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Determination of the Number of Particles/Unit Volume of Latex During the Emulsion Polymerization of Styrene

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Synopsis

The variation of the number of particles/unit volume of latex (N) with conversion was determined during the emulsion polymerization of styrene. The results showed that, contrary to what is required by the Smith-Ewart theory, N increased during the constant rate period. This conclusion was supported by the variation of the particle size distribution with conversion. Further evidence that latex particles could form in the absence of micelles was given by using systems in which the soaps were below the CMC. The chain length of the soaps used had a marked effect on the rate of polymerization. This effect was shown not to be due to the variation of the CMC with chain length, but possibly to the stronger adsorption of the longer chain length soaps at the polymer–water interface.

INTRODUCTION

The theory predominantly employed to explain the kinetics of emulsion polymerization of relatively water-insoluble monomers is that proposed by Smith and Ewart[1] or modifications of it. A review of most of the fundamental aspects of emulsion polymerization has been made by Van der Hoff.[2] The Smith-Ewart theory assumed that free radicals produced in the aqueous phase by decomposition of the initiator entered micelles which were swollen with monomer. Polymerization was propagated in the micelles, monomer being supplied to them by diffusion through the aqueous phase. It was further assumed that polymerization did not take place in the water or monomer droplets.

Using this model, Smith and Ewart derived equations describing the kinetics of the polymerization for three particular values of the number of radicals/particle, $\bar{n}$; i.e., $\bar{n} \gg 1$, $\bar{n} \sim 0.5$, $\bar{n} \ll 1$. For the second case ($\bar{n} \sim 0.5$), which best fitted the data for styrene, the rate of polymerization is proportional to the $^3/_5$ power of the soap concentration and the $^2/_5$ power of the initiator concentration. Previous experimental work[3–9] aimed at verifying the theory has been mainly concerned with this dependence of the rate of reaction on the soap and initiator concentration. More general solutions[10–13] of the Smith-Ewart equations, which allow for the variations in $\bar{n}$, have accounted for some deviations from the results predicted for the stationary value of $\bar{n} = 0.5$, though as yet there has been no direct measurement of $\bar{n}$.

There is evidence in the literature that indicates that some of the assumptions used in the Smith-Ewart theory are invalid. A maximum in the rate of polymerization should be observed,[14] prior to the beginning of the constant rate period, though the best kinetic determinations have failed to show this. Schultz and Romatowski,[15] studying the emulsion polymerization of styrene, allowed polymerization to proceed to 11.5% conversion, then diluted the latex by a factor of 5.7, added monomer and restored the rate of decomposition of the initiator to its original level. The rate of polymerization decreased by only 30%, and two types of latex particles were observed, a large type attributed to the seed latex and a smaller type, claimed to have been produced after dilution. Since the soap concentration fell below the critical micelle concentration (CMC) when the latex was diluted, the smaller particles must have been produced in the aqueous phase, contrary to what is assumed in the Smith-Ewart theory.

During the constant rate period the rate of polymerization is given by:

$$-dM/dt = K_p C_m \bar{n} N$$

where K_p is propagation constant, C_m is the monomer concentration in the micelles, $\bar{n}$ is the average number of free radicals/latex particle, and N is the number of latex particles/unit volume.

All quantities on the right-hand side of the equation are assumed to be constant, although very few precise determinations of the individual quantities have been made. In this paper, N is measured during and after the constant rate period by a spreading method.

Previous Work

Van der Hoff[2] determined N at various conversions during the emulsion polymerization of styrene. However, the important constant rate period was not exactly defined, and the data up to 40% conversion are not sufficient or accurate enough to determine the variation of N during that period. From another emulsion polymerization of styrene, the same author[16] showed that the number of particles per gram of monomer increased sharply at the CMC of the soap used. However, the number of particles per unit volume of latex, the quantity used in the Smith-Ewart theory, cannot be calculated at constant initiator concentration, since the monomer and initiator concentration were not kept constant as the soap concentration was decreased. There does not seem to be any other sufficiently accurate determination of the variation of N with per cent conversion to test the assumptions made in the Smith-Ewart theory.

EXPERIMENTAL

Materials

Styrene was distilled twice from a sample supplied by Australian Petrochemicals. The fraction boiling at 90°C at a pressure of 135 mm was used.

The initiator, potassium persulfate, was recrystallized twice with water from BDH potassium persulfate. Sodium dodecyl sulfate was prepared by the method of Dreger et al[18] with the use of a sample of redistilled BDH dodecanol. The fraction with a boiling point of 254–255°C was used.

Method for Determination of *N*

A new method, described in more detail elsewhere,[17] was developed to determine the value of *N*. The latex was diluted to a suitable concentration (0.05% solids) and made 16% (v/v) with respect to isopropanol and 0.3% (w/v) with respect to poly(vinyl alcohol), the latter being capable of supporting the latex particles at the air/water (A/w) interface. A known volume of this mixture was spread uniformly over a known area of the A/w interface. A monolayer of poly(vinyl alcohol) was formed, in which were embedded all the latex particles, at a surface density of approximately 10 μ^2/particle.

The monolayer of latex particles was transferred to an electron microscope grid in the following way. The grid was held on the end of a brass rod of the same diameter as the grid, by a nitrocellulose film. The grid was pushed 1 cm through the latex film, a glass tube (1 mm in diameter greater than the brass rod) dropped down the brass rod, isolating it from the surrounding latex film, and the brass rod removed. The latex film was photographed in the electron microscope at a suitable magnification (usually 2500×) and by counting the number of latex particles/unit area, the value

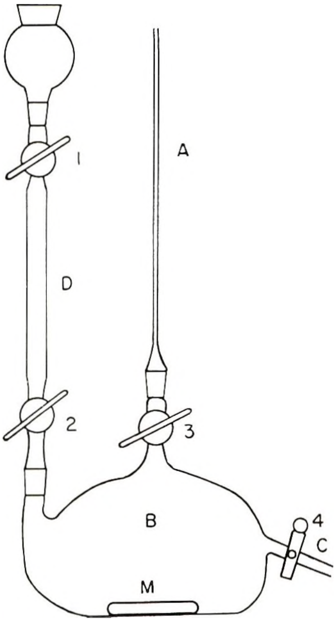

Fig. 1. Apparatus used for sampling latex.

of N could be calculated. The error in N is mainly dependent upon the uniformity of spreading and the number of particles counted, i.e., the number of photographs taken. Experiments with standard Dow latices (0.088 μ diameter) showed that if at least 10 photographs were taken (i.e., count approximately 8000–10000 particles/sample) the error in N was about $\pm 10\%$. The method is probably little less tedious than measuring the particle diameter with the electron microscope and then calculating N, but has the advantage that the results are not influenced by particle size distribution or variations of the particle size in the microscope.

Apparatus

The apparatus (Fig. 1) was designed so that the rate of polymerization could be followed in the same experiment as that from which the samples were taken. It consisted of a capillary tube, A, connected to the reaction vessel B (310ml), to which was also connected a buret, D (15 ml). Sections A, B, and D were situated in a water thermostat, maintained at 40°C. Taps were located at positions 1, 2, 3, and 4, and B was stirred by a magnetic stirer, M. The samples were tapped off through a narrow tube C, which passed through a hole in the side of the Perspex thermostat container into the air, thus allowing samples to be taken with a minimum wastage of material.

Method for Sampling at Various Conversions

The emulsion was prepared in the following way. The total amount of soap was dissolved in water, the initiator dissolved in a minimum volume (less than 10% of total amount) of this soap solution and both solutions thermostatted at 40°C. Styrene was emulsified in the remainder of the soap solution by rapid stirring.

The initiator–soap solution was then mixed with the emulsion and poured into the reaction vessel, filling A, B, and D completely. The rate of reaction in B only (tap 2 closed) was followed by the contraction in A.

To collect a sample, tap 3 was closed, taps 1, 2, and 4 opened until the required volume of latex had been collected, after which they were closed, and tap 3 opened. While a sample was being taken, tap 1 was open for no longer than 20 sec. After collection of each sample, measurements of the rate of polymerization were continued, thus providing a saw-tooth curve, the segments of which were fitted together to give a smooth curve of per cent conversion versus time (Fig. 2). This curve was compared with that from a 48-ml capacity dilatometer, the results for the same mixture agreeing within experimental error.

Samples taken from C were poured directly into a 100 ml flask containing 0.1 g of hydroquinone dissolved in about 50 ml of water. The amount of sample taken was measured by weighing. It was considered that allowing about 10 ml of unstirred latex from D into 310 ml of stirred latex in B would have a negligible effect on the rate of reaction. The sample was diluted to 100 ml, of which a 10-ml portion was dialyzed against warm water (40°C) for 15–20 hr. Any variation in concentration of the latex caused by dialysis was measured by weighing. The number of particles per milliliter was then measured by the spreading method described. All polymerizations were performed at 40°C.

RESULTS

The recipe used for polymerization was styrene (30 g), water (300 g), sodium dodecyl sulfate (2.1 g), and potassium persulfate (0.60g). The rate of polymerization of this mixture is given in Figure 2.

A preliminary run was performed with samples taken after 20, 40, 60, 80, 140, and 1200 min of polymerization. From each sample, N was calculated by use of only eight photographs, thus providing an indicating of the variation of N with conversion. The time of polymerization, per cent conversion, and N are given in Table I.

