentée par la Figure 8. La comparison avec le Vulcan 3 (Fig. 4), montre que dans le cas du Graphon et aux concentrations utilisées, on n'arrive pas à franchir le maximum d'activité du système.

Par comparaison des courbes données par les Figures 2 et 8, il est possible de déterminer la quantité de $Al(Bu)_3$ théoriquement désactivé par le noir Graphon. La Figure 9 représente cette quantité de $Al(Bu)_3$ en fonction de la concentration en noir (courbe (OA). Sur le même graphique, nous avons également porté la quantité de $Al(Bu)_3$ bloqué par adsorption sur ce noir (courbe OB).

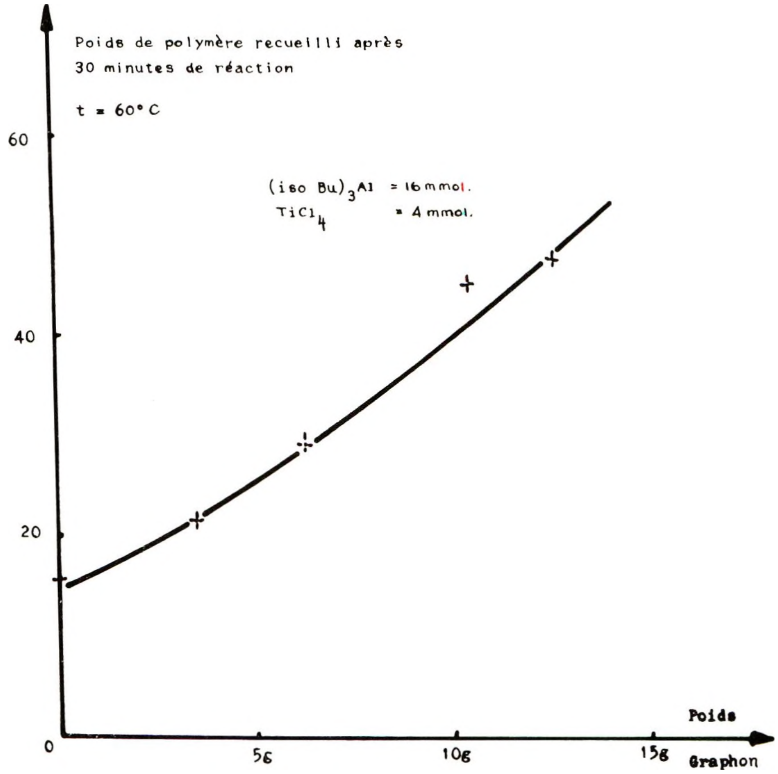


Fig. 8. Variation de l'activité du système catalytique hétérogène pour une composition donnée fonction de la quantité de charge introduite (noir Graphon).

Il est à noter que la consommation en organoaluminique, due à la présence de Graphon, est nettement inférieure à celle que l'on observait dans le cas du Vulcan 3.

Qualitativement les deux noirs interviennent par conséquent de la même manière sur la système catalytique. Quantitativement, la différence de comportement est considérable, mais elle ne saurait être expliquée par le seul défaut de groupements superficiels en surface du noir Graphon.

On peut alors envisager l'hypothèse d'un blocage du complexe coordonné de Ziegler-Natta par adsorption sur le noir, adsorption mettant éventuelle-

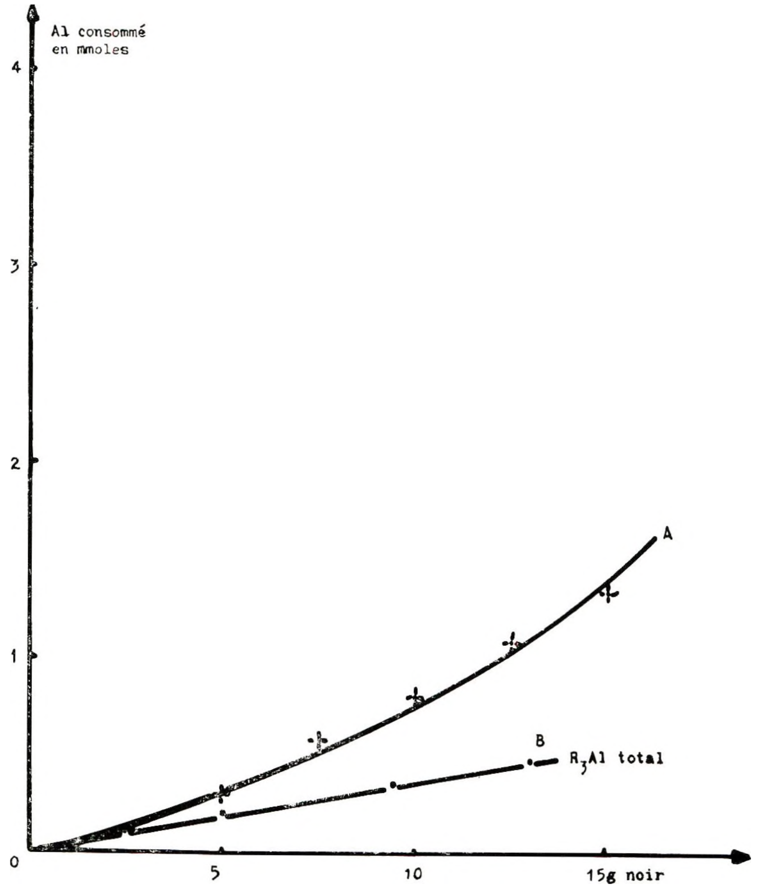


Fig. 9. Quantité d'aluminium désactivé en fonction de la quantité de charge introduite (noir Graphon); Al/Ti initial, 4.

ment en jeu un échange électronique, susceptible de saturer l'élément de transition à l'état réduit.

POLYMERISATION PAR UN CATALYSEUR DU TYPE HOMOGENE

Etant donnée la complexité que nous venons de constater pour l'interaction entre le noir de carbone et un catalyseur Ziegler précipité, nous nous sommes demandés si la variation d'activité était liée à la présence de ces deux phases héterogènes dans le milieu.

La mise en oeuvre d'un système catalytique soluble permettra éventuellement de préciser ce point de vue. Dans ce but, nous avons choisi un système catalytique soluble en milieu toluène, formé par le biscyclopentadiényletitane dichloré comme catalyseur et un aluminium diéthyle monochloré comme cocatalyseur.[4,5] Pour ce système le mode d'interaction serait le suivant.[4,5]

Formation d'un complexe:

$$(\pi\text{-}C_5H_5)_2TiCl_2 + AlR_2Cl \rightarrow (\pi\text{-}C_5H_5)_2TiRCl,\ AlRCl_2$$

Dissociation du complexe:

$$(\pi\text{-}C_5H_5)_2TiRCl,\ AlRCl_2 \rightleftarrows (\pi\text{-}C_5H_5)_2TiR^{(+)} + AlRCl_3^{(-)}$$

Polymérisation:

$$(\pi\text{-}C_5H_5)_2TiR^{(+)} + \text{éthylène} \rightarrow \text{polymère}$$

Resultats de l'Étude Cinétique

Polymérisation en Absence de Noir de Carbone. Les conditions opératoires sont pratiquement identiques à celles de la polymérisation hétérogène, mais pour des raisons de solubilité du dérivé organotitanique, il est nécessaire d'opérer dans le toluène comme solvant. En plus, il est in-

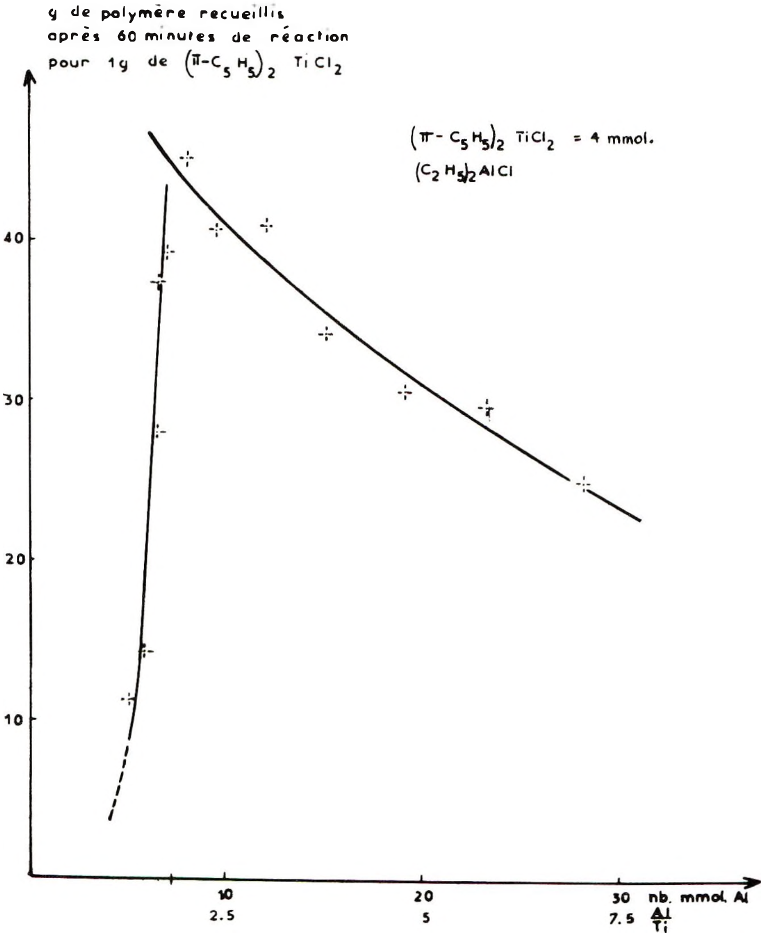


Fig. 10. Activité du système catalytique en fonction de sa composition, cas de la catalyse homogène.

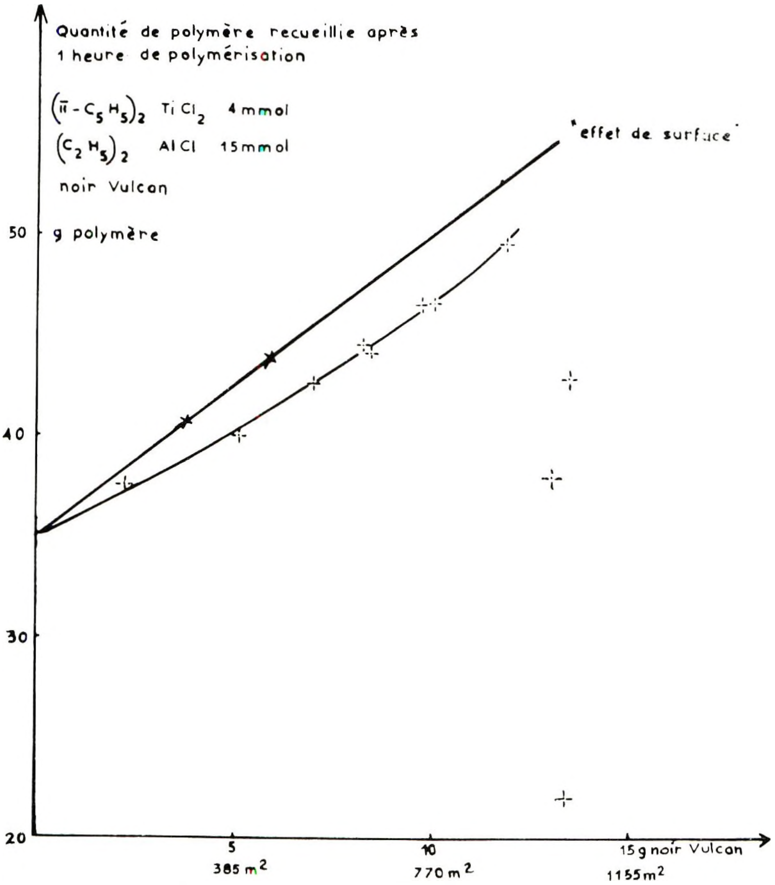


Fig. 11. Variation de l'activité du système catalytique homogène pour une composition donnée en fonction de la quantité de charge introduite.

dispensable de limiter la formation du système catalytique à quelques minutes, en effet audelà de 30 min. d'âge, le catalyseur a perdu la plus grande partie de son activité. La polymérisation proprement dite doit également démarrer au plus tard 5–10 min. après le mélange des constituants.

Dans ces conditions, la Figure 10 représente la variation d'activité du système catalytique homogène en fonction du rapport molaire des composants Al/Ti et pour une température de polymérisation de 38 ± 2°. L'activité est déterminée par le poids de polymère formé après 1 heure de réaction pour 4 mmoles de catalyseur: $(\pi\text{-}C_5H_5)_2TiCl_2$. De façon surprenante on obtient encore ici une courbe à maximum d'activité pour un rapport molaire d'environ 2.

Polymérisation en Présence de Noir de Carbone. Le noir engagé dans ces polymérisations est comme précédemment le Vulcan 3. Pour le système catalytique, nous avons choisi un rapport Al/Ti = 15/4, espérant ainsi pouvoir franchir le maximum d'activité au-delà d'une certaine concentration en noir. La Figure 11 montre que l'effet d'activation en présence de noir est à nouveau très marqué. Toutefois, au-delà d'une concentration en noir égale à 12,5 g., correspondant probablement au maximum d'activité, les essais effectués sont très mal reproductibles. Nous attribuons ceci à une distribution irrégulierè de la charge dans le mileu réactionnel, malgré la violence de l'agitation.

Encore ici, il est possible que l'augmentation d'activité provienne, comme pour un système catalytique hétérogène, de la superposition de deux effets: d'une part adsorption d'organoaluminique, d'autre part adsorption du complexe catalytique sur la charge.

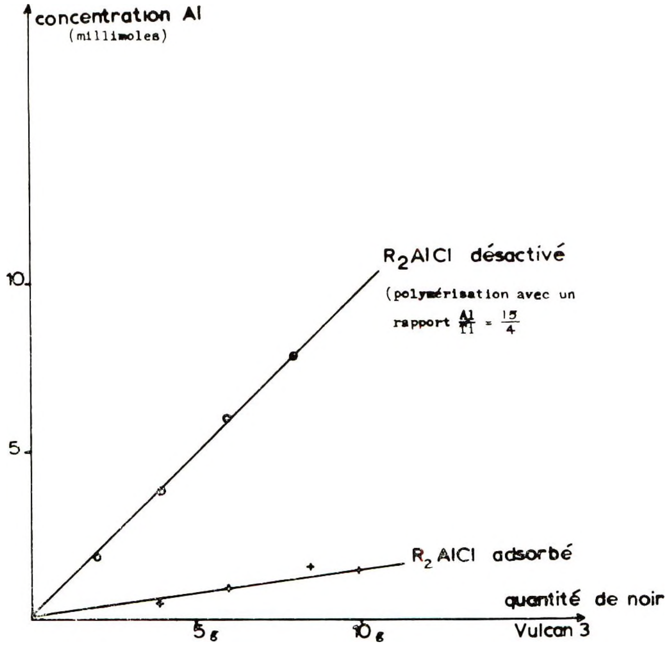


Fig. 12. Concentration en R_2AlCl désactivé et R_2AlCl adsorbé en fonction de la quantité de noir introduite.

Par comparaison de courbes données par les Figures 10 et 11, il est possible de déterminer la quantité de AlR_2Cl théoriquement désactivée par le noir de carbone. La Figure 12 représente cette quantité de AlR_2Cl en fonction de la concentration en noir.

Sur la même figure, nous avons également porté la quantité réelle de AlR_2Cl adsorbé par la charge. On constate encore dans ce cas que la seule adsorption de AlR_2Cl ne peut pas expliquer l'augmentation de l'activité catalytique.

Système catalytique préformé. Contrairement au système catalytique hétérogène étudié précédemment, on ne constate aucune différence dans le cas de catalyseurs solubles entre un mélange préformé et un catalyseur formé en présence de noir (Fig. 11, effet de surface).

C'est donc ici qu'apparaît nettement le rôle de la dispersion et l'importance de facteur surface pour un système catalytique soluble. Cet effet peut éventuellement jouer concurremment aux pertes d'organoaluminique actif.

Effet de Surface

Afin de mieux définir cet effet de surface, nous avons engagé avec un système catalytique soluble des quantités identiques de noir, mais présentant des surfaces spécifiques très différentes.

Pour ces polymérisations, nous avons engagé les noirs suivants après purification par extraction.[6,7]

TABLEAU I

Dénomination commerciale	Type	Surface BET rapportée à 10 g. de noir, m.^{2}	Poids de polymère recueilli, g.
Sterling FT	thermique	157	41,2
Sterling R	noir au four	220	36,5
Vulcan 3	noir au four (hydrocarbure liquide)	770	46,6
Philblack 0	noir au four (hydrocarbure liquide)	770	49,8
Sphéron 6	tunnel	1.200	56,5
Graphon	Sphéron 6 graphité , 2.700°C.	≈ 1.200	55,8

Dans le Tableau I, nous avons également porté le poids de polymère recueilli après 1 heure de polymérisation pour un rapport Al/Ti = 15/4.

Sur la Figure 13, où nous avons porté le poids de polymère en fonction de la surface BET des noirs, on observe que la rendement est directement proportionnel à la surface présentée par la charge.