TABLE 1

Sample	Time of polymerization, min	Conversion, %	$N \times 10^{-14}$
1	20	11.6	0.8
2	40	24	0.9
3	60	36	1.2
4	80	49	1.1
5	140	66	1.2
6	1200	92	1.2

Since the constant rate period began after 10 min polymerization, this experiment indicated that N may have increased during the constant rate period and then remained constant. The experiment was repeated, taking as many samples as possible during the constant rate period. The time of polymerization, per cent conversion, weight of sample taken, and N are given in Table II. Each value of N was calculated from 12–15 photographs.

TABLE II

Sample	Time of polymerization, min	Conversion, %	Weight of sample, g	$N \times 10^{-14}$
1	10	4.6	1.7511	0.97
2	20	11.6	2.6285	1.02
3	30	18.6	2.2084	1.08
4	40	25.4	2.1482	1.16
5	55	34.6	1.7627	1.31
6	84	48	2.0948	1.24
7	1200	92	1.0813	1.33

These results are plotted in Figure 3, together with the error. This error is the standard error of the estimate, calculated for each of the samples,

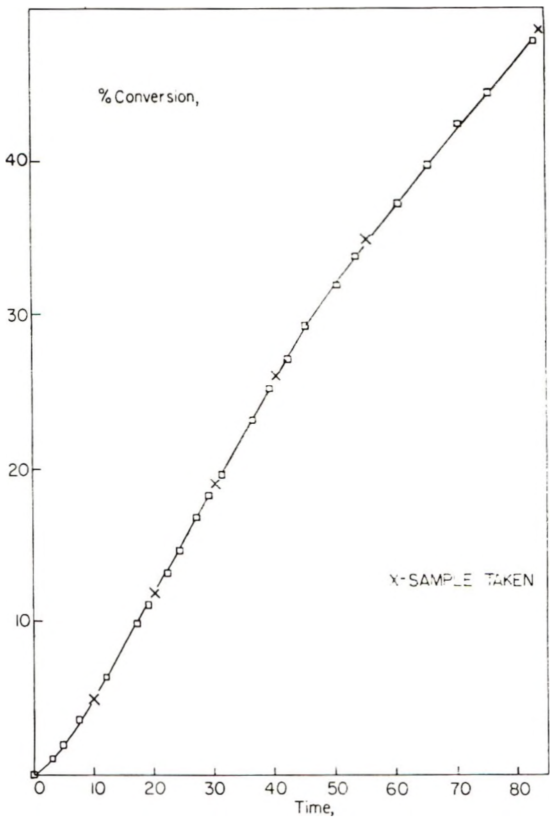

Fig. 2. Rate of polymerization (sampling apparatus).

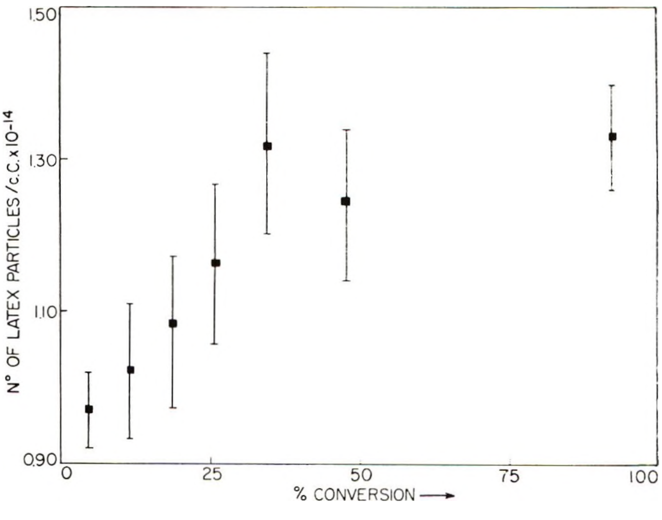

Fig. 3. Variation of particle number with conversion.

from the standard deviations of the number of particles/photograph. The errors calculated in this way, were about ±10%, which is approximately the same error obtained for the calibration of the spreading method.

The experimental results indicated that N increased almost linearly with conversion from 5% to about 35%, after which it appeared to remain constant. The errors in the values of N are low enough to conclude that N was larger at the end of the constant rate period than at the beginning, which means that new particles must have been created during the constant rate period.

This conclusion is very important, and further confirmation was obviously desirable. Such confirmation could be obtained from measurements of the particle size distribution of various samples taken. If no new particles were produced after the beginning of the constant rate period, the minimum particle size in each sample should increase with increasing conversion. The particle size distributions of the first, third and last samples were measured from electron micrographs, taken for the particle number determination.

The procedure for measuring the particle diameters was as follows. The electron microscope grids containing the latex particles, were sprayed with carbon to reduce distortion of the nitrocellulose film in the electron beam. The magnification of the microscope was checked, by using standard Dow latices (0.088 μ and 0.365 μ diameter).[19] The setting up of

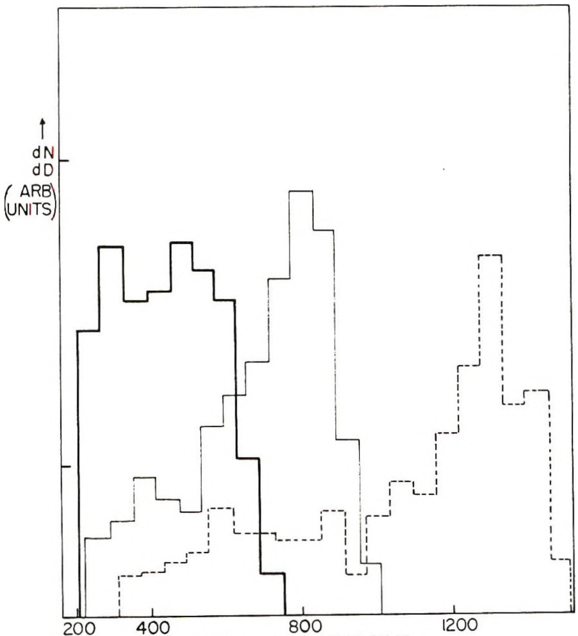

Fig. 4. Distribution of particle diameter of first, third, and last samples: (——) first sample; (——) third sample; (- -) last sample.

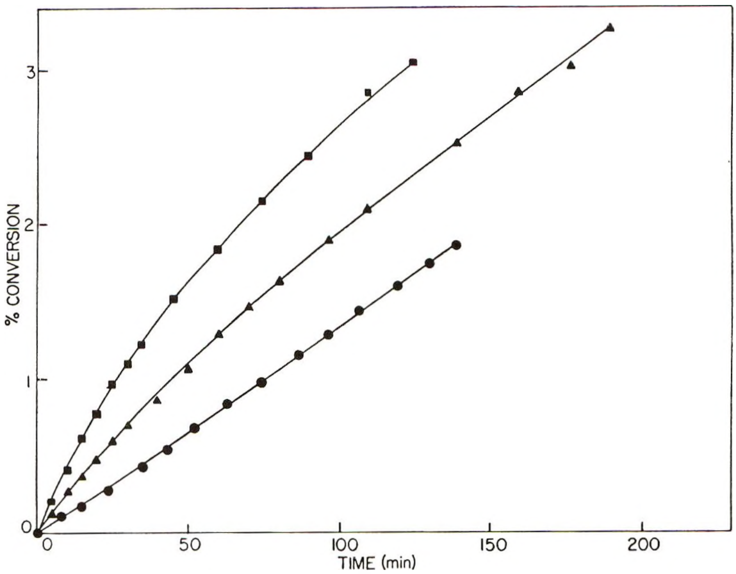

Fig. 5. Rate of polymerization: (■) 35 mmole/l. $NaC_{10}SO_4$, 5 mmole/l. $K_2S_2O_8$, 4% styrene; (▲) 20 mmole/l. $NaC_{10}SO_4$, 20 mmole/l. K_2SO_4, 5 mmole/l. $K_2S_2O_8$, 4% styrene; (●) 20 mmole/l. $NaC_{10}SO_4$, 5 mmole/l. $K_2S_2O_8$, 4% styrene.

the microscope (e.g., focusing) was done on different areas from those used for photographing. The same procedure was used for all samples, thus reducing errors due to variations in the shape of the particles to a minimum. The absolute error in the determination of the particle diameters may have been 10% though the relative error of the measurements should have been no more than 5%, an error which would not influence the overall shape of the distribution curves.

For the first sample, 510 particles were measured, for the third, 480 particles, and for the seventh, 520. The distributions are shown in Figure 4, and although an insufficient number of particle diameters have been measured to obtain a precise distribution curve, two important points may be observed. Firstly, the minimum particle size of the third sample is only 20 Å greater than the first sample, a difference which lies within the experimental error for these measurements. Secondly, the shape of the distribution curves of each sample is different from the other two, in particular, the last sample has a considerable number of particles below 1000 Å diameter. If no more particles were created after the first sample was taken, and if it is assumed that the rate of polymerization/particle is independent of particle size, then the size distribution of the last sample should be narrower than that for the first. The same applied to a comparison between the last and third samples. Hence particles must have been created after the first and third samples were taken, which means that the assumption that new particles are not created during the constant rate period is not supported by these experiments.

Further evidence that particles may be created in the absence of micelles was provided by performing an emulsion polymerization of styrene below the CMC of the soap. The CMC of sodium decyl sulfate at 40°C was measured by the surface tension method, by using a du Nuoy tensiometer. It was found to be 33.5 mmole/l. in pure water, in agreement with the value given by Flockhart,[20] 21 mmole/l. in the presence of 5 mmole/l. potassium persulfate and 12 mmole/l. in the presence of 5 mmole/l. potassium persulfate and 20 mmole/l. potassium sulfate.

The rates of emulsion polymerization at 40°C were measured in the following systems: (a) styrene (4% w/v), sodium decyl sulfate (35 mmole/l.), potassium persulfate (5 mmole/l.), (b) styrene (4% w/v) sodium decyl sulfate (20 mmole/l.), and potassium persulfate (5 mmole/l.) (c) styrene (4% w/v), sodium decyl sulfate (20 mmole/l.), potassium persulfate (5 mmole/l.), and potassium sulfate (20 mmole/l.). The results are shown in Figure 5. If initiation and propagation could only take place in the presence of micelles, no polymerization should take place in system b. However, the initial rate is only 50% slower than that of system c, in which 40% of the soap is in the micellar form.

Staudinger[21] performed a series of emulsion polymerizations of butadiene and styrene at constant soap and initiator concentrations but used soaps of different chain lengths. He attributed the lower initial rates of polymerization for the shorter chain length soaps to the fact that these had higher CMC's. However, in the systems used by Staudinger, there was more potassium dodecanoate in the micellar form than potassium octadecanoate, though the initial rate for the latter is almost double that of the former. Hence some property of the chain length other than its effect on the CMC of the soap, seems to be important.

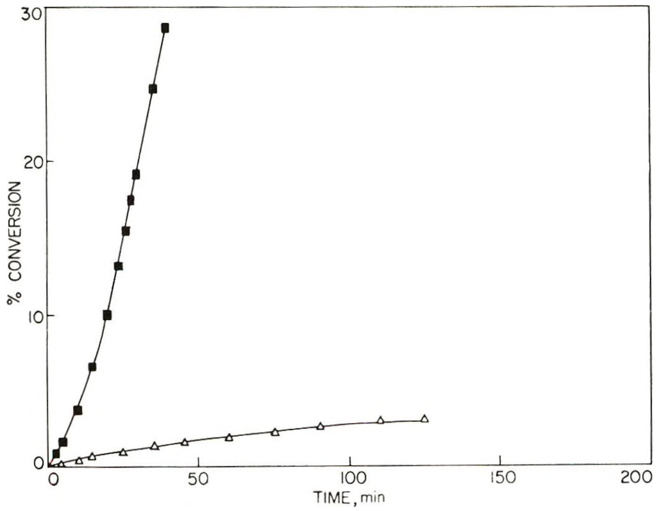

Fig. 6. Rate of polymerization: (■) 20 mmole/l. $NaC_{12}SO_4$, 5 mmole/l. $K_2S_2O_8$, 4% styrene; (△) 35 mmole/l. $NaC_{10}SO_4$, 5 mmole/l. $K_2S_2O_8$, 4% styrene.

The rates of polymerization of two systems were measured, each system having an equal concentration of soap above the CMC, but having soaps of different chain length. The first system was styrene (4% w/v), potassium persulfate (5 mmole/l.), and sodium decyl sulfate (35 mmole/l.); and the second was styrene, (4% w/v) potassium persulfate (5 mmole/l.) and sodium dodecyl sulfate (20 mmole/l.). Each system had 14 mmoles of soap in the micellar form. The aggregation number of the longer-chain soap is between 20 and 50% larger[22,23] than that of the shorter-chain soap, giving more micelles in the solution of the latter. The effect of this, if any, should be to produce a slightly faster rate of polymerization in the decyl sulfate solution. The rates of polymerization are shown in Figure 6. Considering the first 20 min of polymerization, the rate with the C_{12} soap is about 8–10 times greater than with the C_{10} soap, which is contrary to what would be expected if initiation occurred only by entry of the radicals into the micelles.

A more plausible explanation of these results, proposed earlier[14,21,24] may be obtained if it is assumed that initiation of polymerization takes place in the aqueous phase, with soap adsorbing onto the growing polymer chain. On this assumption, the longer the chain length of soap, the stronger the adsorption at the polymer–water interface. This would reduce coagulation and termination, and thus increase the rate of reaction.

CONCLUSION

Using a new method for the determination of the number of latex particles/unit volume of latex (N), it has been shown that in the emulsion polymerization of styrene, N increases during the constant rate period, contrary to what is assumed in the Smith-Ewart theory.

Kinetic experiments with soaps below the CMC showed that latex particles can form in the absence of micelles. The chain length of the soap used, had a marked effect on the rate of polymerization. This effect was not due to the lower CMC's of the longer chain length soap, but possibly due to their stronger adsorption of it at the polymer–water interface.

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The Preparation and Characterization of Some Cellulose Graft Copolymers. V. ESR Study of Preirradiation Grafting of Styrene to Cellulose Acetate

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Synopsis

Previous studies have shown a two-peak molecular weight distribution of the grafted polystyrene side chains from preirradiation-grafted cellulose acetate. ESR has been used to investigate this grafting system in further detail. It was found that the rate of decay of the trapped radicals on adding the monomer solution was quite slow and a substantial proportion remained after 3 days at 25°C. The G value for radicals lost was, however, in good agreement with the G (grafted side chains) produced during the same period. The ESR spectrum does not change on addition of the monomer solution. The explanation offered is that the side chains grow and terminate rapidly compared with the slow overall rate of decay. The grafting yield and the molecular weight of the grafted side chains continue to grow until the reaction is terminated, leading perhaps to the high molecular weight narrow distribution fraction.

Introduction

In an earlier paper[1] a determination of the molecular weight distributions for grafted polystyrene side chains of radiation-induced graft copolymers of styrene with cellulose acetate was reported for both mutual and preirradiation treatments. It was shown that the method of preparation had a pronounced effect on the form of the molecular weight distribution of the grafted side chains. The mutual irradiation treatment gave a single-peak distribution, as expected, whereas, more interestingly, samples prepared by the preirradiation technique could be described by the superposition of two distributions. The explanation offered for the two-peak distribution was that the broad distribution of low molecular weight side chains was formed by the growth and mutual termination of radical chains present in the more mobile, more accessible regions of the polymer. The narrow distribution of high molecular weight material was considered to be due to slow growth of a very small proportion of radical trapped in crystalline regions of the film.

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An alternative explanation[2] would be that irradiation of the solid gave rise to a nonrandom distribution of trapped radicals. Thus, if the larger proportion were in regions corresponding, perhaps, to expanded spurs, this would lead to a large amount of low molecular weight polymer on addition of the monomer and swelling agent due to a fast rate of termination, by radical recombination. Other, more isolated radicals, could continue to grow until terminated by opening the tubes leading to the narrow distribution high molecular weight polymer.

In an attempt to obtain more information on the mechanism of the preirradiation grafting of styrene to cellulose acetate an electron spin resonance (ESR) study has been carried out.

Experimental

Exactly the same grades of cellulose acetate as used previously[1] were cast into films from dimethylformamide and acetone for DS 1.84 and 2.25, respectively. In the earlier experiments, bundles of strips of the films were placed in 3 mm ID Suprasil quartz tubes and degassed to a pressure of $<10^{-5}$ mm Hg without any other pretreatment. However, it was found that such treatment did not remove traces of the solvent, and consequently very low values of spin concentration were obtained, and it was found necessary to thoroughly wash the samples to completely remove traces of the solvent. Two methods of washing were used: the first involved treating the films in boiling water for 30 min, degassing initially for 30 min at 95°C, then overnight at room temperature. In the second method the samples were soaked in cold water for 5 days then degassed at a temperature of 45°C for 3 days. As will be shown later, both methods showed essentially the same behavior as regards the build-up of radicals in vacuum; however, the treatment with boiling water turned the film opaque, and wrinkled. The film used for the grafting experiment leading to the two-peak distribution of grafted side chains described previously[1] were freed from solvent by prolonged heating under high vacuum. The yield obtained is included in Figure 5 and can be seen to fit the curve obtained with washed films within the experimental error. No special differences in the three methods of drying, therefore, seem to be involved except the last traces of solvent must be removed to obtain good yields.

Samples were irradiated in a vacuum in the quartz tubes, either at -78°C or at room temperature, at a dose rate of 0.3 Mrad/hr by γ-rays from a ^{60}Co source. ESR spectra were recorded at room temperature with a Varian V 4502-10 spectrometer, after color centers in the quartz were annealed by flame treatment in the usual manner.

The variation of the concentration of free radicals with dose for a number of samples is shown in Figure 1. It can be seen that both washing treatments gave essentially the same behavior, and that the production of radicals is initially faster at room temperature than at -78°C, but that the radical concentrations are approximately equal after 10 Mrad.

Apparent *G* (radical) values calculated for the cellulose acetate (DS 1.84) pretreated by washing in cold water, and irradiated at −78°C at various doses are given in Table I. The value at 6.5 Mrad compares with the value of 1.76 found by Florin and Wall[3] for a sample of cellulose triacetate irradiated under similar conditions.