La consommation en AlR_2Cl, propre à chaque noir, est comprise dans cet effet d'activation; pratiquement nulle pour un Sterling, elle devient appréciable pour 10 g. de Vulcan 3, néanmoins cet effet reste faible par rapport à l'activité catalytique de surface.

Il semble donc que la mécanisme de la catalyse homogène, en présence de noir, soit fonction de deux phénomènes parallèles, régis tous deux par une loi linéaire: l'influence de la surface de la charge active, et l'adsorption d'organoaluminique en surface du noir.

Une remarque complémentaire s'impose quant au comportement du Sphéron 6 et du Graphon: comme la quantité de polymère obtenue est pratiquement la même dans les deux cas, il semble à priori que la conductivité des noirs et la présence de groupes chimiques superficiels n'influence pas de façon sensible l'activité du système catalytique.

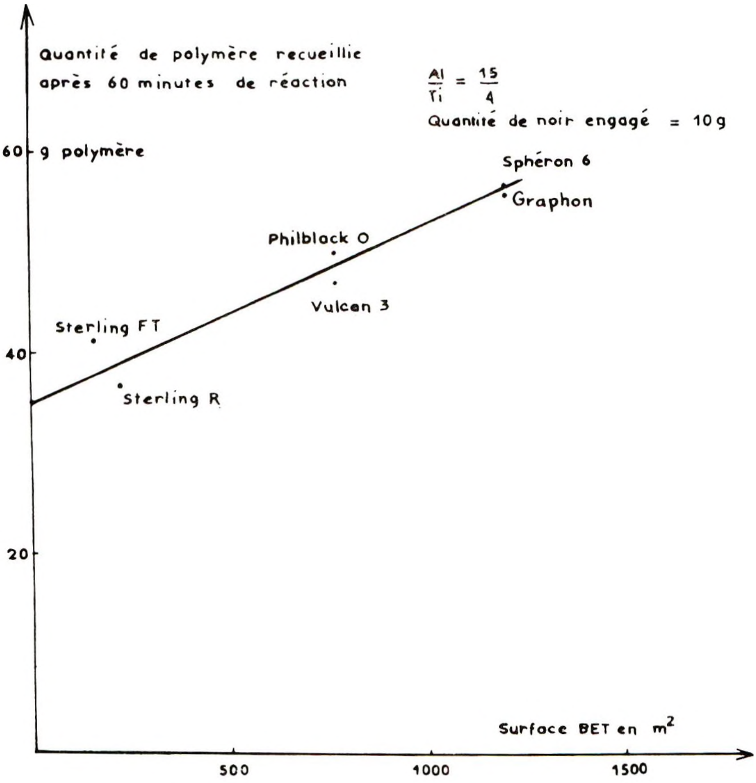


Fig. 13. Activité du système catalytiqe soluble, pour divers types de noirs.

Il est possible par ailleurs de transcrire la Figure 13 directement sur la Figure 11, en portant en abscisse la surface correspondant aux quantités de noir Vulcan engagé. C'est ainsi qu'a 10 g. de Vulcan correspond une surface de 770 m.^{2}

CONCLUSION

Nos résultats expérimentaux établissent l'existence simultanée de trois phénomènes perturbant, en présence de noir de carbone, la cinétique classique de la polymérisation Ziegler-Natta, aussi bien pour des systèmes catalytiques hétérogènes que solubles. Ce sont par order d'importance croissante: (*a*) la réactivité des groupements superficiels de la charge avec les dérivés organoaluminiques; (*b*) l'adsorption d'une fraction élevée d'organoaluminique en surface du noir (les forces qui en sont responsables sont relativement faibles, puisqu'un simple lavage au solvant entraîne la plus grande partie du cocatalyseur fixé); (*c*) l'influence de la surface spécifique de la charge par la dispersion qu'elle impose au système catalytique. En plus de ces résultats d'intérêt plutôt théorique, il a été possible de mettre au point des polyéthylènes chargés de façon homogène par des concentrations et des qualités différentes de noirs de carbone.

Ce travail a pu être réalisé grâce à l'appui matériel de la Compagnie Française de Raffinage, que les auteurs tiennent à remercier très sincèrement.

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Reactions of Trifluoroacetic Acid with Poly(vinyl Alcohol) and Its Model Compounds. Effect of Neighboring Hydroxyl Groups on the Reaction

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Synopsis

Reactions of trifluoroacetic acid with poly(vinyl alcohol) and various model alcohols were investigated by observing the fluorine and the proton magnetic resonance spectra of the reaction mixtures. At equilibrium the degree of conversion to ester under given conditions decreased in the order isopropanol, pentane-2,4-diol, heptane-2,4,6-triol and poly(vinyl alcohol). Therefore the equilibrium constant for esterification of a hydroxyl group is depressed by the presence of neighboring hydroxyl groups. It was observed that the steric structures of the models and polymers also affect the equilibrium position of the reaction and this is mainly ascribable to the fact that *meso* (isotactic) molecules react more slowly with the acid than do racemic (syndiotactic) molecules. In acid-catalyzed acetylation of the model alcohols with acetic acid no similar dependence on the steric configuration was found. Therefore trifluoroacetylation seems to be specific in this respect.

INTRODUCTION

Poly(vinyl alcohol) dissolves in trifluoroacetic acid with esterification of the polymer. Reactions of this type are often used in the preparation of poly(vinyl esters) of relatively strong carboxylic acids (e.g., formic or haloacetic) and seem to be simple acid-catalyzed esterifications in which the carboxylic acid itself acts as catalyst. However, because of the difficulty in following the progress of the reactions they have not been carefully investigated and are not well understood. One especially interesting question concerns the effect of neighboring hydroxyl groups on the esterification, a question which is difficult to examine by isolation and analysis of reaction intermediates because of the instability of the esters. In the present investigation the progress of the reaction was followed *in situ* by the growth of the various ester peaks in the fluorine resonance spectra of the reaction mixtures. The following alcohols were used as model compounds of poly(vinyl alcohol): isopropanol, isomers of butane-2,3-diol, pentane-2,4-diol, and heptane-2,4,6-triol.

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EXPERIMENTAL

Materials

Trifluoroacetic acid (J. T. Baker, Analytical Reagent, bp 72.5°C) was used with and without prior distillation, with no apparent difference in the results obtained.

The *levo*- and *meso*-butane-2,3-diols of biological origin were kindly supplied by Dr. C. T. Bishop; the former was found to have a specific rotation of −12.6° in reasonable agreement with the literature value[1] of −13°. The *meso* glycol was said to contain 5–10% of the *d* isomer,[2] a view confirmed by the fluorine resonance spectrum of the derived trifluoro acetate. However, the semisolid commercial glycol (Eastman Kodak, practical grade) was found by the same method to be essentially pure *meso* isomer and accordingly was used in all further experiments.

Pentane-2,4-diol was obtained commercially. Heptane-2,4,6-triol was synthesized by hydrogenation of diacetylacetone.[3] The diol was separated into *meso* and *dl* components and the triol into *meso,meso* (isotactic), *meso,dl* (heterotactic), and *dl,dl* (syndiotactic) fractions by elution chromatography following a method of Nagai et al.[4,5]

Three poly(vinyl alcohol) samples of different tacticities, as described in a previous paper,[6] were used in this work.

NMR Measurements

Fluorine resonance spectra were obtained at an operating frequency of 94.1 MHz and proton resonance spectra at 100.0 MHz by use of a Varian HR-100 spectrometer modified to operate by a time-division scheme at a pulsing rate of 10 KHz.[7] Base-line stabilization was achieved in this manner. In Figure 1 is shown a block diagram of the integration apparatus. The frequency counter must be capable of manual operation, i.e., as an event counter. A Hewlett-Packard model 521C counter was used. The analog to digital converter should have a high input impedance and be capable of full output for an input signal of about 1 V. The advantage of

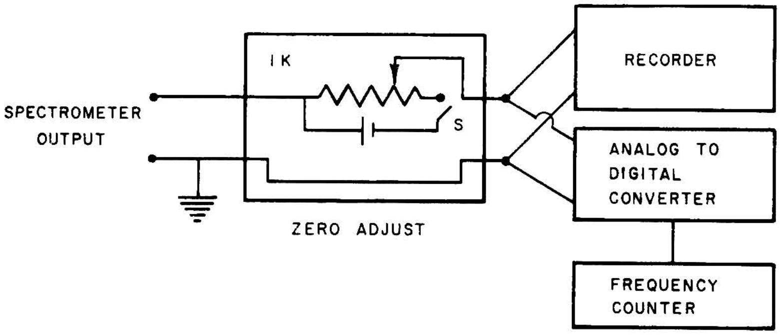


Fig. 1. NMR integrator of large dynamic range.

TABLE I
Accuracy of the Integration System for Mixtures of CF_3COOH and $(CF_3CO)_2O$

Acid in sample, %	Acid found, %
81.5	82.2
51.6	50.8
22.6	21.7

this design is a larger dynamic range than is normally available. The accuracy of the system is shown in Table I.

Rate of Esterification by Acetic Acid

The acetylations of the model alcohols were carried out under two different sets of reaction conditions and were followed by titration. When hydrochloric acid was used as catalyst, the reaction was performed in dioxane at 22°C, and the amount of acetic acid remaining in the reaction mixture was determined by titrating with 0.05*N* aqueous sodium hydroxide solution with the use of phenolphthalein as an indicator. Previous titration of mixtures of acetic acid and ethyl acetate showed that the presence of acetate does not interfere with the titration. In other experiments, trifluoroacetic acid (3 wt-%) was used as catalyst, and the reaction was conducted at 60°C. In this titration, the color of the indicator faded within 10 sec, and addition of a further small amount of the alkaline solution was needed to obtain a real endpoint. Presumably, a small amount of trifluoroacetate was formed in the reaction and hydrolyzed much faster than acetate.

Trifluoroacetylation

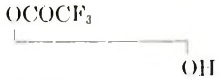
The model alcohols and poly(vinyl alcohol) samples were reacted with trifluoroacetic acid under two different sets of reaction conditions and the fluorine resonance spectra of the equilibrium reaction mixtures were observed. In all spectra the signals of trifluoroacetate groups appeared at lower field than the trifluoroacetic acid signal and their chemical shifts varied depending on their neighboring groups.

The initial conditions for esterification, followed by fluorine resonance spectroscopy as in Figure 3, are the same as those of Table IIIB below. The initial conditions for the hydrolysis, whose course is shown in Figure 4, were diester 0.68 mmole, H_2O 11.1 mmole, CF_3COOH 2.7 mmole, and an equal total volume of acetone to obtain a homogeneous solution.

RESULTS AND DISCUSSION

Each of the fluorine resonance signals can easily be assigned to the corresponding structure in the case of the mono- and dialcohols. Chemical shifts of various trifluoroacetate groups are summarized in Table II. In contrast to the proton resonance of 2,4-diacetoxypentane,[8] the fluorine resonance of the *dl*-ditrifluoroacetate appeared at lower field than that of the

TABLE II
Chemical Shifts of Various Trifluoroacetate Groups in Trifluoroacetylation of Model Alcohols

Starting alcohol	Species	Chemical shift from CF_3COOH, ppm
Isopropanol	$(CH_3)_2HCOCOCF_3$	−0.22
Pentane-2,4-diol	 $OCOCF_3$ OH	−0.30
	 $OCOCF_3$ $OCOCF_3$	−0.36
	 $OCOCF_3$ OH	−0.40
	 $OCOCF_3$ $OCOCF_3$	−0.46
Butane-2,3-diol	 $OCOCF_3$ OH	−0.62
	 $OCOCF_3$ $OCOCF_3$	−0.48
	 $OCOCF_3$ OH	−0.66
	 $OCOCF_3$ $OCOCF_3$	−0.48

meso diester. When the neighboring group was hydroxyl, the trifluoroacetate signal in both isomers shifted to higher field than for the corresponding diester.

With the triols the number of trifluoroacetate groups in different environments is large. One can expect seven different trifluoroacetate groups in the reaction of either isotactic or syndiotactic triols and eleven in the case of the heterotactic triol. It is difficult to assign all the trifluoroacetate signals in the reaction mixtures of isotactic and heterotactic trimers because of the overlapping of some peaks. In the syndiotactic trimer however, the chemical shift differences among the seven peaks were relatively large and all the peaks were clearly observed. They were assigned as illustrated in Figure 2 from a consideration of the peak positions of triester, which were already known,[6] and the change of the peak intensities with time during the esterification reaction. Given the assignment shown in Figure 2, it is found that the signals of trifluoroacetate groups adjacent to other trifluoroacetate groups are somewhat broader than the signals for trifluoroacetate groups neighboring hydroxyl groups.

From the spectrum of Figure 2 we can estimate the relative amounts of various esters. Apparently the amount of 4-substituted monoester is much less than that of 2-substituted monoester at equilibrium. It was also observed that the early rate of growth of the peak for 4-trifluoroacetate was

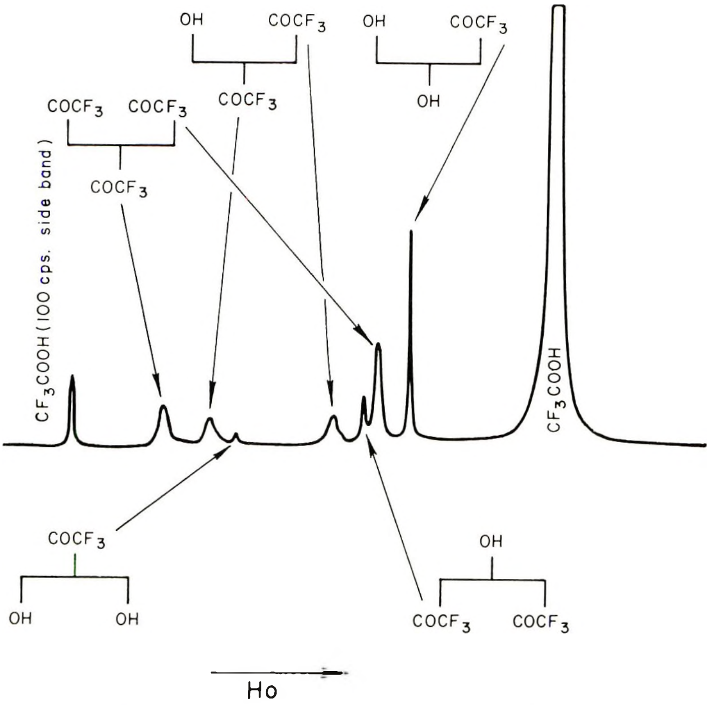


Fig. 2. Fluorine resonance spectrum of the equilibrium reaction mixture with *dl,dl*-2,4,6-heptanetriol.

much smaller than that for 2-trifluoroacetate. Therefore the hydroxyl group in the center of the triol is much less reactive than those in 2 or 6-positions. This result is consistent with the following observations on models of different chain lengths.

The overall conversion of hydroxyl groups to esters at equilibrium was estimated for the various model compounds and polymers from relative peak areas of the acid and esters obtained by integration of the spectra. For convenience in comparing the model compounds with the polymers, all hydroxyl groups were assumed to be independent, and an apparent equilibrium constant, K = [ester][water]/[acid][alcohol] was calculated as shown in Tables III. The presence of neighboring hydroxyl groups depressed the equilibrium conversion and the equilibrium constant decreased in the order isopropanol, pentane-2,4-diol, heptane, 2,4,6-triol, and poly(vinyl alcohol).

The equilibrium is shifted to the alcohol side by the presence of neighboring hydroxyl groups as in 1,3-glycols. To see if a similar effect is observed for a 1,2-glycol structure, *l*- and *meso*-butane-2,3-diols were subjected to equilibrium trifluoroacetylation under the same conditions as for the other alcohols. Chemical shifts of mono- and di-trifluoroacetates and the equilibrium constants obtained in these experiments are summarized in Tables II and IV. In 1,2-substituted compounds the relative position of mono- and diester signals is opposite to that in 1,3-substituted compounds. From

TABLE IIIA
Equilibrium Conversions and Constants of Various Alcohols in Trifluoroacetylation[a]

Alcohol	Conversion, %	K
Isopropanol	82.6	7.22
dl-Pentane-2,4-diol	73.6	4.00
meso-Pentane-2,4-diol	70.1	3.40
Heptane-2,4,6-triol (syndiotactic)	75.8	4.48
Heptane-2,4,6-triol (heterotactic)	67.0	2.80
Heptane-4,4,6-triol (isotactic)	60.2	2.08
Poly(vinyl alcohol)-C[b]	42.5	0.95
Poly(vinyl alcohol)-B[b]	41.5	0.91
Poly(vinyl alcohol)-A[b]	36.4	0.66

[a] Initial amounts of alcohol (based on hydroxyl group), trifluoroacetic acid, and water were 2.3, 11.0, and 11.6 mmole.