TABLE I
Yield of Free Radicals as a Function of Dose for Cellulose Acetate, DS 1.84, at −78°C

Dose, Mrad	*G* (radicals) 100 eV
1.0	3.68
6.5	1.77
10.0	1.31

The shape of the ESR spectrum was found to be independent of the temperature of irradiation, the degree of acetylation (i.e., DS 1.84 or 2.25), and the time of standing in vacuum after irradiation. A typical spectrum is shown in Figure 2.

No attempt was made to identify the free radicals giving rise to the spectra, but it might be pointed out that the spectra are similar to those previously reported for cotton cellulose, although slightly different to that reported for cellulose triacetate.[3]

The decay of radicals for a number of samples maintained in a vacuum at room temperature is shown in Figure 3. The data are also presented in Figure 4 as the reciprocal of the radical concentration against time. The decay appears to follow second-order kinetics over most of the range after

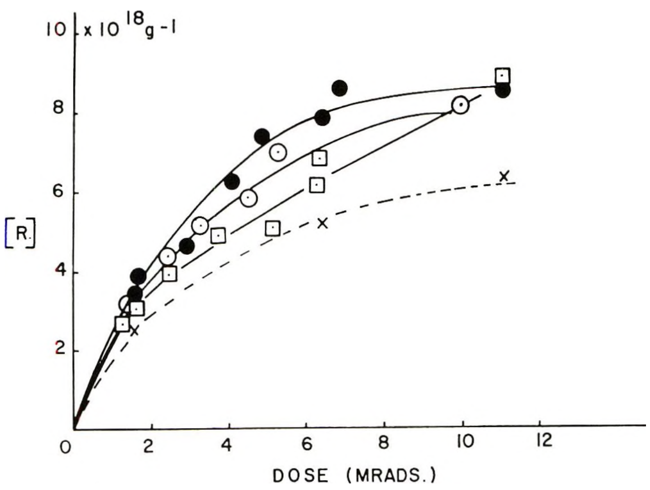

Fig. 1. Variation of free radical concentration with dose: (●) DS 1.84, irradiated at 25°C, washed in boiling H_2O; (⊡) DS 1.84, irradiated at −78°C, washed in boiling H_2O; (⊙) DS 1.84, irradiated at −78°C, washed in cold H_2O; (×) DS 2.25, irradiated at 25°C, washed in boiling H_2O. ESR measurements at 25°C.

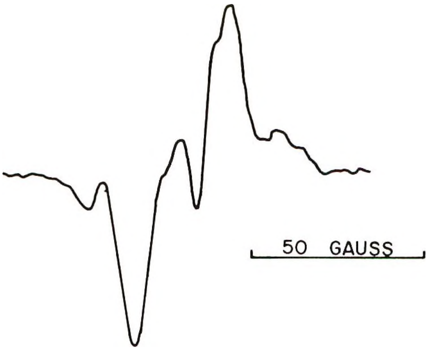

Fig. 2. First derivative ESR spectrum of cellulose acetate at 25°C.

an initial more rapid decay. Such behavior might be expected if there is a nonrandom distribution of the radicals such as would exist if the radicals are formed in spurs or clusters. The initial decay would occur within the spurs and because of the close proximity of the radicals would be relatively fast. As the spurs expand the situation may be treated as corresponding to a more random distribution of radicals which should then follow second-order kinetics. An alternative explanation might be the possibility of reaction of the radicals with gases formed during the irradiation, since no attempt was made to pump out gaseous irradiation products.

Values of second-order decay constants calculated from the data shown in Figure 4 for a number of samples are given in Table II.

TABLE II
Rate of Decay of Trapped Radicals in Cellulose Acetate

Dose, Mrad	Irradiation temperature, °C	DS	k_t, g/rad-hr
11.1	25	1.84	1.60×10^{-22}
7	25	1.84	0.67×10^{-22}
6.4	−78	1.84	2.13×10^{-22}
11.1	25	2.25	2.13×10^{-22}

Although no definite conclusions are drawn from these results it appears that the rate of radical decay increases with increasing dose at room temperature which may be interpreted as being due to a greater amount of disruption of the polymer structure. The relatively high rate of decay for the sample irradiated at −78°C is not understood. The similarly fast decay rate for the sample of 2.25 DS may explain the low maximum radical concentration obtained after irradiation.

In order to follow the rate of grafting of styrene to cellulose acetate a series of samples of the film pretreated by cold water washing were irradiated at −78°C to a dose of 10 Mrad and treated essentially under the same conditions used in the experiments described previously.[1] The per cent

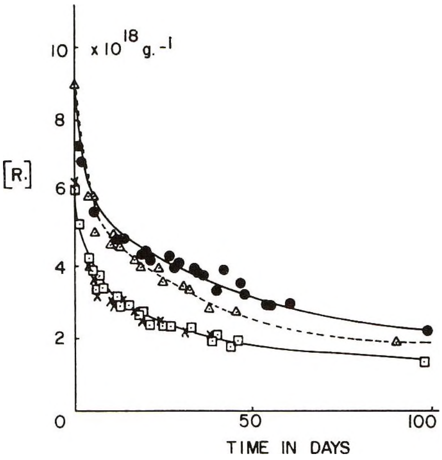

Fig. 3. Decay of free radicals in a vacuum at room temperature: (●) DS 1.84, irradiated at 25°C to 6.94 Mrads, (△) DS 1.84, irradiated at 25°C to 11.1 Mrad; (⊡) DS 1.84, irradiated at −78°C to 6.4 Mrad; (X) DS 2.25, irradiated at 25°C to 11.1 Mrad.

grafting as a function of time is shown in Figure 5. It can be seen that after an initially fast rate the grafting continued to increase slowly even after one week at 25°C. This is in keeping with the slow rate of radical decay to be discussed later. A separate series of experiments was conducted with a larger sample for various times and the resulting films extracted and hydrolyzed as described previously.[1] The molecular weights were determined on the resulting polystyrene. The results are shown in Table III. It can

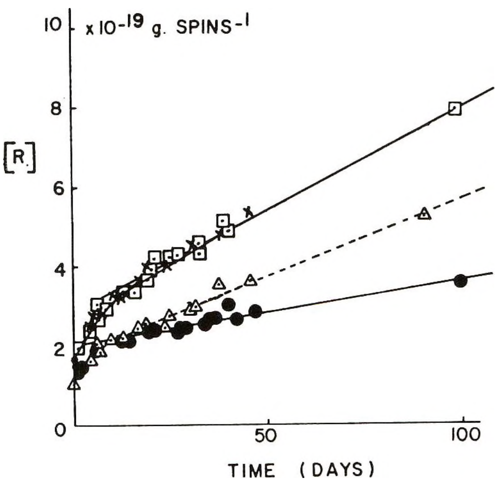

Fig. 4. Second-order decay plots for decay of radicals in cellulose acetate: (●) DS 1.84, irradiated at 25°C to 6.94 Mrad; (△) DS 1.84, irradiated at 25°C to 11.1 Mrad; (⊡) DS 1.84, irradiated at −78°C to 6.4 Mrad; (X) DS 2.25, irradiated at 25°C to 11.1 Mrad.

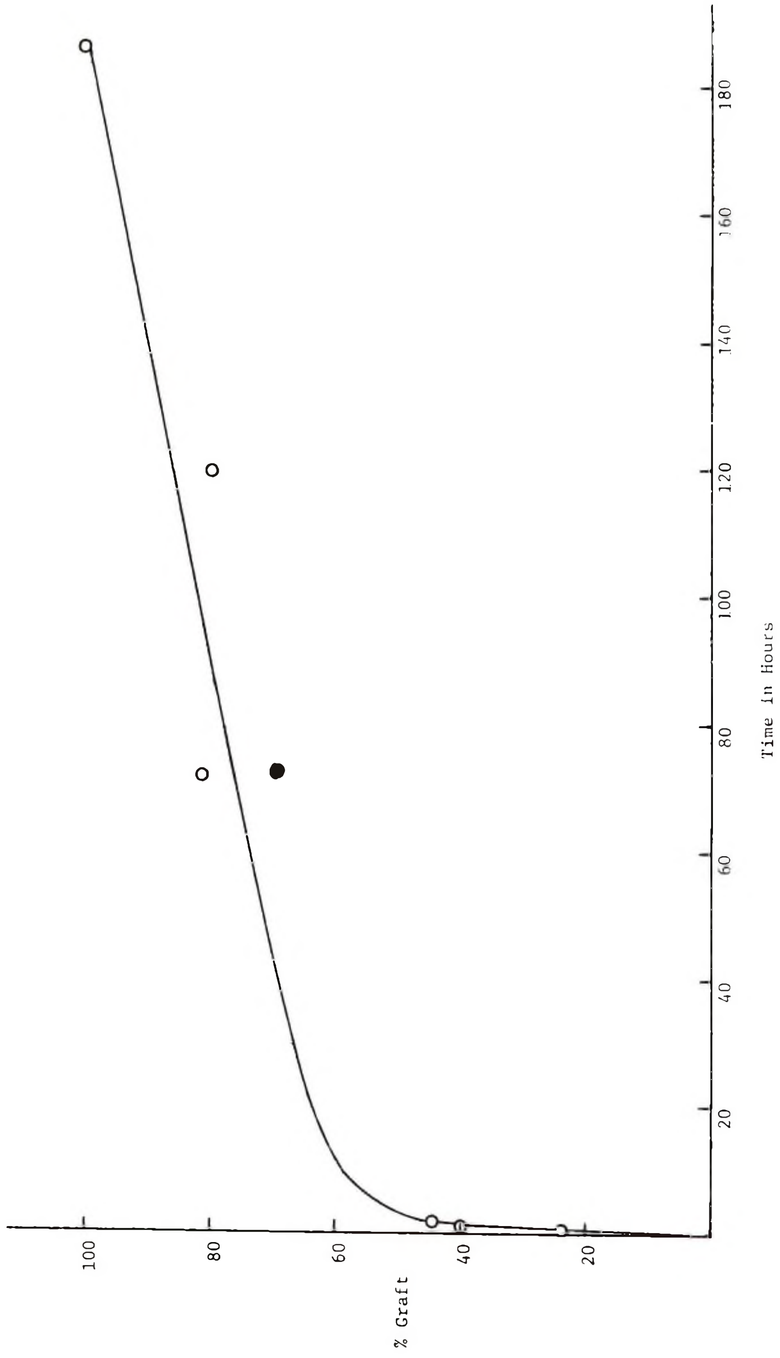

Fig. 5. Per cent grafting vs. time for cellulose acetate irradiated with 10.0 Mrad. The solid circle represents the sample reported previously.[1]

TABLE III
Molecular Weight of Grafted Side Chains[a]

Graft, %	Molecular weight (viscosity average)
40	222,000
56	709,000
81	997,000
102	1,630,000

[a] The measurements were carried out on separately prepared samples.

be seen that the molecular weight slowly increased with time throughout the duration of the experiments.

In a separate experiment a sample was irradiated and the ESR spectrum recorded at room temperature. A solution of 80:20 styrene–pyridine solution was then introduced via a break seal and the change of the spectrum was followed as a function of time. Separate experiments showed that the film contained about 25% styrene and 7% pyridine at equilibrium. The decrease in the signal intensity is shown in Figure 6. Rather surprisingly, the radicals decayed relatively slowly though at a faster rate than a similar sample maintained in vacuum. Further, no detectable changes in the spectral shape occurred during the decay. Thus although grafting was certainly taking place it was not possible to detect the spectrum of the growing polystyryl radical. This is not too surprising if one considers the slow overall decay of the radicals since any contribution from polystyryl radicals, if they have a short lifetime, would be small compared to the total signal intensity. It should be noted that after 72 hr, the time at which the reaction was terminated by opening the tubes and adding methanol in the previous studies,[1] 70% of the radicals had decayed.

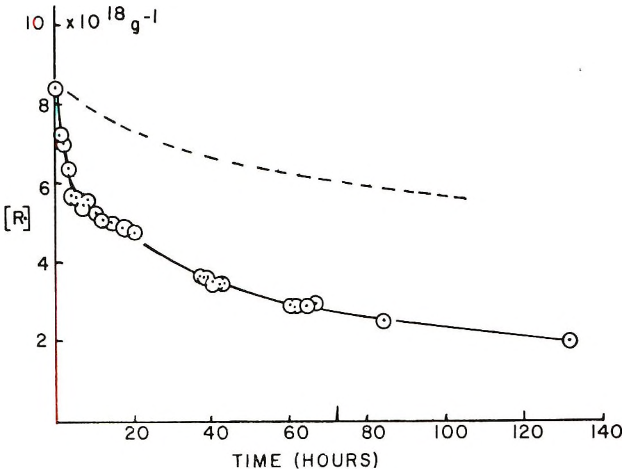

Fig. 6. Decay of free radicals in cellulose acetate, DS 1.84; (——) after introduction of styrene–pyridine; (- - -) decay in dry state.

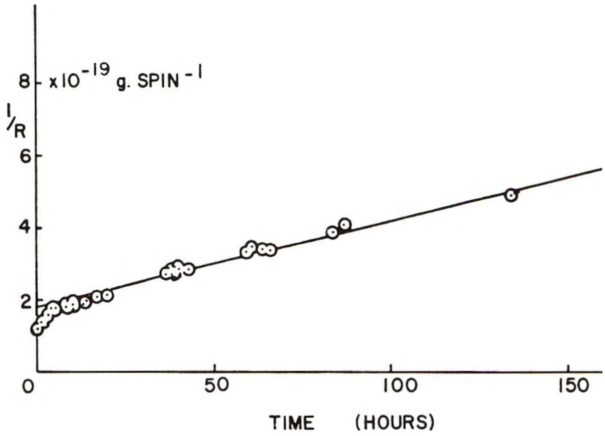

Fig. 7. Second-order decay plot for radicals in cellulose acetate in presence of styrene–pyridine.

The decay data are also plotted in the form of a second-order reaction in Figure 7. As with the decay in the dry state, the results can be described by assuming an initial fast rate which then levels off to follow a second order rate of decay.

A value for the second order rate constant was calculated to be 2.3×10^{-21} g/spin-hr, which is an order of magnitude faster than that in the dry state. In spite of every effort, there were some inevitable differences between the preirradiation grafting experiments and the ESR work. The grafting experiments were carried out by introducing the monomer solution at −78°C and then allowing the solid mixture to melt and reach 25°C, followed by leaving for 72 hr at that temperature. The ESR measurements on the other hand, were made after the film, which was irradiated at −78°C, had reached 25°C. The 70% loss of radicals as measured by ESR after the 72 hr in the monomer solution was, therefore, a minimum value, since some reactive radicals may have decayed during warming. Even so, the agreement between the G (grafted chains) of 1.12 obtained in the grafting experiments and the value of 0.92 for the G (radicals decayed during the 72 hr at 25°C) may be considered quite satisfactory.

The results obtained for the radical decay do not lead to a clear-cut explanation of the two-peak molecular weight distribution found previously. There is indeed a rapid initial drop in radical concentration on adding the monomer solution. The real decrease under the actual grafting conditions described above could be even more impressive. However, a large proportion of the radicals decayed much more slowly than anticipated although about ten fold faster than in the dry film. More unexpectedly, there was no change in the shape of ESR spectrum on adding the monomer solution. This was similar to the behavior found with the preirradiation grafting of styrene to wool.[5] It seems clear that the bulk of the graft polymerization must occur in short bursts which lead to the observed decay of the radical population but without leading to any change in the ESR spectrum. This process would lead to the low molecular weight portion of the product. Why the process takes place in this way is not clear. It may be due to the fact that, as monomer diffuses to a growing radical, the polymerization becomes highly autoaccelerating due to the high local swelling of the polystyrene in the monomer solution or perhaps to the high local exotherm. This, if coupled with a radical population present in the small clusters discussed earlier, would lead to the rapid growth and termination of the chains. In any case, a knowledge of the way in which the trapped radicals are distributed in a glassy polymer is greatly needed. The very high molecular weight, narrow distribution portion, although amounting to 80% of the total grafting by weight, involves only about 3% of the trapped radicals[1] and, therefore, would not affect the spectrum itself. However, the slow increase in the molecular weight with time is consistent with these radicals continuing to grow until the experiment is terminated, thus leading to the narrow molecular weight distribution of the high molecular weight component.

We would like to thank the Camille and Henry Dreyfus Foundation for their support of this investigation. The ESR spectrometer used is the property of the National Aeronautics and Space Administration and has kindly been made available by the Langley Research Center.

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Contributions au fractionnement des copolymères. II. Copolymères ternaires Acrylonitrile–Acétate de vinyle–α-Méthylstyrène

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Synopsis

Acrylonitrile, vinyl acetate, and α-methyl styrene copolymers, were synthesized in aqueous solution, and the resulted products were studied viscometrically by fractionation and by cloud-point titration. The values of the intrinsic viscosities of the polymers in DMF at 20°C are not influenced by the overall composition of the copolymers and the distribution mode of the comonomers. The solubility of the products is directly dependent on the composition, namely, it increases as the acrylonitrile content decreases. The differential fractionation curves are influenced by the chemical composition and by the mode of distribution of the monomers along the macromolecular chain. The successive precipitation method for the fractionation of the ternary copolymers is recommended.

Dans un travail antérieur[1] on a determiné la polydispersité de quelques copolymères binaires d'acrylonitrile (AN) et d'acétate de vinyle (AcV) en appliquant plusieurs méthodes de fractionnement. À cette occasion on a discuté certains aspects de l'influence de la composition chimique des copolymères sur les résultats obtenus par fractionnement, influence concrétisée dans la modification de la forme des courbes de distribution des poids moléculaires.

Le présent travail, poursuit les mêmes aspects et se propose de définir la dépendance des résultats concernant le fractionnement de la nonhomogéneité chimique des copolymères ternaires acrylonitrile–acétate de vinyle–α-méthylstyrène (αmS).

PARTIE EXPERIMENTALE

Synthèse

Les copolymêres ternaires d'AN–AcV–αmS ont été synthétisés au laboratoire en utilisant le procédé de copolymérisation en solution aqueuse. Les monomères ont été introduits en proportion de 11% par rapport au milieu aqueux. La copolymérisation a eu lieu à la température de 60°C sous agitation, pendant 15, 30 et 104 min et présence d'un système initiateur redox constitué de persulfate et métabisulfite (chacun pris en proportion de 0,7% par rapport au total des monomères). Le mélange des monomères a été introduit dès le début dans la solution aqueuse du système initiateur chauffée à 60°C. Ainsi furent synthétisé les copolymères C1, C2, et C3 en partant des proportions différentes des comonomères dans le mélange initial.