[b] Tacticities of poly(vinyl alcohol): A (*i* 0.59, *h* 0.30, *s* 0.11), B (*i* 0.24, *h* 0.46, *s* 0.30), C (*i* 0.16, *h* 0.46, *s* 0.38). Details of these polymer samples are given in the preceding paper.[6]

TABLE IIIB
Equilibrium Conversions and Constants of Various Alcohols in Trifluoroacetylation[a]

Alcohol	Conversion, %	K
Isopropanol	66.0	4.83
dl-Pentane-2,4-diol	50.9	2.10
meso-Pentane-2,4-diol	46.7	1.64
Heptane-2,4,6-triol (syndiotactic)	49.4	1.88
Heptane-2,4,6-triol (heterotactic)	43.5	1.42
Heptane-2,4,6-triol (isotactic)	43.2	1.36
l-Butane-2,3-diol	38.7	1.07
meso-Butane-2,3-diol	41.8	1.27

[a] Initial amounts of alcohol (based on hydroxyl group), trifluoroacetic acid, and water were 4.6, 11.0, and 11.6 mmole.

the data it is evident that the equilibrium conversion is much lower when two hydroxyl groups are attached to adjoining carbon atoms. Thus, both butane-2,3-diols had smaller equilibrium constants than the heptane-2,4,6-triols. Field and Schaefgen[9] have shown that the polyalcohol obtained from poly(vinylene carbonate) is difficult to trifluoroacetylate while poly(vinyl alcohol) is easily transformed to poly(vinyl trifluoroacetate) by treatment with trifluoroacetic acid. The present result is consistent with their observation. It should be noted that the variation of the calculated equilibrium constants for different reaction conditions is greater than the experimental error in measuring the extent of reaction. Presumably this arises because of lack of ideal behavior in the concentrated solutions or because the reaction is more complicated than was assumed. Therefore the relative values of the various equilibrium constants are more significant than their absolute magnitude.

Another interesting point is the effect of steric configuration of the molecule on the equilibrium. In the model dimers and trimers of poly(vinyl

TABLE IV
Relative Amounts of Diol, Mono- and Diesters in the Equilibrium Trifluoroacetylation of Various Diols

Alcohol	Degree of esterification, %	Ratio diester:monoester:diol[a]
dl-Pentane-2,4-diol	73.6	61.2:27.2:11.6 (54:39:7)
meso-Pentane-2,4-diol	70.1	53.9:32.6:13.5 (49:42:9)
l-Butane-2,3-diol	38.7	8.4:60.6:31.0 (15:47:38)
meso-Butane-2,3-diol	41.8	9.7:64.2:26.1 (17:49:34)

[a] The numbers in parentheses are the percentages to be expected for the observed degree of esterification if the esterification is completely random.

alcohol), *meso* isomers are esterified to a lesser extent than *dl*-isomers. A similar difference was also observed in the reaction of the polymers. In alkaline-catalyzed hydrolysis of poly(vinyl acetate), some difference was observed in the shape of time–conversion curves depending on the stereoregularity of the polymer.[10] However it was not possible to confirm a similar difference in the reaction of the model compounds, so the effect was assumed to be specific in the polymer reaction.[11] In the present trifluoroacetylation studies a difference of reactivity was observed both in the models and polymers. In order to see if a similar effect is observed in acetylation by acetic acid, acetylation of model alcohols was carried out, hydrochloric acid and trifluoroacetic acid being used as catalysts.

Acid-Catalyzed Acetylation of Model Alcohols

The isomers of pentane-2,4-diol and of heptane-2,4,6-triol were acetylated with acetic acid and hydrochloric acid in dioxane. As shown in Table V, the initial rate of acetylation of the diol is about 50% higher than that of the triol, but no difference in the rate was observed between the two diols or among the three triols. Overall equilibrium conversion was compared

TABLE V
Initial Rate and Equilibrium Constant of Acetylation of Diol and Triol Models

	Initial rate (relative), %/min.	K_1[a]	K_2[b]	K
dl-Pentanediol	0.029	2.08	0.69	1.20
meso-Pentane-2,4-diol	0.029	2.14	0.71	1.24
Syndiotactic heptane-2,4,6-triol	0.020	—	—	—
Heterotactic-heptane-2,4,6-triol	0.020	—	—	—
Isotactic-heptane-2,4,6-triol	0.020	—	—	—

[a] K_1 = [monoester][H_2O]/[diol][acid].
[b] K_2 = [diester][H_2O]/[monoester][acid].

for the two diols by titration of the unreacted acetic acid and by gas chromatographic analysis but, as shown in Table V, no significant difference was found. It was also possible to find the extent of mono and diester formation from the relative areas of the peaks in the chromatograms.

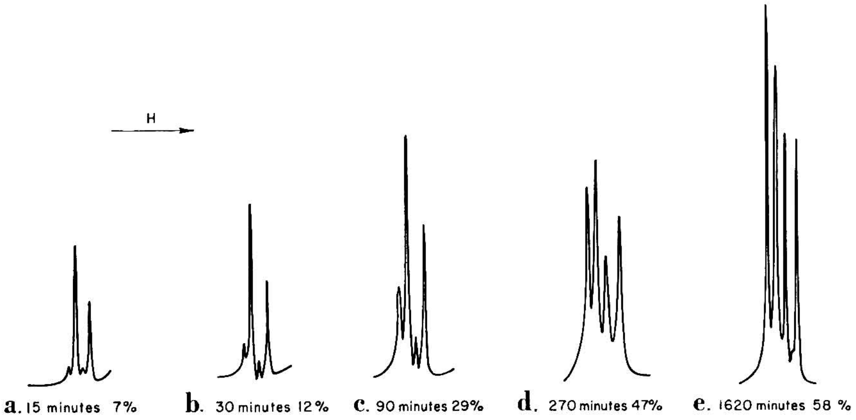
These results showed that reactivity does not depend on steric configurations in HCl-catalyzed acetylation. Similarly, when a small amount of trifluoroacetic acid was used as a catalyst and the reaction was carried out in dioxane at 60°C, no difference was observed among the initial rates of the three triols.

NMR Observations of Trifluoroacetylation of a Mixture of *meso*- and *dl*-Pentane-2,4-diol

A significant difference was observed between acetylation and trifluoroacetylation in the dependence of the rate on steric configuration. To confirm this difference and to see some details of the reaction, trifluoroacetylation of an equimolar mixture of *meso*- and *dl*-pentane-2,4-diols, and hydrolysis of an equimolar mixture of *meso*- and *dl*-2,4-di(trifluoroacetoxy)-pentane were observed by fluorine resonance spectroscopy.

The change of the fluorine resonance spectrum with time, for the trifluoroacetylation system, is shown in Figure 3. Initially two signals from the mono-esters are observed. Apparently the *dl* diol is reacting about 1.6 times as fast as the *meso* diol. Next the two diester signals begin to grow. Since the ratio of the two diester signals at equilibrium is close to that of the two monoester signals early in the reaction this suggests that the initial ratio is maintained in all subsequent processes.

The relative rate of the reverse reaction was observed in the hydrolysis reaction shown in Figure 4. The two diester signals decrease at almost the same rate as is shown by the growing rate of the two monoester signals It is rather difficult to compare the rate of hydrolysis of monoester from these spectral changes. Nevertheless after the reaction has reached



a. 15 minutes 7% b. 30 minutes 12% c. 90 minutes 29% d. 270 minutes 47% e. 1620 minutes 58 %

Fig. 3. Trifluoroacetylation of equimolar mixtures of *meso*- and *dl*-2,4-pentanediols.

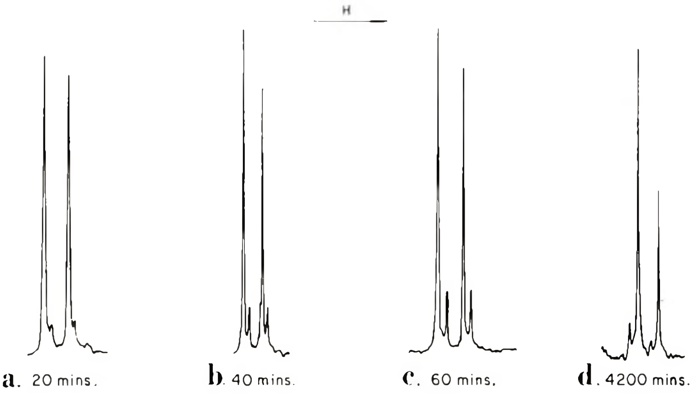


Fig. 4. Hydrolysis of equimolar mixtures of *meso*- and *dl*-2,4-trifluoroacetoxypentanes.

equilibrium (right in Figure 4) a considerable difference is observed between the two isomers. The two diester signals become very weak, and the intensity of the signal of the *dl* monoester is 60–70% greater than that of the *meso* monoester.

We have no clear explanation of the difference between acetylation and trifluoroacetylation, but trifluoroacetylation seems to be specific in its sensitivity to steric configuration.

Fluorine and Proton Resonance Spectra of Partially Trifluoroacetylated Poly(Vinyl Alcohol)

The chemical shifts of various trifluoroacetate groups in the model compounds showed that a similar magnitude of chemical shift is expected from the steric configuration of the molecule as from the neighboring hydroxyl groups. Therefore it seems rather difficult to discuss the distribution of trifluoroacetate groups along the chain of a partially esterified polymer apart from the influence of stereoregularity. When a starting polymer is stereoregular one may hope to find the distribution of trifluoroacetate groups in the partially esterified polymer. The fluorine resonance spectrum shown in Figure 5*a* is obtained from a reaction mixture by using a poly(vinyl alcohol) with a relatively high isotactic content. The three signals may arise from trifluoroacetate groups centered in three different sequences of monomer units. The degree of esterification of this polymer was estimated as 69% and the ratio of the three peak areas is approximately 0.10:0.45:0.45. This is consistent with the trifluoroacetate groups being randomly located along the polymer chain. Needless to say, this is a rather rough estimate because the original polymer is not perfectly stereoregular.

The proton resonance spectrum may also provide information on this problem. The methylene signals of poly(vinyl alcohol) and of poly(vinyl trifluoroacetate) are known to appear at $\tau = 8.60$ (in dimethyl sulfoxide) and $\tau = 7.60$ (in acetone), respectively.[12] Since the chemical shift between these two signals is relatively large, there may be a chance that the methy-

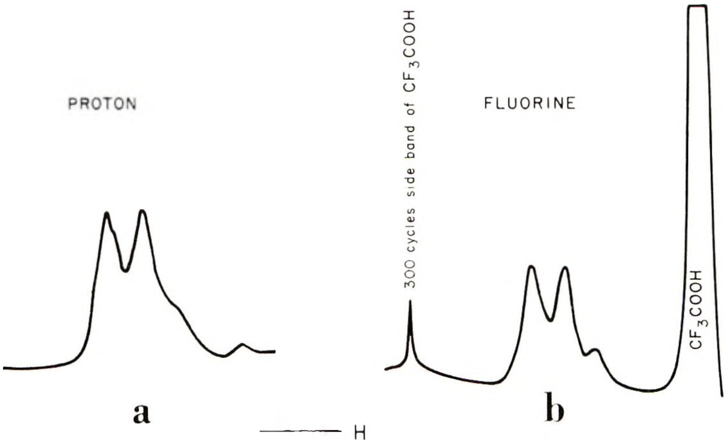


Fig. 5. Fluorine and proton resonance spectra of a trifluoroacetylation reaction mixture with an isotactic poly(vinyl alcohol).

lene group which is between hydroxyl and trifluoroacetate groups can be separately observed. Three methylene peaks were observed in the proton resonance spectrum of the copolymer as shown in Figure 5*b*. The ratio of the three peaks is very similar to that of the three trifluoroacetate signals, which also suggests the random distribution of trifluoroacetate groups. This method may be applied even for atactic samples. Since copolymer samples which have different distributions were not available no further measurements were made on this problem. A study of the copolymers obtained by various hydrolyses of poly(vinyl trifluoroacetate) may be interesting in this respect.

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Fluorine Magnetic Resonance Spectra and Tacticities of Poly(vinyl Trifluoroacetate)

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Synopsis

Fluorine magnetic resonance spectra of poly(vinyl trifluoroacetate) samples of different tacticities were investigated, along with those of model compounds. These polymers represent the first case where the line order in respect to stereostructure does not agree with that expected from the spectra of model compounds. More than four peaks were observed for signals from the trifluoromethyl groups of the polymers and the relative peak positions differed from those previously reported. The intensity ratios of the peaks were affected by the solvent employed. Therefore the spectra cannot be interpreted in terms of triad stereosequences. Seemingly longer stereosequences or other influences have to be considered to interpret the spectra.

INTRODUCTION

Three signals in the methyl regions of the proton resonance spectra of various poly(vinyl acetate) samples have been reported and attributed to triad stereosequences in the polymer.[1] The peaks were assigned to isotactic, heterotactic, and syndiotactic triad sequences in order of increasing magnetic field strength.[2,3] The stereostructure of poly(vinyl acetate) as estimated from the methyl proton signal, has been reported to be consistent with that of the derived poly(vinyl alcohol), as estimated from the latter's methine proton signal.[4] A similar but more detailed comparison has been made by using deuterated polymers, and good agreement obtained between the results for poly(vinyl acetate) and poly(vinyl alcohol).[5]

Separate signals in the fluorine magnetic resonance spectra of poly(vinyl trifluoroacetate) have been observed and attributed to the stereostructure of the polymer.[6] The three peaks were interpreted in terms of triad stereosequences and were assigned in the same order as the assignment for the methyl peaks in poly(vinyl acetate). However, the stereostructure of polymer samples calculated from the fluorine resonance spectra did not agree with those obtained from analysis of the proton resonance spectra of structurally similar poly(vinyl alcohol) samples, and thus remained in doubt.[7] After equilibrium trifluoroacetylation of model diols and triols, the observed chemical shifts for the trifluoromethyl signals suggested

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a different line order for the triad stereosequences.[8] These results led us to an examination of the proton and fluorine resonance spectra of poly(vinyl trifluoroacetate) and some model compounds.

EXPERIMENTAL

The preparative methods for the polymer samples used in this experiment have been reported on many occasions. Nevertheless an outline of the preparation of the polymers used in this study is described in view of the difference in spectra reported in previous work,[6] and our results.

Polymer A

Vinyl *tert*-butyl ether (5 vol.-%) was polymerized in toluene (95 vol.-%) at −78°C. with boron trifluoride etherate as initiator. The resultant poly(vinyl *tert*-butyl ether) was acetylated with acetic anhydride and zinc chloride in methylene chloride at 30°C. The reaction was complete within 48 hr., and a homogeneous solution of poly(vinyl acetate) was obtained. The reaction mixture was poured into water and the polymer was precipitated and then purified by repeated precipitation using methanol and water. Hydrolysis to poly(vinyl alcohol) was carried out by the usual method with a methanolic solution of sodium hydroxide.

Polymer B

A conventional polymer which was obtained from vinyl acetate (50 vol.-%) in methanol polymerized at 60°C. with azobisisobutyronitrile as an initiator. The polymer was purified and hydrolyzed in the same manner as for polymer A.

Polymer C

Vinyl formate was polymerized in methyl formate (50 vol.-%) at −78°C. with triethylboron as an initiator. The resultant poly(vinyl formate) was purified by solution in acetonitrile and precipitation with methanol. It was then dissolved in dioxane and hydrolyzed with a methanolic solution of sodium hydroxide.

Trifluoroacetylation of Heptane-2,4,6-triol

To 1 g. of each (*meso-meso*, *meso-dl*, and *dl-dl*) heptane-2,4,6-triol[9] was added 20 ml. of trifluoroacetic acid. After standing for 24 hr. the acid was distilled off along with a small amount of water formed by the esterification, then 2,4,6-tri(trifluoroacetoxyheptane) was distilled under reduced pressure at temperatures below 200°C. Only the *dl-dl*(syndiotactic) triester was obtained as crystals. After redistillation, each triester was examined by infrared and proton resonance spectroscopy. There was no evidence for any unreacted hydroxyl group and hence the triesters were used without repeated esterifications.

Trifluoroacetylation of Poly(vinyl Alcohol)

Three different poly(vinyl alcohol) samples used in the equilibrium esterification[8] and described above were also used in this experiment. Since trifluoroacetic anhydride tends to give insoluble products, and because it also has a fluorine resonance signal very close to those of the various trifluoroacetates, no anhydride was used in the esterification. Poly(vinyl alcohol) was treated with a thirtyfold excess of trifluoroacetic acid. Reaction mixtures were heated to 70°C. for 4 hr. and then poured into petroleum ether to precipitate the polymer. The product was purified by reprecipitation from acetone to petroleum ether and dried under vacuum. The esterification procedure was repeated three times.

NMR Measurement

Proton resonance spectra were obtained at 100 MHz and the chemical shifts reported in ppm from internal tetramethylsilane. Fluorine resonance spectra were obtained at 94.1 MHz and the chemical shifts reported in ppm from internal trifluoroacetic acid.

RESULTS

Fluorine resonance spectra of the three types of 2,4,6-tri(trifluoroacetoxyheptane) were obtained in trifluoroacetic acid and in acetone. Chemical shifts of the trifluoroacetate groups of the trimers and dimers* relative to that of the acid are summarized in Figure 1. Trifluoroacetic acid was used as an external reference for the acetone solutions, and a correction was made for the difference in diamagnetic susceptibility. Unfortunately, differences in solvent polarizability also affect fluorine chemical shifts,[10] so only the relative difference in chemical shifts can be compared. The proton chemical shifts of the CH_3 groups for the trimers and dimers are shown in Figure 2. The spectra of the methylene and methine protons were similar to those reported for the corresponding acetates[11] and were not analyzed.