Le copolymère C2-30A a été obtenu par l'introduction continuelle de l'AN, pendant toute la durée de la copolymérisation, tandis que les deux autres comonomères se trouvaient déjà dans le système. Après le lavage à l'eau froide et le séchage à 60°C (à l'air et sous vide) les produits ont été soumis à l'extraction au benzène. L'analyse chimique des copolymères nonextraits de même que l'évaporation de l'extrait benzénique ont prouvé l'absence d'homopolymères et de copolymères binaires AcV–αmS.

Les copolymères ainsi obtenus ont été caractérisés par la teneur en AN (la détermination en pour cent d'azote d'aprés Kjeldahl), par $[\eta]$ en solution dans le diméthylformamide (DMF) à 20°C dans un viscosimètre à niveau pendant et par la valeur de log ϕ_{crit} (Tableau 1).

Les spectres infrarouges effectués avec l'appareil Unicam SP 200 confirment la formation de copolymères ternaires par la présence des bandes d'absorption caractéristiques pour αmS à 3100, 1610, 1590 et 715 cm^{-1} à côté de celles d'AcV et d'AN (Fig. 1).

Fractionnement

Une partie des copolymères synthétises à savoir C1-30, C1-104, C2-30, C2-104, C2-30A, de même que le produit ternaire industriel de l'UFS Săvinesti, CS, se caractérisent par le titrage du point de précipitation et par fractionnement en utilisant dans les deux cas le système DMF–n-heptane à 70°C.

La titrage par point de précipitation a été effectué conformément à la méthode de Elias,[2] à l'exception de certaines modifications non-essentielles.

Le fractionnement des copolymères a été réalisé par deux méthodes: précipitation successive et élution sur colonne à gradient de solvant.

Une solution de 1% de copolymère dans le DMF est précipitée par addition successive, sous agitation, de *n*-heptane. Pour assurer la miscibilité des composants du système, la réservoir de non-solvant et le vase de précipitation ont été maintenus à 70°C. Après apparition d'une opalescence persistante, le système a été gardé pendant la nuit à la même température pour établir l'équilibre. Après décantation de la phase diluée, le gel déposé, représentant la fraction, a été dissous dans le DMF. On a déterminé la concentration en pourcent de la solution obtenue et $[\eta]$. Pour les fractions 1 et 6, obtenues au fractionnement de C2-30 et C2-30A on à établi aussi log ϕ_{crit}. Par cette méthode les copolymères ont été séparés en sept fractions.

Pour réaliser le fractionnement sur colonne avec gradient de solvant, on a utilisé la méthode de Barbé et Zanetti[3] en notant que, dans notre cas, la

TABLEAU I

Caractéristiques Physico-chimiques des Copolymeres Etudiés

Copolymere	Temps de polymérisation, min	Mélange de monomeres, g/100 g			Composition du copolymere, g/100 g		$[\eta]$ (DMF, 20°C)	$\log \phi_{crit}$
		AN	AcV	αmS	N	AN		
C1-15	15	91	6	3	25,02	94,82	2,30	—
C1-30	30	91	6	3	24,79	93,95	2,60	1,20
C1-104	104	91	6	3	24,50	92,85	2,60	1,28
C2-15	15	82	12	6	24,08	91,26	2,45	—
C2-30	30	82	12	6	23,38	88,61	2,40	1,66
C2-104	104	82	12	6	23,21	87,96	2,60	1,71
C3-15	15	73	18	9	22,84	86,56	2,45	—
C3-30	30	73	18	9	22,38	84,82	1,80	—
C3-104	104	73	18	9	21,26	80,57	2,60	—
C2-30A	30	82	12	6	22,54	85,42	2,50	1,52
CS	104	91	6	3	24,40	92,47	1,75	1,35

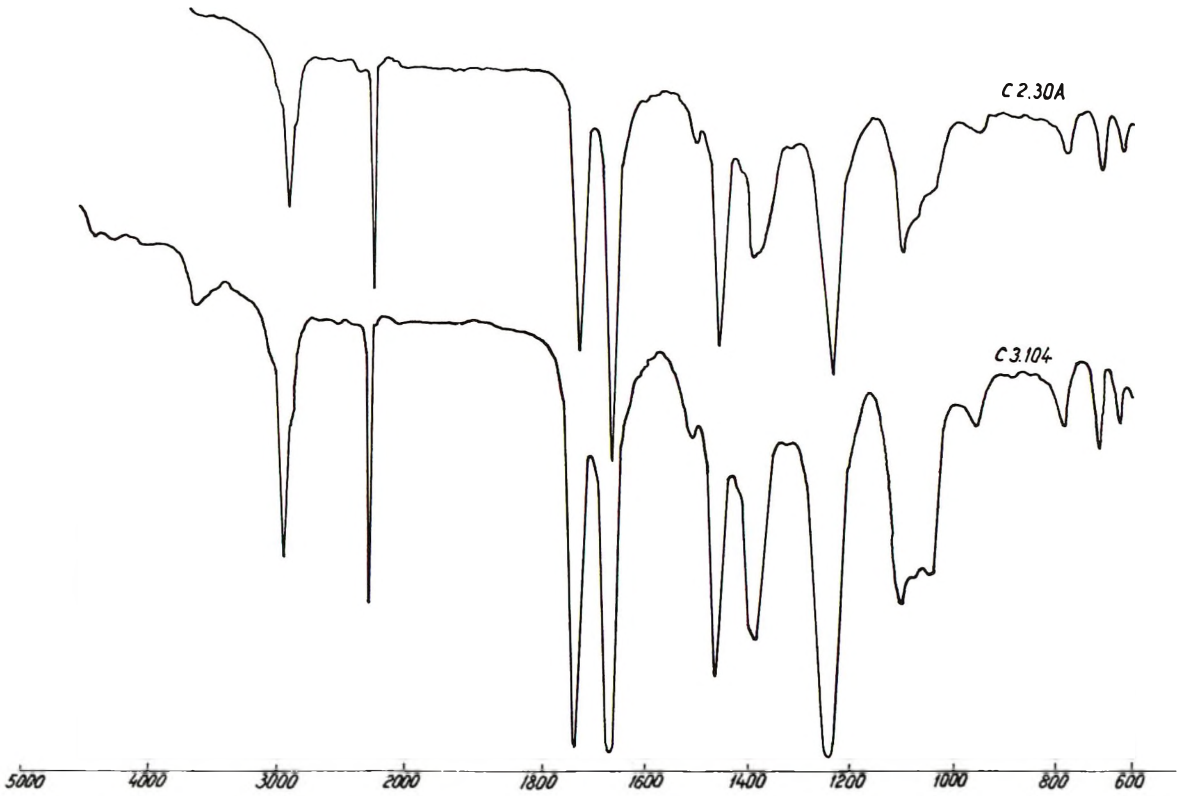

Fig. 1. Spectres d'absorbtion en infrarouge des C2-30A et C3-104.

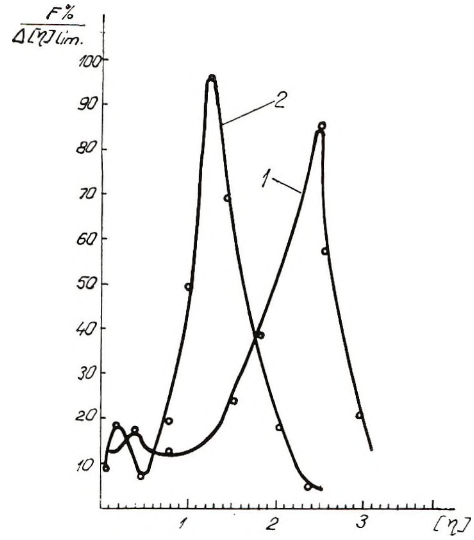

Fig. 2. Courbes différentielles de fractionnement du CS: (*1*) précipitation successive; (*2*) élution sur colonne.

température de la colonne a été maintenue à 70°C. La polymère a été déposé non-selectivement sur le support. De cette manière, les copolymères étudiés ont été séparés en dix fractions dont on a déterminé également [η].

Les données expérimentales obtenues ont été représentées sous forme de courbes différentielles de distribution (Figs. 2–7, les courbes *1* pour les

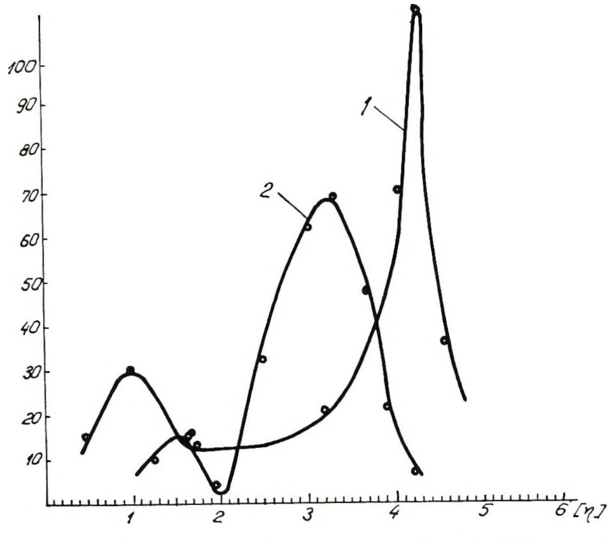

Fig. 3. Courbes différentielles de fractionnement du C1-30: (*1*) précipitation successive; (*2*) élution sur colonne.