In both acetone and trifluoroacetic acid the fluorines of the central ester group of the syndiotactic trimer came into resonance at about 0.16 ppm lower field than in the *meso-dl* (heterotactic) trimer. The corresponding fluorine signal of the *meso-meso* (isotactic) trimer appeared at about 0.11 ppm higher field than did that of the heterotactic trimer. Thus the line order is syndiotactic, heterotactic, and isotactic with increasing field strength. This order is consistent with the results for the dimer models which showed the fluorine signal of the *dl*-diester at lower field than in the *meso*-diester. It is noted that the line order of the 4-CF_3 signal of 2,4,6-tri(trifluoroacetoxyheptane) with respect to steric configuration is contrary to that of the 4-CH_3 signal of the 2,4,6-triacetoxyheptane isomers.[2] The shielding effect of an anisotropic functional group is similar for both proton and fluorine resonance, but the fluorine resonance position is much more

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* Chemical shifts for the dimers were obtained in the equilibrium acetylation studies,[8] where some water was present in the solvent.

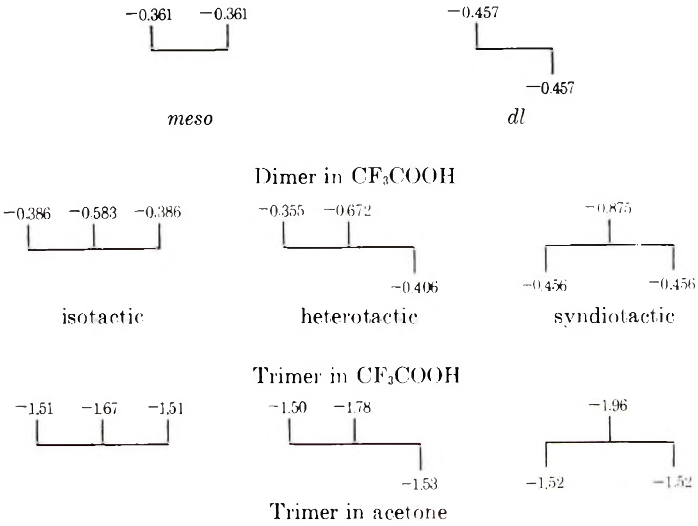

Fig. 1. Chemical shifts of fluoromethyl groups of model dimers and trimers (in ppm from trifluoroacetic acid as reference).

sensitive to inductive effects along bonds, and through space, than the proton resonance position. Therefore the different order of chemical shifts with stereostructure does not necessarily indicate a change in the preferred conformation of the trifluoroacetoxy compound relative to the corresponding acetoxy compound. In fact a similarity of the methylene and methine spectra between the two compounds and the similar order of chemical shifts for the terminal methyl groups of the isomers in the two series suggest that the conformations may be similar for the corresponding isomers. If this is true, then the differences of the relative chemical shifts for the acetyl and trifluoroacetyl groups can be attributed to the differing importance of anisotropic and inductive effects upon proton and fluorine chemical shifts.

The fluorine resonance spectra of equilibrium esterification mixtures of poly(vinyl alcohol) with trifluoroacetic acid showed that the remaining

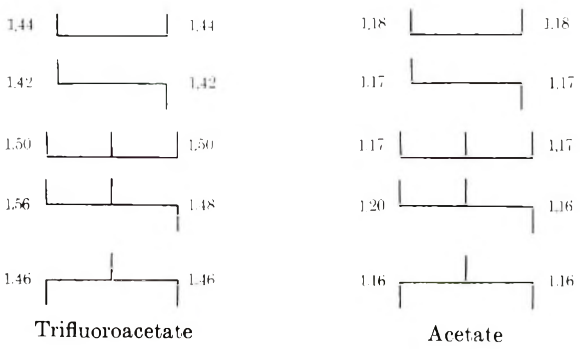

Fig. 2. Chemical shifts of terminal methyl protons of model dimers and trimers (in ppm from tetramethylsilane).

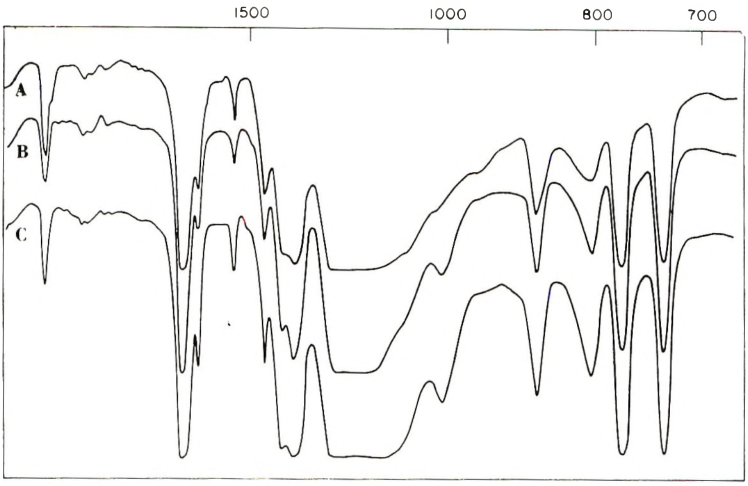

Fig. 3. Infrared spectra of various poly(vinyl trifluoroacetate) samples.

hydroxyl groups in the polymer had a large effect upon the chemical shifts of neighboring trifluoroacetate groups. Therefore much attention was paid to insure a complete transformation of poly(vinyl alcohol) to poly(vinyl trifluoroacetate) in order to observe the effect of the stereostructure upon the spectra as distinct from the effect of the remaining hydroxyl groups. Although the esterification was repeated three times, infrared and proton magnetic resonance spectra showed that the reaction was essentially complete after the first repetition. Infrared spectra of three poly(vinyl trifluoroacetate) samples prepared by esterification are shown in Figure 3. These spectra are similar to each other except for a small difference at 1010 cm.$^{-1}$ and agree with that previously reported for poly(vinyl trifluoroacetate).[12] No hydroxyl absorption is seen at about 3300 cm.$^{-1}$ in the spectra. Therefore the concentration of hydroxyl groups should be very low, if any, and would not affect the fluorine resonance spectra of the polymers. Only the intensity of an absorption band at 1010 cm.$^{-1}$ seems to be dependent upon the stereostructure of the polymer. The shape and position of this band resembles a crystallization sensitive band at 1026 cm.$^{-1}$ of poly(vinyl formate) which relates to the syndiotactic structure of the polymer.[13] Details of this 1010 cm.$^{-1}$ band will be discussed elsewhere along with structure-property relationship for poly(vinyl trifluoroacetate).

In Figure 4 are shown the fluorine resonance spectra of 10% solutions of three polymer samples in acetone at room temperature. Splitting into separate peaks is observed, as reported previously at 56.4 MHz for polymer samples analogous to ours.[6] However, at least five peaks are observed in the present spectra. A striking difference lies in the fact that the principal peak of the polymer of highest isotacticity does not correspond to the peak at lowest field in an atactic polymer, but rather, corresponds to one of the two principal peaks of the atactic polymer. Of these two peaks, the one at lower field increases in relative intensity with increasing isotactic content of

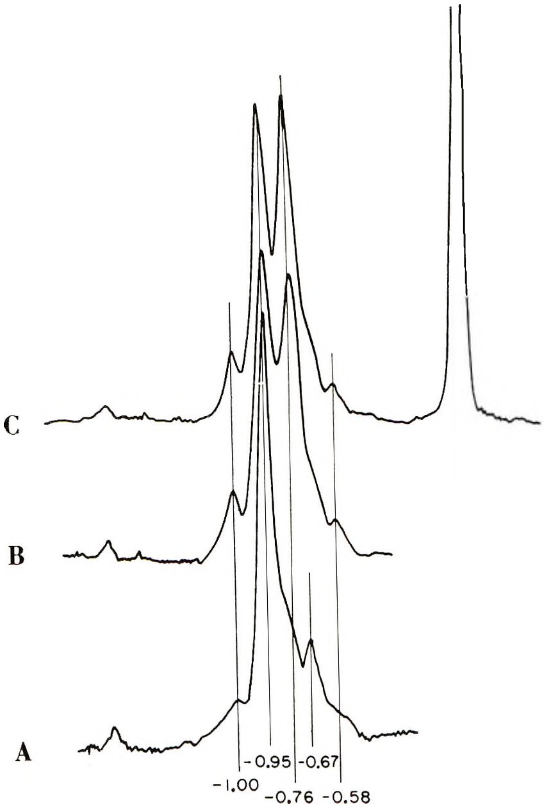

Fig. 4. Fluoromethyl resonance signals of various poly(vinyl trifluoroacetate) samples in acetone at room temperature.

the polymer and that at higher field does so with increasing syndiotactic content of the polymer. If these lines are assigned to isotactic and syndiotactic triad sequences, respectively, the line order is contrary to that expected from the spectra of the dimer and trimer models. In the proton spectra of the various vinyl polymers, no such reversion of the line order has been observed between model compounds and polymers.

Another difference between the present and previous results is that the line intervals (in Hz) observed in the present study were of approximately the same magnitude as those previously reported despite the difference in frequency employed. The only apparent difference between the two sets of measurements was the use of 5% trifluoroacetic acid as internal reference in our samples. Although it seemed rather unlikely that the presence of a small amount of the acid in the solution could affect the line spacings, the spectrum of the atactic polymer in pure acetone was observed using the acid as an external reference. No difference was observed in the spacing between lines with internal or external referencing.

In the top half of Table I are shown the tacticities of the poly(vinyl acetate) samples from which the poly(vinyl trifluoroacetate) polymers were

TABLE I
Tacticities of Polymer Samples Estimated from Their Proton Resonance Spectra

Sample		Tacticity		
		I	*H*	*S*
A		0.59	0.30	0.11
B		0.24	0.46	0.30
C		0.16	0.46	0.38
I-A$_3$	(A)[a]	0.58	0.35	0.07
H-B	(B)[a]	0.29	0.41	0.30
S-A	(D)[a]	0.11	0.46	0.43

[a] Data of Harris et al.[14]

prepared for this study. These tacticities were determined from the relative areas of the acetoxy proton signals of poly(vinyl acetate).[2,3] In the lower half of Table I are shown tacticities for samples prepared in the same way as those of Pritchard et al., by another group of workers from the same laboratories.[14] Tacticities of these samples were determined from analysis of the methylene and methine proton signals of the derived poly(vinyl alcohol).[15] The two sets of polymers are essentially of identical tacticity. No differences in the stereochemistry of the polymer chain are expected to result from the preparation of the trifluoroacetate via the acetate and alcohol. Therefore the differences in peak positions observed for the two sets of polymer samples cannot be ascribed to a structural difference between them.

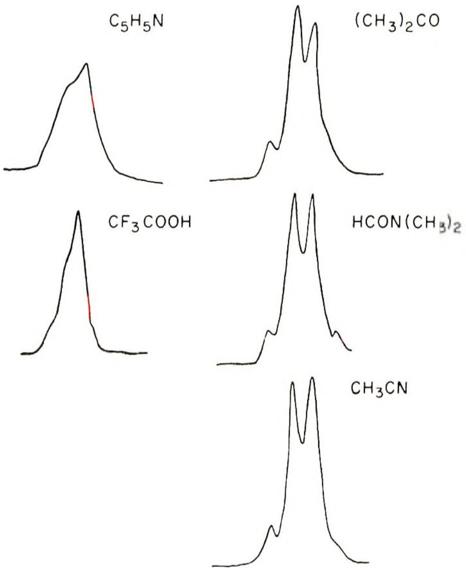

Fig. 5. Effect of solvent on the spectrum of polymer sample B. All spectra were run at room temperature except that with trifluoroacetic acid as solvent, where a temperature of 60°C. was required to obtain a homogeneous solution.

In the spectrum previously reported for the polymer of highest isotacticity the presence of a weak shoulder at lowest field is clearly noticeable, and the peak profile is very similar to that obtained by us.[6] Therefore we may safely conclude that the principal peak of the most isotactic polymer corresponds to that assigned by them to the atactic polymer. The previous measurements may have been handicapped by the lower magnetic field available and by use of an external reference, which makes it more difficult to achieve good resolution.

The effect of a variety of solvents upon the polymer spectra was examined and is illustrated in Figure 5. It was found that not only the peak separations but also the ratio of peak areas were affected by the solvent. The relative intensity of one of the principal peaks at high field to that at low field increased by changing solvent in the order; acetone, dimethyl formamide, acetonitrile. Since all solvents used in this experiment were carefully purified and dried, and 5% trifluoroacetic acid was added as an internal reference, partial hydrolysis of the trifluoroacetate groups was unlikely to occur. As a confirmation of this view the fluorine resonance spectrum was obtained for a partially hydrolyzed atactic polymer and was found to be quite complicated.

DISCUSSION

It appears that the trifluoromethyl resonance signals of poly(vinyl trifluoroacetate) cannot be adequately explained in terms of triad stereosequences since more than three peaks are observed. It is also unlikely that an adequate fit of the observed spectra can be obtained by considering pentad sequences. The effect of longer range ordering is most likely to be fine structure within the isotactic, syndiotactic, and heterotactic peaks rather than additional peaks beyond them. It would also be difficult to devise a plausible scheme in terms of local stereosequences which gives rise to the change in relative intensity of the fluoromethyl resonance signals with change in solvent. Seemingly, a long-range effect, perhaps related to the secondary structure of the polymer in solution, is important in affecting the chemical shift of the trifluoromethyl groups.

One possible reason for the complexity of the spectra is the interaction between the side chains of a polymer molecule. Such an interaction seems to play an important role in a few characteristic properties of vinyl trifluoroacetate such as some stereoregulation in polymerization of the monomer,[12] the strong lateral order in the polymer,[16] and the thermal reversible gelation of the polymer solution in trifluoroacetic acid.[17] It is noteworthy that solution polymerization of the monomer gave less water resistant poly(vinyl alcohol) while highly water resistant poly(vinyl alcohol) was obtained from the bulk polymerization.[12,18] This evidence suggests that some type of interaction or association of the monomer was disturbed by introduction of the solvent, as has been observed previously in the polymerization of vinyl formate.[19]

To see if a change in the average conformation of the polymer molecule can affect the spectrum, the atactic polymer was observed in the mixed solvent system acetonitrile (solvent)–dichloromethane (nonsolvent). The polymer solution became less viscous and the resonance signal became sharper with increasing content of dichloromethane in the mixed solvent but the ratio of peak intensities was not affected.

Another factor to be considered in interpretation of the spectra is the structural irregularities in the polymer. The presence of head-to-head structure was clearly established in poly(vinylidene fluoride) from its fluorine resonance spectrum.[20] In the present case, the atactic polymer derived from vinyl acetate polymerized at 60°C. is known to have approximately one and a half 1,2-glycol units per hundred monomer units.[21] This might cause a discernible effect on the spectrum. However, poly(vinyl alcohol) derived from vinyl formate polymerized at -78°C. has only 0.2 mole-% of 1,2-glycol units.[22] No 1,2-glycol units were detected in the poly(vinyl alcohol) sample derived from vinyl *tert*-butyl ether.[23] Nevertheless all peaks present in the spectrum of the atactic polymer were also present in the spectrum of the isotactic polymer. Therefore, none of the peaks in the spectra can be ascribed to deviation from the regular head-to-tail structure. Branching in poly(vinyl alcohol) has also been assumed as another irregularity[7,24,25] but is rejected as a significant factor for a variety of reasons. At the present time, therefore, it is not possible to interpret the details of the fluorine resonance spectra of various poly(vinyl trifluoroacetate) polymers.

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Polymerization of Cyclobutene Rings. VI. Influence of the Organometallic Compound of the Ziegler-Natta Catalysts on the Mechanism of Polymerization of Cyclobutene and 3-Methylcyclobutene

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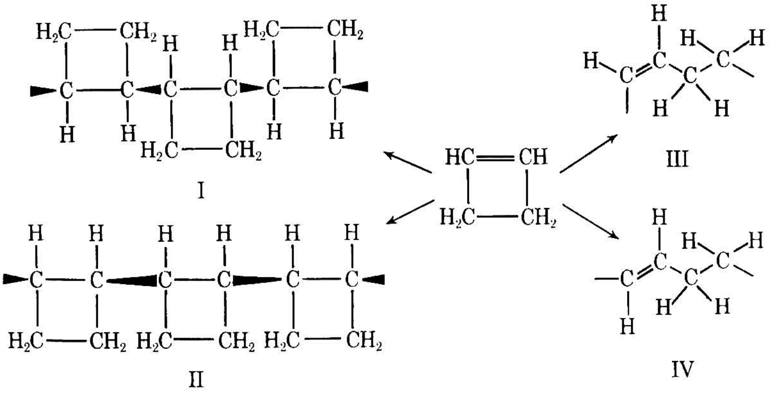
Synopsis

The polymerization of cyclobutene and 3-methylcyclobutene in the presence of Ziegler-Natta catalysts was studied especially in view of the influence of the metal alkyls on the course of polymerization. Several metal alkyls of the main groups I–IV of the periodic table of elements were investigated, vanadium halides being used as transition metal compounds. The influence of the metal alkyl was found not to be limited to the activity of the catalyst system, which is maximum for aluminum alkyl, but also to extend to the polymerization mechanism. Depending on the metal alkyl, the two cyclobutene monomers can in fact be polymerized by two different mechanisms, i.e., by opening of the double bond or by ring opening with retention of the double bond. No migration of the double bond is involved in these polymerizations. An interpretation of the different experimental observations is tentatively proposed, and the relationship with the stereospecific polymerization of the α-olefins is stressed.

INTRODUCTION

In preceding studies in this laboratory[1,2] the polymerization of cyclobutene was found to be a suitable tool for the investigation of the mechanism of the stereospecific polymerization of olefins in general. The polymerization of cyclobutene monomers is in fact very sensitive to modifications of the catalyst systems. Even small variations of the composition of the Ziegler-Natta type catalysts, which are the most effective in these polymerizations, can determine significant changes in the polymerization mechanism, leading to polymers that differ in their chemical as well as steric structures. Four main types of polymers derived from cyclobutene could be recognized, and the four following structures (see next page) were attributed to them (the steric structures of the saturated polycyclobutene types I and II were tentatively assigned). (I) *erythro* diisotactic polycyclobutene; (II) *erythro* disyndiotactic polycyclobutene; (III) *cis* polybutenamer (*cis*-1,4-polybutadiene); (IV) *trans* polybutenamer (*trans*-1,4-polybutadiene).



The polymers having saturated polycyclobutene structure are the result of a polymerization via opening of the double bond of cyclobutene. The polymers having the unsaturated structure of polybutenamers (corresponding to 1,4-polybutadiene), on the contrary, derive from a ring-opening polymerization with retention of the double bond. This twofold aspect relates the cycloolefin polymerizations to the coordinate polymerizations of α-olefins and of conjugated diolefins.

Table I illustrates some of the most typical polymerizations of cyclobutene previously explored in this laboratory. It appears that the above types of polymers can be obtained by varying the transition metal of the catalyst system or the environment this metal operates in. The most significant variations are induced by the transition metal, which determines the chemical structure of the polymers. The environment of the transition metal, i.e., the groups bound to it, the relative amount of halogen atoms of the catalyst system, its degree of dispersion (insoluble, colloidally dispersed, or dissolved) and the nature of the diluent, show scarce effect on the

TABLE I
Some Examples of Cyclobutene Polymerizations Previously Described[a]

Catalyst system	Structure of the polymer	Reference
$CrO_2Cl_2/AlEt_2Cl$/toluene	Crystalline I only	2
$CrAc_3/AlEt_2Cl$/toluene	Crystalline I only	2
$VCl_4/AlEt_3/n$-heptane	Crystalline I only	2
$VAc_2Cl_2/AlEt_2Cl$/toluene	Crystalline I only	2
$VAc_3/AlEt_2Cl$/toluene	Crystalline II only	1, 2
$VO(OBu)_3/AlEt_2Cl$/toluene	Crystalline II only	2
$TiCl_4/AlEt_3/n$-heptane	Predominantly III amorphous	1
$TiCl_4/AlEt_3$/toluene	Predominantly IV crystalline	2
$MoCl_3/AlEt_3$/toluene	Predominantly III amorphous	2
Ni-π-allyl bromide/EtOH	Crystalline I only	6
$RhCl_3/H_2O$	Crystalline I only	3
$RuCl_3/H_2O$	III + IV amorphous	4
$RuCl_3$/EtOH	Crystalline IV only	4

[a] Et = ethyl; Bu = n-butyl; Ac = acetylacetonate. The numbers (I–IV) refer to the reaction scheme.

chemical structure of the polymer, but can induce significant variations of its steric structure.

The influence exerted by the metal of the organometallic compound used in the preparation of the Ziegler-Natta type catalyst systems on the polymerization of cyclobutene has been unknown until now. The present paper describes investigations of this factor. In addition to cyclobutene, 3-methylcyclobutene was also studied.

RESULTS AND DISCUSSION

The transition metal compounds used for these investigations are vanadium halides in a high valence state, i.e., VCl_4 and $VOCl_3$. The organometallic compounds are fully alkylated metals of groups I, II, III, and IV of the periodic table of elements. The molar ratios between the organometallic compound and the transition metal of the catalyst system exert some influence on the cyclobutene polymerization, especially in the low ratio region (<2). This factor was not thoroughly investigated, and relatively high molar ratios ($2.5 \div 5$) were chosen. The main results are listed in Table II. They show that also the metal of the organometallic compound has a decisive influence on the polymerization mechanism of cyclobutene and 3-methylcyclobutene.

Organometallic compounds, like $AlEt_3$, $AlEt_2Cl$, or *n*-BuLi, are completely inactive in the cycloolefin polymerization, provided that they are employed in the absence of a transition metal compound.[3,7]

The polymerization of cyclobutene monomers with typical Ziegler-Natta catalysts never involves migration of the double bond, e.g., the ring-opening polymerization of cyclobutene always leads to polymers having 1,4-polybutadiene structure, whereas the analogous polymerization of 3-methylcyclobutene always yields polymers having 1,4-polypentadiene structure. Moreover, according to a recent publication from this laboratory,[5] the ring-opening polymerization of 1-methylcyclobutene in the presence of a catalyst prepared from tungsten halides and organoaluminum compounds provides a polymer built up by (partially cyclized) 1,4-isoprene units. On the other hand, polymers obtained by opening of the double bond of 3-methylcyclobutene have their methyl group still in the 3 position.

Unlike the polymers obtained from cyclobutene, all those prepared from 3-methylcyclobutene are amorphous. This holds for those having saturated poly-3-methylcyclobutene as well as those having 1,4-polypentadiene structures. It is the author's opinion, mainly based on analogies found in the infrared spectrum of crystalline polymers of cyclobutene and of the corresponding amorphous polymers of 3-methylcyclobutene, that the lack of crystallizability of the polymers obtained from 3-methylcyclobutene is due to the failing stereoregularity of the tertiary carbon atom in the 3 position, to which the methyl group is bound. The configuration of this tertiary carbon atom exists prior to the polymerization and is not induced during the polymerization itself. Starting from a racemic monomer, in order to produce a completely stereoregular and hence crystallizable poly-

TABLE II

Polymerization of Cyclobutene and 3-Methylcyclobutene with Catalysts Prepared from Vanadium Halides and Organometallic Compounds of Different Metals

	Catalyst system[a]					Polymer structure		
							Alkenamer units[c]	
Monomer	Organometallic compound RM	Vanadium halide VX	Molar ratio, RM/VX	Solvent	Polymer yield, %	Cyclic units, %[b]	*trans*, %	*cis*, %
Cyclobutene	$AlEt_3$	VCl_4	2.5	*n*-Heptane	100	99	1	0
Cyclobutene	$BeEt_2$	VCl_4	3	Toluene	100	>70	25	Trace
Cyclobutene	LiBu	VCl_4	3.5	Toluene	32	~ 0	~50	~50
3-Methylcyclobutene	$AlEt_3$	VCl_4	2.5	*n*-Heptane	37	90	10	0
3-Methylcyclobutene	$GaEt_3$	VCl_4	3	*n*-Heptane	25	90	6	4
3-Methylcyclobutene	$BeEt_2$	VCl_4	3	Toluene	17	85	12	3
3-Methylcyclobutene	$MgEt_2$	VCl_4	3	Toluene	14	94	6	0
3-Methylcyclobutene	LiBu	VCl_4	5	*n*-Heptane	3	~ 0	~55	~45
3-Methylcyclobutene	$ZnEt_2$	VCl_4	3	Toluene	Trace	—	—	—
3-Methylcyclobutene	$SnBu_4$	VCl_4	3	*n*-Heptane	0	—	—	—
3-Methylcyclobutene	$SiMe_4$	VCl_4	3	Toluene	0	—	—	—
3-Methylcyclobutene	$AlEt_3$	$VOCl_3$	3	Toluene	85	88	12	0
3-Methylcyclobutene	$BeEt_2$	$VOCl_3$	3	Toluene	29	70	20	10
3-Methylcyclobutene	LiBu	$VOCl_3$	3	Toluene	2	~ 0	~40	~60

[a] Polymerization conditions: 20 hr at −20°C; 25 parts of solvent/part of monomer; 20 moles of monomer/mole of V halide.

[b] Cyclobutylene units in the case of cyclobutene, 3-methylcyclobutylene units in that of 3-methylcyclobutene.

[c] 1,4-Butadiene units in the case of cyclobutene, 1,4-pentadiene units in that of 3-methylcyclobutene.

mer, the catalytic centers should be able to exert stereoselectivity with regard to this carbon atom, in addition to the stereospecificity they exert with respect to the carbon atoms of the double bond. Such a stereoselectivity seems to be lacking, indicating that the tertiary carbon atom in the 3 position is not involved in the stereoregulating coordination of the double bond of the monomer to the metal of the catalytic centers. However, it cannot be excluded *a priori* that the lack of crystallizability of 3-methylcyclobutene polymers is due to lack of stereoregularity in the succession of tertiary carbon atoms of the main chains, or to some extent of head-to-head enchainment along with the usual head-to-tail enchainment, or finally to difficulty in crystallization due to the bulkiness of the monomer units.

The mechanism of the polymerization of cyclobutene monomers certainly depends in a complex manner on the metal forming the organometallic compound used for the preparation of the Ziegler-Natta catalysts. Two important experimental facts likely reveal the existence of at least two catalytic factors influencing the course of polymerization. The first fact is that the polymer yield obtained from cyclobutene or 3-methyl cyclobutene in the presence of catalysts prepared from VCl_4 or $VOCl_3$ depends on the metal of the organometallic compound used in the catalyst preparation in the following characteristic manner. $AlEt_3 > GaEt_3 > BeEt_2 > MgEt_2 \gg LiBu > ZnEt_2 > SnBu_4$ and $SiMe_4$.

The second is that some of these catalysts generally yield polymers having essentially a saturated polycycloolefin structure, i.e., one derived by the opening of the double bond of the cyclobutene monomer, whereas some others preferentially induce the ring-opening polymerization to yield unsaturated polyalkenamers. In the above runs the highly active catalysts preferably induce polymerization via opening of the double bond and those having low activity generally promote ring-opening polymerization.

Extensive experimental work carried out over a period of many years in our laboratories on Ziegler-Natta catalysts* allows one to distinguish three classes of metal alkyls with respect to their reactivity in alkylating transition metal compounds: (*a*) metal alkyls having no or very low alkylating power (metal alkyls of tin and silicon belong to this class); (*b*) metal alkyls exerting a very high alkylating power, e.g., those of lithium and of zinc,[8] but in the presence of which the reductive decomposition of the transition metal-alkyls occurs very rapidly; (*c*) Metal alkyls, like those of aluminum, gallium, beryllium, and magnesium, having intermediate alkylating power, in the presence of which the reduction of the transition metal halides proceeds slowly.

The catalytic activity in the polymerization of unsaturated monomers is related in a complex manner to the alkylating power of the metal alkys used in the catalyst preparations. Actually, the metal alkyl compounds of the

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* An analogous pattern of metal alkyl dependence of polymerization activity is known also for the stereospecific polymerization of propylene. A quantitative ralationship of this type was recently reported,[8] e.g., for the case of catalysts prepared from VCl_3 and metal alkyls.

first of the above three classes form catalysts that are practically inactive, due to their inability to form transition metal–alkyl bonds necessary for the anionic coordinate polymerization. The metal alkyls of the second class yield very unstable transition metal alkyls and hence poorly active catalysts. The metal alkyls of the third class form transition metal–alkyl bonds that are much more stable, probably due to the formation of bimetallic complexes between transition metal compound and metal alkyl[9–11] which prevent the decomposition of such bonds.

The stability of these bonds not only confers long lifetimes to the catalytic centers, thus allowing high monomer conversion to polymer, but also allows stereospecific vinyl-type polymerization of the cyclobutene monomers, thus relating the above-stressed experimental facts. Actually, in the present case also, the most active catalysts are those prepared with the use of metal alkyls of aluminum, gallium, beryllium, and magnesium, characterized by fairly good alkylating power as well as by strong complexing capacity. These catalysts, which are supposed to contain the most stable bimetallic complexes, are also those which polymerize the present cyclobutene monomers via opening of the double bond. Scarcely active catalysts are obtained by using *n*-BuLi* or $ZnEt_2$, whereas from $SnBut_4$ or $SiMe_4$ catalytically inactive products are obtained.

It may therefore be concluded that the polymerization of the present cyclobutene monomers via opening of the double bond follows a pathway which is very similar to that of the stereospecific polymerization of the α-olefins and is likely to proceed through a mechanism of the same type. The mechanism of the ring-opening polymerization, on the contrary, which is certainly quite different, is not well understood so far.

EXPERIMENTAL

Materials

The solvents (toluene and *n*-heptane) were pure grade products, refluxed over metallic Na, distilled, and stored under dry N_2. The V halides (VCl_4 and $VOCl_3$) are freshly distilled pure grade products. The metal alkyls (except for *n*-BuLi which was used in *n*-pentane solution) were undiluted

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* In the case of Li alkyls another aspect should be taken into account. Li alkyls are *per se* good complexing agents, but they cannot display this property in the presence of V halides owing to their high tendency to form Li halides. As long as V–Cl bonds are available (especially on the surface of the V compound) the formation reaction of LiCl hinders the formation of the complex. Only when all the accessible halogen has been consumed does formation of a (halogen-free) complex between V and Li become possible. According to a previous paper from this laboratory,[2] however, halogen-free catalysts, e.g., those prepared from $VO(OBu)_3$ and $AlEt_3$ or from VAc_3 and $AlEt_3$, exhibit only low catalytic activity in the cyclobutene polymerization and yield polymers having exclusively polybutadiene structure. This analogy may suggest that the polymerization mechanism of cyclobutene monomers, with V as transition metal, is also regulated by the presence or absence of halogen in the catalytic centers.

products of at least 90% purity, the impurities being mainly monoalkoxides and, in lower concentration, the corresponding monohydrides.

Cyclobutene was prepared from 1,3-propylene glycol over 1,3-dibromopropane, 1,1-dicarboxyethylcyclobutane,[12] cyclobutanecarboxylic acid,[12] aminocyclobutane,[13] *N*-dimethylaminocyclobutane,[14] *N*-trimethylammoniumcyclobutane iodide,[15] and Hofmann elimination of this last.[15] The overall yield, considering the recovered amino cyclobutane, was 9%. The raw product was purified by washing with aqueous hydrochloric acid, drying over NaOH, and twofold distillation at low temperature. The cyclobutene proved butadiene-free.

3-Methylcyclobutene was prepared by photoisomerization of pentadiene (*cis–trans* mixture) according to Srinivasan.[16] After a 28-day irradiation of a 2% cyclohexane solution with a convenient UV lamp, pentadiene was converted for 25% to 3-methylcyclobutene. The purification to a 98–99% pure product was accomplished by fourfold rectification in a Todd column.

Polymerization Procedure

The runs were carried out in a three-necked glass vessel, provided with mechanical stirrer, nitrogen inlet, and dropping funnel with cooling jacket. About 80% of the solvent and the V halide were introduced into the vessel swept with N_2 and cooled led to −20°C. The metal alkyl was added to the stirred solution. Immediately afterwards the cooled solution of the monomer in the remaining solvent was dropped over a period of 5 min from the funnel to the stirred catalyst mixture. After 20 hr the polymer was precipitated with an excess of methanol acidified with HCl. The polymer was washed first with aqueous NH_4Cl–NH_3 solution, then with acidified methanol, finally with pure methanol. It was dried under vacuum.

Analysis of the Polymer

The composition of the 3-methylcyclobutene polymers was determined on films from benzene, the infrared absorptions of the bands at 10.35 and 7.15 μ, characteristic respectively of *trans* and *cis* unsaturations (corresponding respectively, to *trans*- and *cis*-1,4 pentadiene units) being measured. Values of 15.2×10^4 cm^2/mole (*trans*) and 0.82×10^4 cm^2/moles (*cis*) were used for the coefficients. As 1,2- or 3,4-pentadiene and other units were virtually absent, the difference to 100% was attributed to 3-methylcyclobutene units.

The absorption coefficients used in the case of the cyclobutene polymers are 10×10^4 cm^2 mole (*trans*-1,4 butadiene units) and 0.82×10^4 (*cis*-1,4 butadiene units), and the technique was the same.

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Polymerization of Cyclobutene Rings. VII. Polymerization of Bicyclo[4,2,0]octa-7-ene and Bicyclo[3,2,0]hepta-2,6-diene with Ziegler-Natta Catalysts and with Group VIII Metal Halides

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Synopsis

The polymerization of bicyclic olefins containing a cyclobutene and a higher-membered ring was studied by using Ziegler-Natta systems as well as group VIII metal halides as catalysts. Only the cyclobutene moiety of the monomers proved reactive in polymerization, whereas the higher-membered ring moieties enter unchanged in the polymer chains as side groups. In spite of the considerable bulkiness of the monomers, homopolymerization by opening of the double bond as well as by ring opening take place readily. Steric isomerism of the monomer units and the problem of the site of opening of the cyclobutene ring are discussed.

INTRODUCTION

The first publication of this series[1] reported the possibility of polymerizing cyclobutene stereospecifically by opening of the double bond or by ring opening, depending on the transition metal of the Ziegler-Natta catalyst. The investigations were successively extended to many groups of this type of catalysts and several relationships existing between catalyst composition and polymerization mechanism were elucidated.[2] The possiblity of stereospecific polymerization of cyclobutene by opening of the double bond or by ring opening also by use of simple Rh or Ru halides[3,4] in protic solvents revealed the parallel between the polymerization mechanism of these catalysts and of the Ziegler-Natta catalysts.