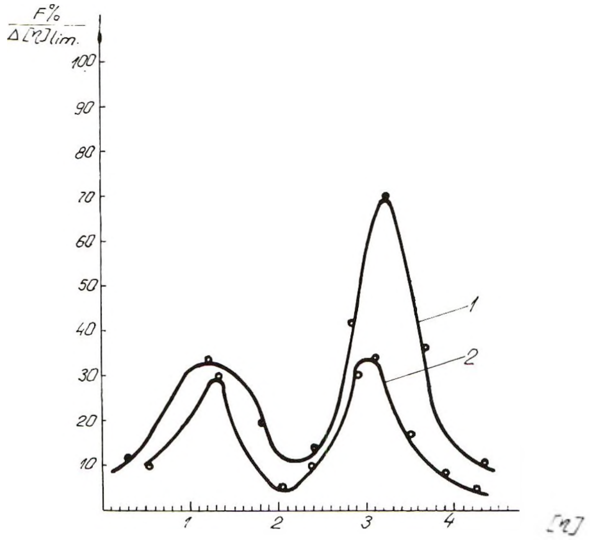

Fig. 4. Courbes différentielles de fractionnement du C1-104; (*1*) précipitation successive; (*2*) élution sur colonne.

résultats par précipitation successive, les courbes *2* pour ceux obtenus par élution sur colonne).

RESULTATS ET DISCUSSIONS

Les dates expérimentales mettent en évidence la complexité de la dependance entre le facteur composition chimique et les résultats du fractionnement. Les copolymères synthétisés par changement de la teneur en AN modifient autant leur comportement à l'écoulement que leur solu-

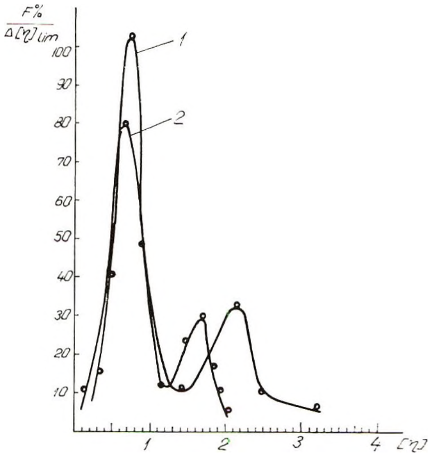

Fig. 5. Courbes différentielles de fractionnement du C2-30: (*1*) précipitation successive; (*2*) élution sur colonne.

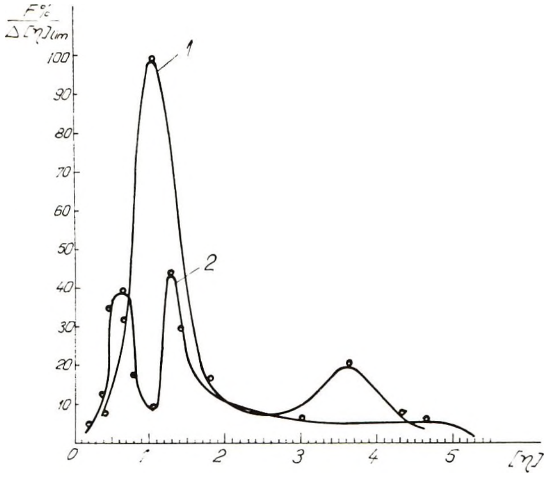

Fig. 6. Courbes différentielles de fractionnement du C2-104: (*1*) précipitation successive; (*2*) élution sur colonne.

bilité. Les résultats du fractionnement dépendent de ces deux propriétés mentionnées du moins lorsque l'évaluation du degré de polymérisation est faite à l'aide du viscosimètre. Étant donné la simplicité de la technique expérimentale, nous avons recours à la détermination de la moyenne viscosimétrique dê poids moléculaire sans mettre en discussion l'influence de la forme des macromolécules.

Les données concernant les valeurs [η] des copolymères étudiés sont représentées dans la Figure 8.

Les valeurs obtenues pour [η] sont inclues dans le domaine 1,7–2,6. On constate une augmentation des pentes des droites η_{sp}/c par rapport à

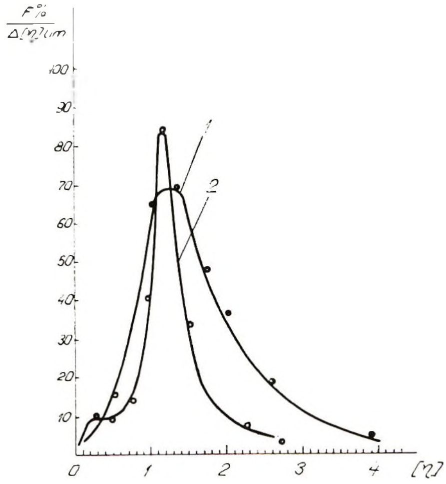

Fig. 7. Courbes différentielles de fractionnement du C2-230A: (*1*) précipitation successive; (*2*) élution sur colonne.

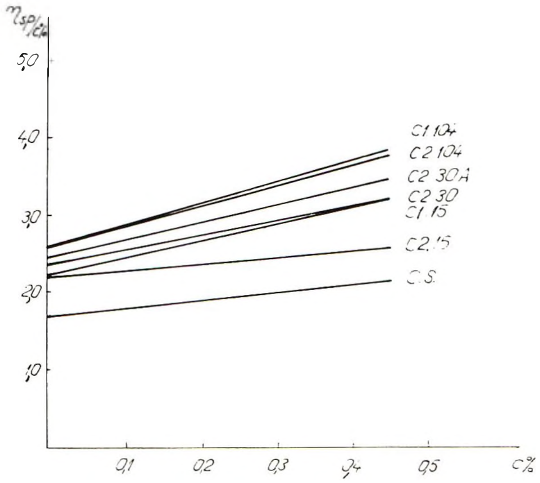

Fig. 8. Variation de η_{sp}/c avec la concentration des solutions dans DMF, 20°C.

la concentration en même temps que l'accroissement de la teneur en comonomère d'AcV dans les copolymères ternaires. Cette constatation confirme la relation de Huggins modifiée par Tompa.[4]

$$\eta_{sp}/c = [\eta] + K'Q[\eta]^2$$

où Q est le facteur de polydispersité. Il faut préciser que, dans notre cas, Q se rapporte autant à la polydispersité du poids moléculaire qu'à la composition chimique.

Les copolymères ternaires AN–AcV–αmS se distinguent des copolymères binaires AN–AcV pour lesquels on a constaté une dépendance directe entre $[\eta]$ et la composition.[1]

Le titrage par point de précipitation a permis d'établir la dépendance linéaire entre les valeurs de log ϕ_{crit} et la composition des copolymères, exprimée en pour cent d'azote (Fig. 9). Ce diagramme indique que la

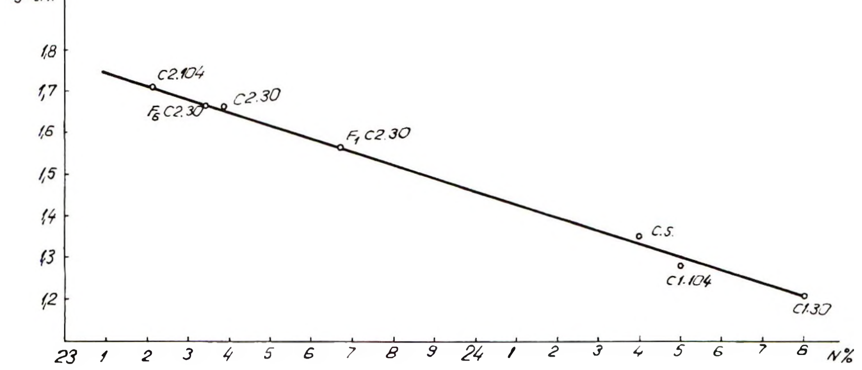

Fig. 9. Variation de logϕ_{crit} á teneur d'AN (exprimé par N %).

solubilité des copolymères croît en même temps que l'abaissement de la teneur en AN.

Les courbes différentielles *1* des Figures 3 et 4 obtenues pour les copolyméres ternaires avec une teneur élevée an AN (Cl-30 et Cl-104) possèdent deux maximums dont le principal est situé dans le domaine des valeurs plus grandes de $[\eta]$. L'abaissement de la teneur en AN des copolymères détermine le déplacement de ce maximum vers les valeurs plus petites de $[\eta]$ (voir les Figs 5 et 6).

Les courbes *2* des Figures 2–7 représentent les résultats du fractionnement des polymères ternaires sur colonne. L'évolution de ces deux maximums est moins régulière que dans les cas des courbes *1*, les données fournies par le fractionnement sur colonne s'étendant sur un domaine plus restreint de valeurs appartenant à $[\eta]$.

Les courbes *1* et *2* des Figures 2 et 7 se rapportent à deux copolymères qui diffèrent par la durée de la synthèse et par la composition, pourtant dans tous les deux cas l'introduction de l'AN a été faite continuellement dans le réacteur. L'allure de ces courbes est pareille, fait qui, à côté du caractère unimodal soutient une répartition moins désordonnée des comonomères le long de la catène.