In addition to cyclobutene, 1-methylcyclobutene[5] and 3-methylcyclobutene[4,6] were also studied, which contributed to the understanding of the polymerization mechanism, particularly with regard to the influence exerted by the metal alkyls used in the preparation of the Ziegler-Natta catalysts. The present contribution faces the problem of the relative reactivity of different-membered rings contained in the same molecule by examining bicyclic olefins containing a cyclobutene ring. The homopolymerization of such ring systems also allowed us to verify the different path-ways of cycloolefin polymerizations in the case of sterically hindered, bulky monomers. Another problem investigated concerns the bond which is cleaved in the monomer during the ring-opening polymerization. Bicyclic monomers containing a cyclobutene ring actually appear particularly suitable for clarifying this problem, because one of the single bonds of the cyclobutene ring may be easily recognized since it participates in both ring moieties.

EXPERIMENTAL

Materials

The transition metal compounds were pure grade commercial products, except for π-allyl Ni bromide prepared from biscyclooctadiene Ni(O) and allyl bromide according to Wilke.[7] VCl_4 was freshly distilled before its use. The organo aluminum compounds were undiluted, and were at least 90% pure (the impurities being mainly the respective monoalkoxides and, in smaller amounts, the monohydrides). Toluene was a pure grade product, refluxed over Na metal, distilled, and stored under dry N_2.

Bicyclo[4,2,0]octa-7-ene was prepared by photoisomerization of cyclooctadiene-1,3 according to Dauben and Cargill.[8] Bicyclo[3,2,0]hepta-2,6-diene was analogously prepared by photoisomerization of cycloheptatriene-1,3,5.[9,10] The monomers were purified by preparative gas chromatography; their purity was 99%.

Polymerization Procedure

The polymerizations in the presence of Ziegler-Natta catalysts were run in glass vessels under nitrogen at −20°C. The catalysts were prepared in the polymerization vessel by adding the organo aluminum compound to the stirred solution (or suspension) of the transition metal compound in toluene. Immediately afterwards, the monomer dissolved in a small amount of toluene was dropped within a few minutes from a cooled dropping funnel into the catalyst mixture. During preparation of the catalyst, addition of the monomer, and the polymerization, the reactants were maintained in good agitation. The polymerizations in the presence of group VIII metal halides as catalysts were run in vials, sealed under N_2 and kept in agitation in an oil bath. The polymerization temperature was initially 20°C; after some hours it was raised to 50°C (Further details in Tables I and II).

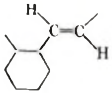
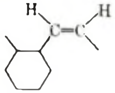
The polymers were recovered by precipitating the reaction mixture with an excess of methanol acidified with HCl. The polymers were washed with methanol and dried under vacuum.

Analysis of the Polymer

The determination of the relative amounts of the different monomer units in the polymers was carried out by infrared spectroscopy. The absorption

TABLE I

Polymerization of Bicyclo[4,2,0]octa-7-ene

Catalyst system									Polymer structure		
Organo-metallic compound	Transition metal compound[a]	Molar ratio, Al/transition metal	Molar ratio, monomer/transition metal compound[b]	Solvent or diluent	Volume ratio, solvent/monomer[b]	Polym-eri-zation tempera-ture, °C	Polym-eri-zation time, hr	Polymer yield, %	 units, %[b]	 *trans* units, %[b]	 *cis* units, %[b]
$AlEt_3$	VCl_4	2.2	10	Toluene	5	−20	24	50	90	10	—
$AlEt_2Cl$	VAc_3	5	10	Toluene	5	−20	24	60	95	5	Trace
$AlEt_2Cl$	$CrAc_3$	5	10	Toluene	5	−20	24	20	87	13	—
$AlEt_3$	$TiCl_4$	2.2	10	Toluene	5	−20	24	75	20	80	Trace
$AlEt_2Cl$	WCl_6	5	10	Toluene	5	−20	5	45	50	40	10
—	π-allyl Ni bromide	—	30	Ethanol	2.5	20	20	45	99	1	—
—	$RhCl_3 \cdot nH_2O$	—	30	Water[c]	2.5	20/50	17 + 48[d]	Trace	—	—	—
—	$RhCl_3 \cdot nH_2O$	—	30	Ethanol	1.5	20/50	17 + 48[d]	6	99	1	—
—	$RuCl_3 \cdot nH_2O$	—	30	Water[c]	2.5	20/50	20 + 48[d]	0	—	—	—
—	$RuCl_3 \cdot nH_2O$	—	30	Ethanol	3	20/50	3 + 20[d]	10	30	70	—
—	$(NH_4)_2RuCl_6$	—	30	Ethanol	5	50	48	5	10	90	—
—	$(NH_4)_2IrCl_6$	—	45	Ethanol	5	20/50	3 + 24[d]	37	25	75	—

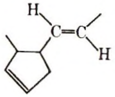
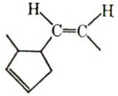
[a] Ac = acetyl acetonate.

[b] Approximate values.

[c] With dodecylbenzene sulfonate as emulsifier.

[d] Polymerization initiated at 20°C during the time value indicated first and continued at 50°C during the time value indicated after the + sign.

TABLE II
Polymerization of Bicyclo[3,2,0]hepta-2,6-diene

Catalyst system									Polymer structure		
Organometallic compound	Transition-metal compound[a]	Molar ratio, Al/transition metal	Molar ratio, monomer/transition metal compound[b]	Solvent or diluent	volume ratio, Solvent/monomer[b]	Polymerization temperature, °C	Polymerization time, hr	Polymer yield, %[b]	 units, %	 *trans* units, %[b]	 *cis* units, %[b]
$AlEt_3$	VCl_4	2.5	2.5	Toluene	40	−20	15	15	98	2	—
$AlEt_2Cl$	VAc_3	5	3.5	Toluene	30	−20	15	87	97	3	—
$AlEt_3$	$TiCl_4$	2.5	2,5	Toluene	40	−20	15	70	15	85	—
—	$RhCl_3 \cdot nH_2O$	—	55	Water[c]	2.5	20/50	2 + 20[d]	0	—	—	—
—	$RuCl_3 \cdot nH_2O$	—	35	Ethanol	3	20	20	55	Not determined[e]	Predomimant[e]	Not determined[e]
—	$(NH_4)_2PdCl_6$	—	35	DMSO[c]	3	20/50	80 + 50[d]	10	100	—	—

[a] Ac = acetylacetonate.

[b] Approximate values.

[c] With dodecylbenzene sulfonate as emulsifier.

[d] Compare with Table I; see footnote d of Table I.

[e] Insolubility of the polymer due to crosslinking did not allow an evaluation of the polymer structure.

bands at 10.35 and 7.1 μ, characteristic, respectively, of internal *trans* and *cis* unsaturations, were used for the determination of the monomer units derived from the ring-opening polymerization of the four-membered ring of both bicyclic monomers. Values of 1.0×10^5 (*trans*) and 0.82×10^4 (*cis*) $cm^2/mole$ were used as absorption coefficients. The difference to 100% was attributed to monomer units derived from the opening of the double bond of the four-membered ring, since other monomer units were not found present.

Properties of the Polymers

The polymers obtained by ring opening as well as by opening of the double bond of both bicyclic monomers are white, powdery products. They have a linear chain structure, as can be deduced also from their solubility in solvents like benzene or carbon tetrachloride. Only the bicycloheptadiene polymers obtained with the ruthenium catalysts are insoluble and hence presumably crosslinked. All polymers are insoluble in *n*-heptane, methyl ethyl ketone, or isopropyl ether.

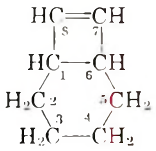
The molecular weights (determined with the Mechrolab vapor osmometer) are generally quite low (about 1000), mainly due to the relatively high catalyst concentrations. Only in the case of the polymer obtained with the $(NH_4)_2IrCl_6$ catalyst was a molecular weight as high as about 9000 found. All polymers were found to be amorphous by x-ray analysis. The softening temperatures ranged between 60 and 130°C.

No appreciable amounts of polyethylene, which might derive from a decomposition of the aluminum alkyl component of the catalyst, were present in the polymers.

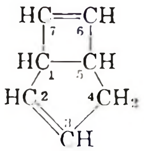
Elementary quantitative analysis indicated for the polymer of bicyclo[4,2,0]octa-7-ene obtained with the $VAc_3 + AlEt_2Cl$ catalyst: $C = 88.6\%$, $H = 11.4\%$; for the polymer of the same monomer obtained with the $WCl_6 + AlEt_2Cl$ catalyst: $C = 88.2\%$, $H = 11.8\%$. Calculated values for $(C_8H_{12})_n$ were: $C = 88.82\%$, $H = 11.18\%$.

RESULTS AND DISCUSSION

The two bicyclic monomers containing a cyclobutene ring used for the present investigations are bicyclo[4,2,0]octa-7-ene (I) and bicyclo[3,2,0]hepta-2,6-diene (II).



I



II

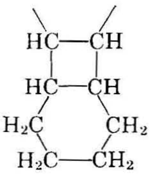
Both monomers were homopolymerized by using two different classes of catalysts: (*1*) Ziegler-Natta catalysts prepared from chlorides or acetylacetonates of titanium, vanadium, chromium, or tungsten and organoaluminum compounds; (*2*) salts of the group VIII metals nickel, rhodium, ruthenium, iridium, and palladium in water, ethanol, or dimethyl sulfoxide.

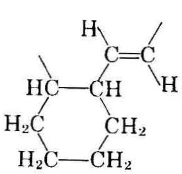
The results of these polymerizations are summarized in Tables I and II.

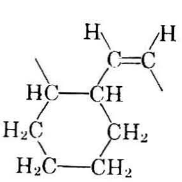
The polymer yields were not investigated systematically in dependence of the catalyst concentrations; in order to overcome a supposed low monomer reactivity, attributed to the considerable bulkiness of the ring systems, high catalyst concentrations were used, especially in the case of the Ziegler-Natta catalysts. Hence, the polymer yields given in Tables I and II should only be read as generally indicative.

In spite of their considerable bulkiness, both bicyclic monomers could be polymerized to linear polymers. Significant results were obtained with both classes of catalysts. With regard to the structure of the polymers obtained, the employed catalysts may be divided into two groups: those preferably or exclusively promoting polymerization by opening of the double bond, and those predominantly inducing ring-opening polymerization. Catalysts containing vanadium, chromium, nickel, rhodium, or palladium as transition metal belong to the first group, whereas those containing titanium, ruthenium, or iridium as transition metal pertain to the second group. The catalysts containing tungsten as transition metal exhibit an intermediate character.

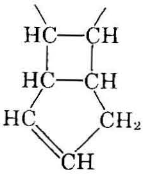
The polymers show a quite simple pattern of chemical structures. All monomer units are derived from reactions at the four-membered rings (except for the polymer of (II) prepared with the $RuCl_3 \cdot nH_2O$ catalyst, which is crosslinked and in which also the double bonds of the five-membered ring may have reacted). The polymerizations by opening of the double bond involve only the double bond of the cyclobutene rings. In the ring-opening polymerizations only the cyclobutene rings are opened. In this case the internal double bonds of the linear chain segments are predominantly *trans*, and only small amounts of the *cis* type are found. In conclusion, in the case of I the observed monomer units are Ia, Ib, and Ic,

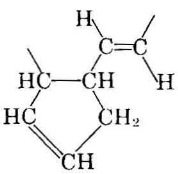

Ia

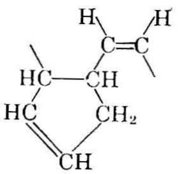

Ib


Ic

and in the case of II, the units found were IIa, IIb, and IIc.


IIa


IIb


IIc

In the case of I, the unreactivity of the cyclohexane ring was not surprising if one considers its saturated nature and the very low strain of a fused six-membered ring. In the case of II, however, the five-membered ring, which is also unreactive, not only has considerable ring strain, but it is also unsaturated and could therefore reasonably be supposed to polymerize, at least to a low extent. Unlike cyclohexene, which could not be polymerized to polyalkenamers,[11] cyclopentene, with the above catalysts, has actually been homopolymerized by ring opening[12] as well as copolymerized by opening of the double bond.[13] Evidently, the ring strain of the cyclobutene rings is so much higher than that of the higher-membered rings as to monopolize the polymerization reaction.

The chemical structure of the monomer units in the obtained polymers was deduced primarily by infrared analysis. In the case of I, that all cyclobutene rings had been polymerized (by ring opening or opening of the double bond) was verified by the disappearance of the absorption band at 6.43 μ, characteristic of the double bond in a highly strained cyclobutene ring. Moreover, a theoretically possible opening of the fused cyclohexane ring could be excluded on the basis of the absence of an infrared absorption in the 13.3–13.9 μ region, attributable to a linear chain sequence of four methylene groups.

The monomer units Ib and Ic were determined on the basis of the infrared absorptions at 10.35 (*trans*) and 7.1 μ (*cis* internal double bonds). A polymer built up only by (Ia) monomer units is characterized by the absence of any type of double bonds.

In the case of (II), the unreactivity in these polymerizations of the cyclopentene ring (except for the polymers prepared with $RuCl_3 \cdot nH_2O$ catalyst) was deduced from the fact that the *cis* double bond of the five-membered ring of the monomer (infrared absorption at 6.22 μ) was retained in the polymer, whereas the *cis* double bond of the four-membered ring of the monomer (infrared absorption at 6.43 μ) completely disappeared in the polymer.

According to indications given by Weissberger[14] and confirmed in our laboratories, the infrared absorption bands due to the stretching vibration of the *cis* double bonds of hydrocarbons shift to higher wavelengths with increasing strain, being found at 6.0 μ for a linear chain, 6.06 μ for a six-membered ring, 6.22 μ for a five-membered ring, and 6.43 μ for a four-membered ring.

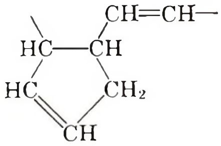
The presence of the monomer units IIa, IIb, and IIc was deduced on the basis of the absorption bands characteristic of the *trans* and *cis* internal double bonds in the linear chain segments, by a method analogous to the method described for the polymers derived from I.

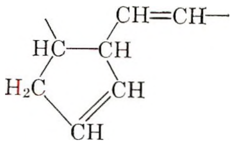
All polymers obtained with the above catalysts are amorphous by x-ray examinations, despite the high degree of regularity of the chemical structure of most of them. It has not been possible so far to decide whether this is due, in the case of the chemically regular polymers, to an irregularity of the sterical structure (optical isomerism) or to the steric hindrance caused by the bulkiness of the monomer units, which could prevent the crystallization of the polymers. In the above given six monomer units, optical isomerism, which would greatly increase the number of possible monomer units, is not considered.

Two types of optical isomerism must be distinguished. The first one arises during polymerization by opening of the double bonds, in that the carbon atoms of the monomer double bond become tertiary carbon atoms of the polymer chains.

The second type involves the two bridgehead carbon atoms (in positions 1 and 6 of I and 1 and 5 of II, which are tertiary carbon atoms. Their steric configuration is determined prior to the polymer formation. In the bicyclic monomers I and II, the two ring moieties are certainly fused together in a *cis* fashion. It is in fact known for bicyclic systems that the seven-membered ring is the smallest cycle that may span a four-membered unsaturated ring in a *trans* fashion.[15,16] Hence the bridgehead carbon atoms of both monomers should always become tertiary carbon atoms with an *erythro* relationship in the polymer.

A third type of possible irregularity concerns only the polymers of II and derives from the intrinsic asymmetry of this monomer. The type of double bonds being the same, e.g., the ring-opening polymerization may in fact yield the two isomeric monomer units:





Analogous considerations are valid for the two corresponding monomer units derived from the opening of the double bond.

All above considerations are made supposing that the ring-opening polymerizations cleave the cyclobutene ring at the single bond adjacent to the double bond. Evidence had been accumulated previously[1,4,12,17] supporting this hypothesis. The present results should allow us to exclude the possibility of ring opening at the single bond far from the double bond (allylic position). In fact, in this case one should obtain ring-opening polymers free of linear chain segments containing internal double bonds and built up only by cyclic monomer units linked together by the two bridgehead carbon atoms.

The ring opening at the single bond adjacent to the double bond is in contrast with many ring-opening reactions of classical organic chemistry. It is known, for example, that in cyclobutene and its derivatives the single bond far from the double bond is weakened by allylic activation, from both sides, induced by the double bond.[18] However, in these cases the reactions are thermal and proceed through a radical mechanism, in contrast with the ionic character of the present polymerizations and with their coordination mechanism, which implies a coordination bond between the transition metal and the double bond of the monomer.

The above evidence, however, is not conclusive in deciding whether the ring opens at the single bond adjacent to the double bond or at the double bond itself. Further experiments are in progress in order to clarify this question.

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NOTES

Method for Computing the Specific Rate of Hydrolysis of Glucosidic Bonds in Some Trisaccharides

It was shown recently[1] that the kinetics of the acid-catalyzed hydrolysis of some trisaccharides can be described by rate equations derived on the basis of a reaction scheme consisting of a combination of two interdependent parallel and consecutive reactions. The computation of the rate constants of hydrolysis of the two glucosidic links in the trisaccharide, isomaltotriitol, by means of the derived rate equations required the experimental values of the concentrations of isomaltotriitol, isomaltitol, isomaltose, glucose, and sorbitol for various periods of time of hydrolysis.

In studying the rate of hydrolysis of some trisaccharides it may occur that the concentration of only one of the hydrolysis products is measured and that of the unhydrolyzed trisaccharide is not measured. The present paper offers a method by which the specific rate of hydrolysis of each of the two glucosidic bonds in some trisaccharides (e.g., isomaltotriitol) can be computed when the following are known: (*a*) the concentration of one of the hydrolysis products (isomaltose or isomaltitol) and (*b*) the rate constants of hydrolysis of these products.

The course of the hydrolysis of this trisaccharide and the kinetic scheme for the reactions are illustrated in Figure 1.

In Figure 1 A denotes the concentration of isomaltotriitol at any instant, (B), B, and B^* are concentration of glucose at any instant, C is the concentration of isomaltitol at any instant; (D) and D are concentration of sorbitol at any instant, E denotes concentration of isomaltose at any instant; k_2 and k_4 are the known specific rates of hydrolysis of isomaltitol and isomaltose, respectively; k_1 and k_3 are the specific rates of hydrolysis of the two glucosidic bonds in isomaltotriitol; A_0 is the initial concentration of isomaltotriitol.

The pertinent rate equations are as follows:

$$A = A_0 e^{-(k_1 + k_3)t} \tag{1}$$

$$C = \frac{A_0 k_1}{k_2 - (k_1 + k_3)} e^{-(k_1 + k_3)t} - e^{-k_2 t} \tag{2}$$

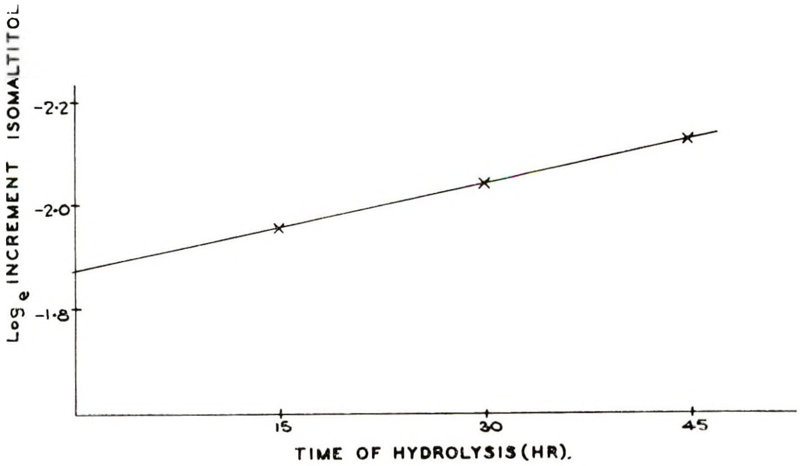

Figure 1

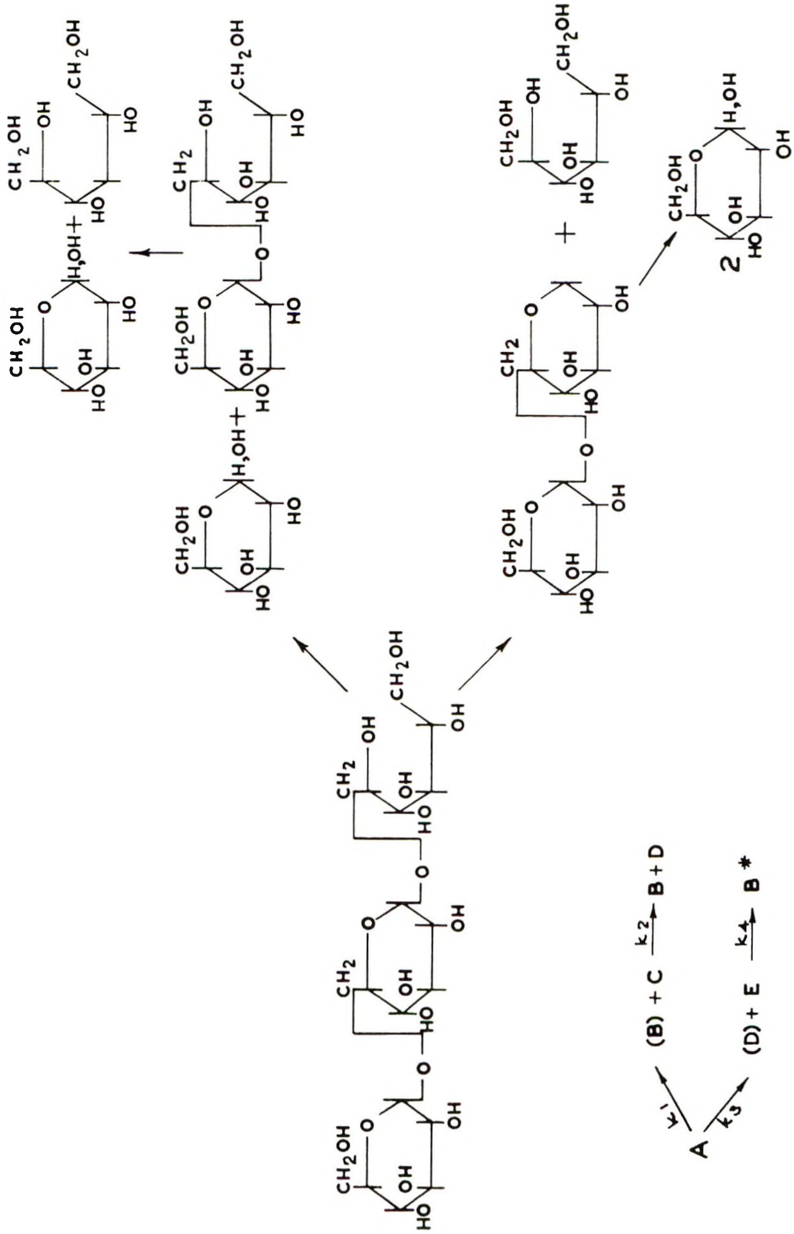

Fig. 2. Rate plot according to eq. (5).

$$E = \frac{A_0k_3}{k_4 - (k_1 + k_3)} e^{-(k_1 + k_3)t} - e^{-k_4t} \tag{3}$$

From eq. (2)

$$\frac{C}{A_0e^{-k_2t}} = \frac{k_1}{k_2 - (k_1 + k_3)} e^{-(k_1 + k_3 - k_2)t} - 1 \tag{4}$$

and it can easily be shown that

$$\ln \text{Increm } (C/A_0e^{-k_2t}) = -(k_1 + k_3 - k_2)t + \text{const.} \tag{5}$$

and

$$\text{Antiln} \left[\text{const.} - \ln (1 - e^{-(k_1 + k_3 - k_2)\Delta t}) \right] = \frac{k_1}{k_1 + k_3 - k_2} \tag{6}$$

Similarly, from eq. (3)

$$\frac{E}{A_0e^{-k_4t}} = \frac{k_3}{k_4 - (k_1 + k_3)} e^{-(k_1 + k_3 - k_4)t} - 1 \tag{7}$$

$$\ln \text{Increm } (E/A_0e^{-k_4t}) = -(k_1 + k_3 - k_4)t + \text{const.}' \tag{8}$$

$$\text{Antiln} \left[\text{const.}' - \ln (1 - e^{-(k_1 + k_3 - k_4)\Delta t}) \right] = \frac{k_3}{k_1 + k_3 - k_4} \tag{9}$$

In eqs. (6) and (9), Δt refers to the time interval chosen for the increments.

Thus, knowing the initial concentration of the trisaccharide, the hydrolysis rate constants of the disaccharides formed through hydrolysis of the trisaccharide, and the experimental values for the concentration of one of the hydrolysis products corresponding to equal time intervals of hydrolysis, the rate constant of hydrolysis of each of the two glucosidic bonds of the trisaccharide can be computed. If experimental values of C and E for equal time intervals are not available, they can be obtained by interpolation. The computation can be performed by either (*a*) substituting values of $C/A_0e^{-k_2t}$ or $E/A_0e^{-k_4t}$ into eqs. (5) and (6) or (8) and (9), respectively, and solving them by the customary algebraic procedure, or (*b*) plotting values of either ln Increm $(C/A_0e^{-k_2t})$, or ln Increm $(E/A_0e^{-k_4t})$ against t and evaluating the gradient of the straight line so obtained and of its intercept with the ordinate [cf. eqs. (5) and (8)]. One such plot is shown in Figure 2, the experimental rate data of Jones et al.[2] being used.

The values for the hydrolysis rate constant of each of the two glucosidic bonds in isomaltotriitol so computed are: $k_1 = 9.84 \times 10^{-3}$ hr^{-1} and $k_3 = 4.86 \times 10^{-3}$ hr^{-1}. They agree quite well with the values arrived at previously,[1] viz., $k_1 = 9.8 \times 10^{-3}$ hr^{-1} and $k_3 = 5.0 \times 10^{-3}$ hr^{-1}.

While the method described above is an exact method, its accuracy depends, among other things, on the number of increments available, which, in turn, depends on the number of measured values of the concentration of one of the hydrolysis products.

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Copolymerization of Phenanthrene and Maleic Anhydride

The alternative copolymerization of maleic anhydride (MAH) with the common vinyl monomers has been widely studied.[1,2] Recently these investigations tended towards radical copolymerization with monomers which are not capable of radical homopolymerization, for example, dioxene[3] and dimethoxyethylene.[4] The argument that these copolymerizations are promoted by the formation of a complex between two monomers or on the propagating radical has been accepted.

TABLE I
Copolymerization of Phenanthrene and Maleic Anhydride in Various Solvents[a]

Solvents	Temperature, °C	Yield, g	[η]	Molecular weight[b]	Polymerization system
DMF	60	—	—	—	Homogeneous
Dioxane	"	0.682	0.06	3600	"
CCl_4	"	1.016	0.13	5800	Partly heterogeneous
CCl_3H	"	1.100	0.13	6100	Oily precipitant
Acetic anhydride	"	1.008	0.09	4600	Homogeneous at 60°C
Acetone	30	—	—	—	Homogeneous
Dichloroethane	60	1.076	0.11	—	Oily precipitant
THF	"	Trace	—	—	Homogeneous
Benzene	"	1.000	0.13	—	Heterogeneous
Toluene	"	1.011	0.07	—	"
Xylene	"	0.822	0.06	—	"

[a] AIBN = 50 mg; phenanthrene = 0.90 g, maleic anhydride = 0.50 g (1:1 in molar ratio); solvents = 5 ml; polymerization time, 48 hr; in N_2, precipitated in MeOH.

[b] Molecular weights were determined by ebulliometric method in acetone.

On the other hand, the MAH electron-acceptor character has been well known for the formation of complexes with aromatic compounds. We have succeeded in copolymerizing aromatic compounds such as phenanthrene with MAH in the form of a new copolymer. The rate of copolymerization and molecular weight were influenced by the nature of sol-

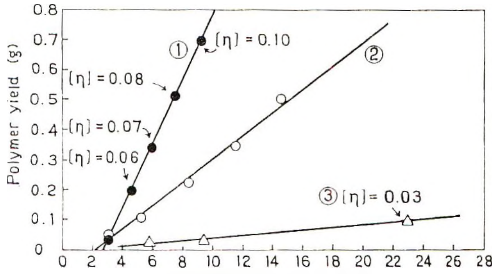

Fig. 1. Copolymerization of phenanthrene and maleic anhydride: (*1*) 1.8 g phenanthrene, 1.0 g maleic anhydride; (*2*) 0.9 g phenanthrene, 0.50 g maleic anhydride; (*3*) 0.45 g phenanthrene, 0.25 g maleic anhydride. AIBN 100 mg, in dioxane solution, total volume 5.00 ml.

vent (Table I) and was enhanced by the increase of concentration of the complex between the two monomers (Fig. 1). With decreasing concentration of monomers, the ultraviolet absorption spectra of this polymerization solution shows a remarkable diminution of absorption intensity at 390 mμ attributed to the complex.

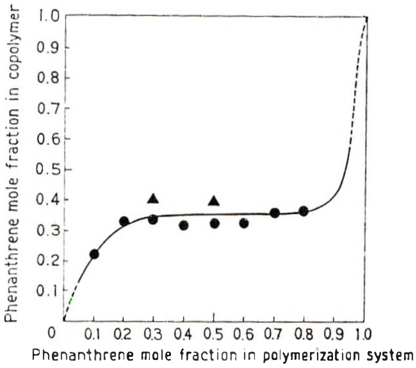

Fig. 2. Phenanthrene mole fraction in copolymer obtained in benzene solution at 60°C: (●) precipitated in methanol; (▲) precipitated in benzene. Polymerization time: 20 hr.

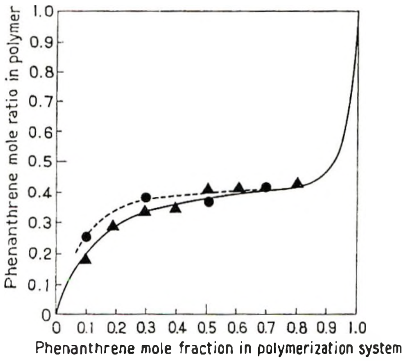

Fig. 3. Phenanthrene mole fraction in copolymer obtained in dioxane solution at 60°C: (●) precipitated in methanol; (▲) precipitated in benzene. Polymerization time: 20 hr.

Figures 2 and 3 show that these copolymers have a composition in the range 1:1.2–1:2 phenanthrene:MAH (mole ratio).

The details of the copolymerization based on the complex formation will be published elsewhere.

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Effect of Agitation on the Heterogeneous Polymerization of Trioxane in Solution

In solution cationic polymerization of trioxane, a certain time after the introduction of the catalyst, a weak opalescence appears which increases as the reaction proceeds; this instant, corresponding to the initial precipitation of the polymer, is considered to mark the end of the induction period.[1,2] At this moment, the reaction ceases to be homogeneous. In effect, the polymerization appears to take place at the solution–polymer crystal interface with a rate proportional to the surface area of the separated phase.[2]

Nevertheless, after the induction period, transfer reactions, especially with water, can give rise to reaction in solution; however, it has been shown that the water concentration assumes a stationary value.[3]

Other authors have pointed out the heterogeneous nature of the cationic polymerization of trioxane.[4–8] In the present note this polymerization is analyzed, the influence of agitation being especially studied. In effect, as the polymerization proceeds through growth of polymer crystals, diffusion of the monomer from the body of the solution to the polymerization surface is required; this diffusion, if the reaction is fast enough, may be a controlling factor.

Moreover, the process rate is influenced by the agglomeration of the polymer particles which reduces the active surface of polymerization. Agglomeration also involves chemical linking, through chain-transfer reactions.[5] This fact may explain the results of Kučera and et al.,[3,9–11] who noted a decrease in the amount of catalyst during the polymerization.

EXPERIMENTAL

Materials

Trioxane (Schuchardt) was employed without purification (amount of water determined by the Karl-Fisher method: 0.03–0.04% by weight). Cyclohexane RP (Carlo Erba) was purified by the usual methods. Nitrobenzene RP (Carlo Erba) was distilled under vacuum; BF_3 etherate (Eastman) was doubly distilled under vacuum, and the intermediate fraction of the second distillation was employed.

POLYMERIZATION METHOD

Polymerization experiments without agitation were carried out in the same equipment and under the same conditions as previously described.[12] Experiments with agitation were performed in a cylindrical (6 cm diameter) reactor equipped with baffles and a 3 cm blade agitator. The stirring rate was followed by stroboscopy.

The beginning of the opalescence was taken as zero time.

The reaction was stopped by addition of acetone.

Inherent viscosity ($\ln \eta_{rel}/c$) measurements were taken at 60°C in *p*-chlorophenol (containing 2% α-pinene) solutions and at 0.5 g/dl polymer concentration.

RESULTS AND DISCUSSION

In Figure 1 polymerization yields are plotted against reaction time for two different initial concentrations of monomer and catalyst solutions in cyclohexane. Agitation has no effect on the induction period but becomes effective when the reaction becomes heterogeneous; stirring shortens the time between the end of the induction period and the time of the highest polymerization rate and gives higher rates at the same conversions.

The behavior of the polymerization in the first stages might be interpreted on the basis of a diffusional resistance which adds to the reaction step; agitation, lowering the diffusion time of the monomer from the main body of the solution to the polymerization ac-

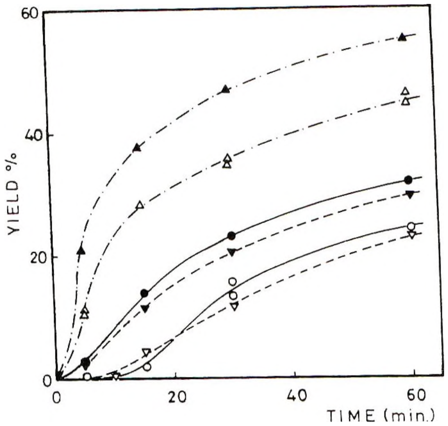

Fig. 1. Polymerization yield vs. reaction time with cyclohexane as solvent (○, ●): $[\text{trioxane}]_0 = 2.88$ mole/l, $[H_2O]_0 = 10.4 \times 10^{-3}$ mole/l, $[BF_3 \cdot OEt_2]_0 = 2 \times 10^{-3}$ mole/l; (△, ▲) $[\text{trioxane}]_0 = 5.2$ mole/l, $[H_2O]_0 = 16 \times 10^{-3}$ mole/l, $[BF_3 \cdot OEt_2]_0 = 2 \times 10^{-3}$ mole/l; (▽, ▼) $[\text{trioxane}]_0 = 5.2$ mole/l, $[H_2O]_0 = 16 \times 10^{-3}$ mole/l, $[BF_3 \cdot OEt_2]_0 = 1 \times 10^{-3}$ mole/l; (○, ▽, △) no agitation; (●, ▼, ▲) 300 rpm.

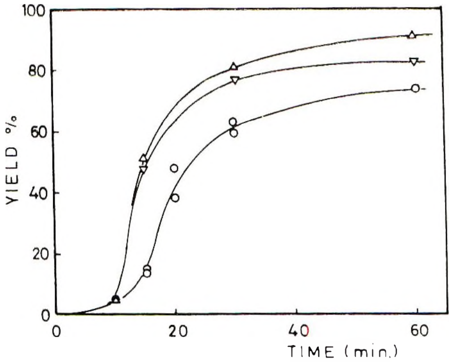

Fig. 2. Polymerization yield vs. reaction time with nitrobenzene as solvent (56°C): (○) no agitation; (▽) 300 rpm; (△) 900 rpm. $[\text{Trioxane}]_0 = 2.88$ mole/l, $[H_2O]_0 = 23 \times 10^{-3}$ mole/l, $[BF_3 \cdot OEt_2]_0 = 0.5 \times 10^{-3}$ mole/l.

tive surface, increases the process rate. Part of this increase may be, however, attributed to the lower tendency to agglomeration of growing crystals in presence of stirring.

Agglomeration, which is rather marked when apolar solvents such as cyclohexane are used, can be noticeably reduced by employing highly polar media. With nitrobenzene, in fact (Fig. 2), the decrease of the diffusion time brought about by the agitation has a strong effect in increasing the process rate, with respect to the hindrance to the agglomeration of the polymeric particles.

In both solvents, with increasing reaction time, the polymerization yield tends to assume an asymptotical value which depends on the agitation rate.

Figures 3 and 4 show the variation of the inherent viscosity as a function of polymerization yield in cyclohexane and nitrobenzene solutions with or without stirring. With cyclohexane, at least for not so high yields, agitation causes a remarkable lowering of the inherent viscosity. Without stirring or with low rates of stirring the inherent viscosity, as result of degradative reactions due to the catalyst,[12–14] at first increases and then de-

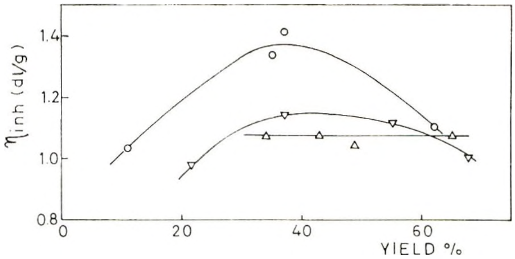

Fig. 3. Inherent viscosity vs. polymerization yield with cyclohexane as solvent (56°C): (○) no agitation; (▽) 300 rpm; (△) 900 rpm. $[\text{Trioxane}]_0 = 5.2$ mole/l, $[H_2O]_0 = 16 \times 10^{-3}$ mole/l, $[BF_3 \cdot OET_2]_0 = 2 \times 10^{-3}$ mole/l.

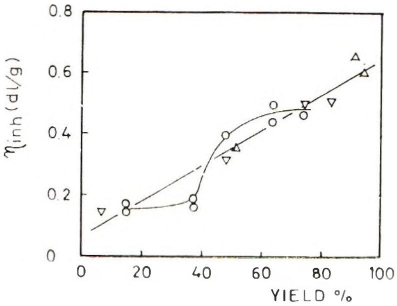

Fig. 4. Inherent viscosity vs. polymerization yield with nitrobenzene as solvent (56°C): (○) no agitation; (▽) 300 rpm; (△) 900 rpm. $[\text{Trioxane}]_0 = 2.88$ mole/l, $[H_2O]_0 = 23 \times 10^{-3}$ mole/l, $[BF_3 \cdot OEt_2]_0 = 0.5 \times 10^{-3}$ mole/l.

creases with increasing polymerization yield; on the contrary, with high agitation rates it is practically independent of yield. Inherent viscosity plotted against polymerization, when nitrobenzene is used as solvent and with no agitation gives, as already found by Okamura et al.,[15,16] S-shaped curves, while with agitation it exhibits linear behavior.

CONCLUSION

The heterogeneous nature of the cationic polymerization of trioxane has been analyzed in relation to the conditions of agitation in the polymerizing system. Agitation rate influences the process kinetics and the dependence of the molecular weight on polymerization yield. The observed increase of the reaction rate with stirring has been attributed to the lowering of the diffusion time of the monomer from the main body of the solution to the polymerization active surface and to the hindrance to agglomeration of the polymeric particles.

The possibility of coexistence of chemical and diffusional regimes must be considered in any investigation of the kinetics of a process.

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Identification of Diene Comonomer by Time-Averaged NMR Spectroscopy

Identification of the nonconjugated diene introduced into ethylene–propylene copolymers to permit sulfur vulcanization is difficult owing to the small amounts which are normally present and to the fact that several different types of termonomer can be employed. Usually it is possible to detect this residual unsaturation by infrared spectroscopy[1] and measure it by a chemical method (such as with iodine monochloride),[2] but such methods can present some difficulties. Identification of the incorporated third monomer is not always practical in infrared spectroscopy at the low concentrations involved, and in the high-resolution NMR spectra of these terpolymers the presence of unsaturation is not usually detected, since the signals from the olefinic protons are of such low intensity that they become lost in the background noise. We have found that it is possible to detect the NMR signals from the olefinic protons of a number of ethylene–propylene terpolymers by means of a time-averaging technique, similar to that described for butyl rubber.[3] The spectra so obtained are usually sufficiently characteristic to allow identification of the particular third monomer incorporated in the terpolymer. Moreover, as the third monomer initially contains two double bonds, differing in structure and reactivity, the one used up in copolymerization may be distinguished from the one remaining for subsequent use in vulcanization. Therefore information concerning the structure of the remaining unsaturated entity may be obtained. The table shows the chemical shifts of olefinic protons of a number of different third monomers in the copolymers. The spectra are shown in the diagram.

TABLE I

Third monomer	Chemical shift, τ
Cyclooctadiene 1,5	4.55
Dicyclopentadiene	4.55
1:4 Hexadiene	4.7
Methylene norbornene	5.25 and 5.5
Ethylidene norbornene	4.8 and 4.9

The cyclooctadiene and dicyclopentadiene terpolymers have olefinic protons with the same chemical shift, 4.55 τ, and so these cannot be differentiated by this technique but may be distinguished by the use of iodine monochloride.[2] The hexadiene type of terpolymer may be identified by its olefinic resonance at 4.7 τ. These three monomers have what appears as a single olefinic resonance in the terpolymer. On the other hand, the two norbornadiene types of monomer each show two characteristic resonances. In the methylene norbornene terpolymer the olefinic resonances arise from two protons, each giving a separate signal, whereas in the ethylidene norbornene terpolymer there is only one proton, the signal of which appears as a doublet. In view of these considerations it is more difficult to detect the olefinic resonance in the latter instance.

In the terpolymers it appears that the chemical shifts of the olefinic resonances are very similar to those given by the corresponding protons in the (starting) monomers, and it follows that the other olefinic resonances in the monomer must belong to the double bond used up in the polymerization. The norbornene types of monomer and dicyclopentadiene evidently copolymerize through the more reactive double bond in the bridged ring.

Butyl rubber is similar to ethylene–propylene terpolymers in that a time-averaging technique is necessary for the detection of the olefinic proton resonance, and we have detected a resonance at about 5 τ, in agreement with the result of Chen and Field.[3]

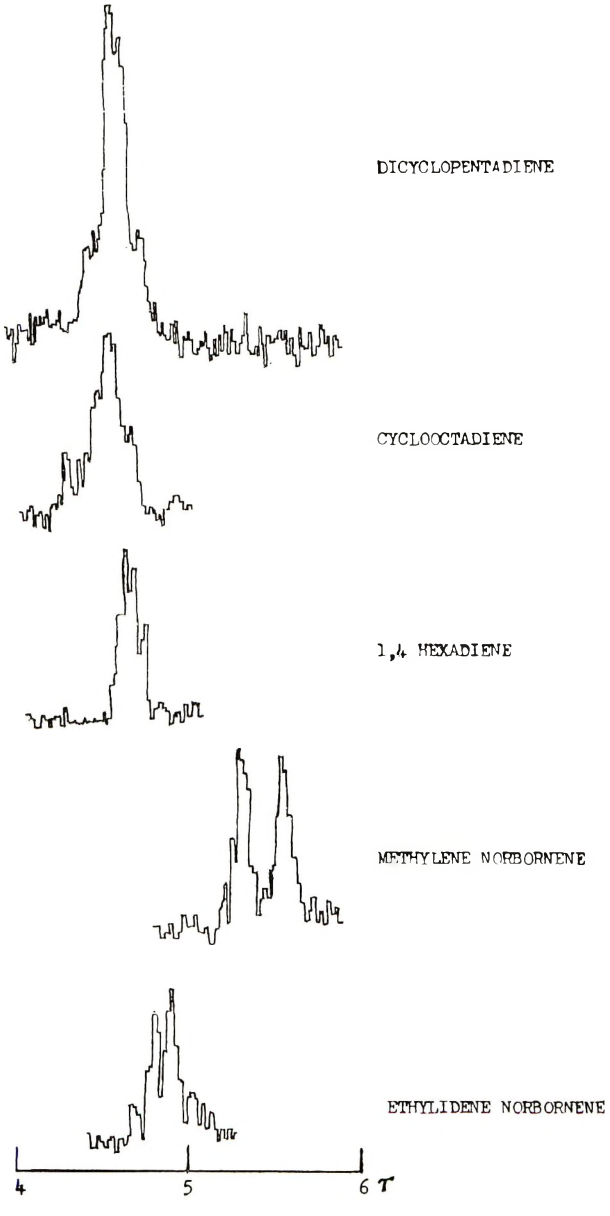

Figure 1

Polymers were dissolved in carbon tetrachloride at about 3% concentration. A Perkin-Elmer R10 instrument was used, working at 60 Mc./sec. Measurements were made at 33°C. The equipment for time-averaging has been described[4] and is presumably similar to other equipment[3,5] applied to the examination of polymers. Only the regions of 4–6 τ were examined, 2–3 hr. being taken per spectrum. In view of the possibility of magnetic field drift over this time, very accurate chemical shifts cannot be determined.

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BOOK REVIEWS

Coupling Research and Production. George Martin and R. H. Willens, Eds., Wiley, New York, 283 pp., $12.00.

This handy volume reports the proceedings of a symposium dealing with how to accelerate the finding of practical applications for the discoveries of basic research and getting them into production. The symposium was organized by the American Institute of Mining and Metallurgical Engineers and sponsored by Federal Agencies having an interest in materials development. It was held in Los Angeles, October 5–7, 1966. The twenty papers presented were mostly authored by administrators of applied research, materials development in agencies of the Armed Forces and Space, or undergraduate and graduate education.

Those interested in research management will find this a convenient reference by which to check their methods against those of the competition. They will also be interested in the attempt to train "entrepreneural engineers" at Dartmouth and in three "coupling" programs now being supported by the Advanced Research Projects Agency, which pair basic research carried on in a specific university with applied research and engineering development carried on in specific firms to accelerate progress in a field of technology of interest to the Government. Educators and students can obtain a glimpse of industrial research from the inside by reading the papers presented by J. J. Harwood (Ford Motor), L. P. Jahnke (General Electric), E. R. Morgan (Jones & Laughlin), M. J. Pryor (Olin Mathieson), and R. P. Olsen and H. Reiss (North American Aviation). Papers by H. M. Burte (Chief, Materials and Ceramics, Air Force Materials Laboratory), G. C. Deutsch (Chief, Materials NASA), L. J. Klinker (Chief, Materials Science and Technology, Army Research Office), and N. Promisel, H. Liebowitz, and T. F. Kearns (Navy) will introduce the reader to the operations of these governmental agencies.

Definition of a technological need was repeatedly cited as an important catalyst for technological advance. See particularly M. Tanenbaum's account of ten case histories. Effective "coupling" requires good communications to encourage interaction between the basic researchers, those identifying needs, those making applications, and those engaged in production, but it also requires effective motivation to get these groups to work together for the payoff in production. Motivation for accomplishment and ideas for interdisciplinary solutions can be fostered by focussing the attention of all on desirable payoffs. Flexibility for major changes in goals and in the directions of applied research is often necessary to achieve a successful innovation.

A key individual in successful projects was variously identified as the "coupler," and "idea champion," the "vertical interdisciplinary man," the "generalist," the "technological entrepreneur," etc. In this connection the paper by R. C. Dean describing Dartmouths' efforts to revise their engineering curriculum to foster the training of technological entrepreneurs was particularly encouraging to me.

There were implications that it was very difficult to convert scientists to technological entrepreneurs while they are working on the job. This is contrary to my experience. If one selects the right candidate there should not be great difficulty. It has seemed to me that basic or fundamental researchers cleave into two groups; (*1*) descriptive scientists, who excell in characterizing and diagnosing the factors at work in natural phenomena, but who find difficulty in extending their observations to originate new concepts, and (*2*) innovators, who investigate more broadly, and are primarily interested in synthesis and originating new concepts. Although they can do descriptive work they prefer to range more broadly and soon develop into generalists. It has been my experience that the scientists in this second group convert readily to technological entrepreneurs. They need only exposure to economic studies, application work, and case histories and to be given responsibility for choosing and defending lines of research which will maximize the payoff of the research for which they are responsible. As J. J. Harwood stated in his paper, the coupling of research to technology is indeed a people problem.

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Modern Organic Chemistry, by John D. Roberts and Marjorie C. Caserio, W. A. Benjamin, Inc., New York, N.Y., 1967. XXII + 844 pp. Price $10.75

This new introductory textbook is a condensation of *Basic Principles of Organic Chemistry* by the same authors, published in 1964. The new work is about two-thirds the size of its parent.

The organization and emphasis are essentially unchanged, and the condensation appears to have been accomplished to a considerable extent by excision of paragraphs and sections. This is a dangerous practice, for it may result in the loss of subjects, the acquaintance with which is assumed in later sections. Nevertheless, the text flows well.

The introduction of spectroscopy, particularly IR and NMR, at the very beginning, and the continued emphasis on thermodynamics and mechanism are the features that differentiate this book from most, if not all, of its competitors. Such features, together with the intellectually provocative problems scattered throughout the book, exert a strong attraction to established chemists, whom the book may impress as the wave of the future in the presentation of organic chemistry.

The test of actually teaching from a book is apt to be more enlightening than that of simply reading through it, and under this test, a number of flaws in "Roberts and Caserio" come to light. Except for the most highly motivated, students do not react as favorably as their professors are apt to; they find that their background (or that part of it that they have retained) is less than optimum for some of the more sophisticated material, and the exercises become especially frustrating. In fact, the exercises are a major source of irritation to the instructor as well, for too many of them assume knowledge which cannot be found in the text (presumably excised in the condensation), and the *Supplement,* which provides the answers to the exercises, is a mass of errors. The result is that an instructor must spend an inordinate amount of time explaining why a given exercise cannot be answered with information given in the text, and in correcting the errors. As an example, Exercise 1-2 states that there are three isomers of C_3H_9N (there are actually four); the heat of combustion given as a datum in Exercise 3–4 is quite different from the answer given for Exercise 3–6b, in which this quantity is calculated from bond energies; for Exercise 6–1f, the name for 3,3-dimethylcyclopropene is incorrectly given as 1,1-dimethylcyclopropene.

Although this book is commendably free from purely typographical errors, there are errors or inconsistencies of other kinds, which upset students considerably when the reckoning comes. On page 65, for example, the C—H bond energy for methane is taken as 98.7 kcal/mole, but on page 71, a new value, 102 kcal, is given without remark. On page 65, the ground state of molecular oxygen is represented as a singlet electronic structure.

The coverage of descriptive chemistry is weaker than usual in organic textbooks; this is of course a necessity if other subjects are expanded while the size is kept constant. The area of reactions has been curtailed, and with it the preparation of the student to handle problems in synthesis. The presentation of industrial processes is very skimpy, which may dismay many chemists. This is nevertheless true to the authors' intention of giving primary emphasis to principles.

Among unfortunate omissions is any information on the stereochemistry of catalytic hydrogenation, although much is made of the stereochemistry of all manner of other additions to multiple bonds. Neither the Hofmann nor the Curtius rearrangement is listed in the index, nor appears to be mentioned anywhere in the text. Isocyanates as a class have entirely been overlooked, whereas such exotic structures as diazirines are discussed. No book, obviously, can include every item of information that each and every instructor might want, but in the present case, the omissions are more numerous than in other works of equivalent size.

A 23 page chapter on polymers is a welcome feature of this book; there are in addition a three page section in another chapter on polymerization of conjugated dienes, and four pages on polymerization of alkenes. The coverage of any particular chemical type of polymer is necessarily light, but principles and important terms are explained and the relation between physical properties and structure is given proper attention.

The up-to-date insights into mechanism and structure are such a strong feature that they may well redeem the shortcomings mentioned. It is not everybody's book, but the adventurous should at least enjoy the experiment of presenting organic chemistry in a new way. Any chemist is likely to benefit from as well as be entertained by tackling the numerous thought-provoking exercises, even if he doesn't always agree with the answers the authors provide.

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