Pour comparér l'efficience des méthodes utilisées, nous avons représenté sur la Figure 10, la variation de log ϕ_{crit} par rapport à la viscosité intrinsèque $[\eta]_{\text{max}}$ correspondante au maximum des courbes différentielles.

Conformément à Gruber et Elias[2] on établit log ϕ_{crit} par l'extrapolation pour 100% polymère, des données obtenues à la titration par le premier point de précipitation des solutions des composés macromoléculaires. On remarque sur la Figure 10 la tendence de parallélisme de la courbe *1* avec l'axe des abscisses qui confirme que la précipitation fractionnée présente une sensibilité plus réduite à la non-homogénéité chimique que la méthode de l'élution sur colonne.

L'analyse des courbes de fractionnement révèle aussi l'influence de l'équilibre au cours de la séparation des différentes fractions. Au cas de la précipitation successive, puisque chaque fraction s'est séparée en un intervalle plus long, on a réalisé l'équilibre thermodynamique entre les

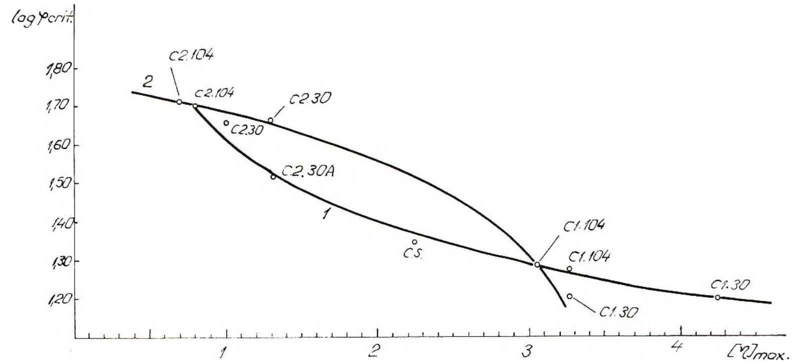

Fig. 10. Dépendance de logϕ_{crit} vis-á-vis de $[\eta]_{\text{max}}$.

phases et par conséquent on a exercé l'influence préponderante du facteur "dimension." Cette dernière s'est reflétée dans une détermination plus précise des courbes de fractionnement.

Au cas d'élution sur colonne, les conditions de fractionnement ne favorisent pas la réalisation de l'équilibre thermodynamique.[5]

En tenant compte de nos observations nous considérons que pour l'étude de la polydispersité des copolymères ternaires par les méthodes classiques, il est recommandable d'appliquer ces méthodes où la séparation des fractions est précédée par l'accomplissement de l'équilibre thermodynamique.

CONCLUSIONS

Pour l'étude de la polydispersité on a synthétisé une série de copolymères ternaires à base de AN, AcV, et αmS, qui, quoiqu'ils diffèrent au point de vue de la proportion des comonomères et de la manière de leur distribution le long des catènes macromoléculaires, ont des viscosités intrinsèques voisines.

Le titrage par point de précipitation a permis de constater que la solubilité des copolymères étudiés est directement liée à la composition et qu'elle s'accroit en même temps que l'abaissement de la teneur en AN.

On a constaté également que l'aspect des courbes différentielles de fractionnement est influencé par la composition chimique et la manière de distribution des monomères le long des chaines macromoléculaires.

Les données expérimentales démontrent la sensibilité plus accentuée envers la composition chimique de la méthode de fractionnement par élution, comparativement à la mèthode par précipitation successive.

Pour le fractionnement des copolymères ternaires par des méthodes classiques, on recommande celles où la séparation des fractions est précédée par l'accomplissement de l'équilibre thermodinamique.

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Alkyllithium and Alkali Metal *tert*-Butoxide as Polymerization Initiator

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Synopsis

We have shown that the presence of other alkali metal alkoxides in the alkyllithium-initiated polymerization drastically increases the rate of polymerization and vinyl unsaturation in polybutadiene. Mechanistically, the propagating center is the dynamic equilibriums between carbon–metal bonds and oxygen–metal bonds. With potassium, rubidium, and cesium salts it reaches a limiting anionic behavior.

INTRODUCTION

The alkyllithium compound including polymer–lithium associates with itself as well as with other metalalkyls or polar compounds such as ethers and amines. For some time we have been interested in the effects on polymerization and polymer structure when the propagating center (carbon–lithium bond) is associated with a compound other than polymer–lithium itself.[1]

One of the significant discoveries, first observed by Wofford,[2] was associated with introduction of alkali metal *tert*-butoxides in a copolymerization system. The objectives of this present work were to examine the homopolymerization reactions and to explore the mechanism of these polymerization initiators.

EXPERIMENTAL

Polymerization grade cyclohexane was dried by countercurrent scrubbing with nitrogen. Phillips special purity butadiene was dried by scrubbing the gaseous monomer with sodium ethylene glycoxide in ethylene glycol. It was condensed at Dry-Ice temperature and stored over Drierite. Styrene was doubly distilled. All monomers were stored at $-15°C$.

Butyllithium was obtained from Lithium Corporation of America as solution in hexane and diluted to about 0.2 M with cyclohexane. Orgmet supplied phenylpotassium as a suspension in hexane. Lithium *tert*-butoxide was obtained from Lithium Corporation of America. Other alkali metal *tert*-butoxides were purchased from MSA Research Corporation.

The technique used to obtain rate of polymerization has been described

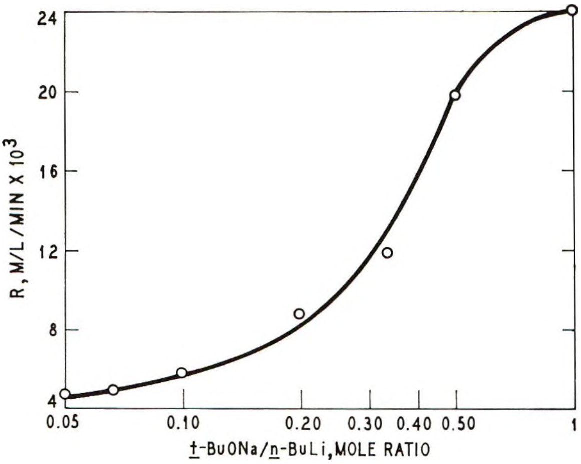


Fig. 1. Rate of polymerization of butadiene with sodium *tert*-butoxide–*n*-butyllithium at 30°C.

extensively in an earlier publication.[3] Polymer microstructure was obtained from infrared absorption spectra.[4]

RESULTS

Rate of Homopolymerization of Butadiene and Styrene

The rates of polymerization of butadiene and styrene in cyclohexane at 30°C with butyllithium and alkali metal *tert*-butoxides are shown in Figures 1–8. The presence of lithium *tert*-butoxide (up to mole equivalence to butyllithium) did not change the rate appreciably. Roovers and Bywater have made a similar observation.[5] However, in the presence of *tert*-butoxides of other alkali metals, polymerization is accelerated. The

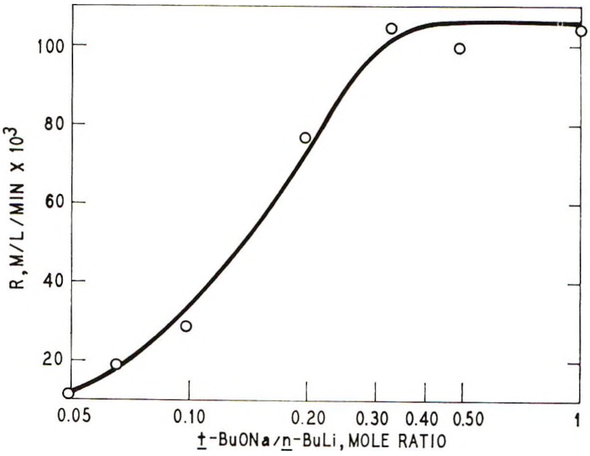


Fig. 2. Rate of polymerization of styrene with sodium *tert*-butoxide–*n*-butyllithium at 30°C.

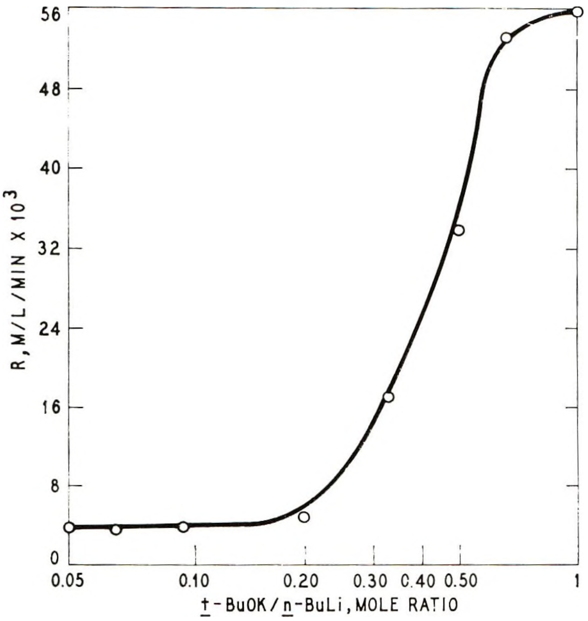


Fig. 3. Rate of polymerization of butadiene with potassium *tert*-butoxide–*n*-butyllithium at 30°C.

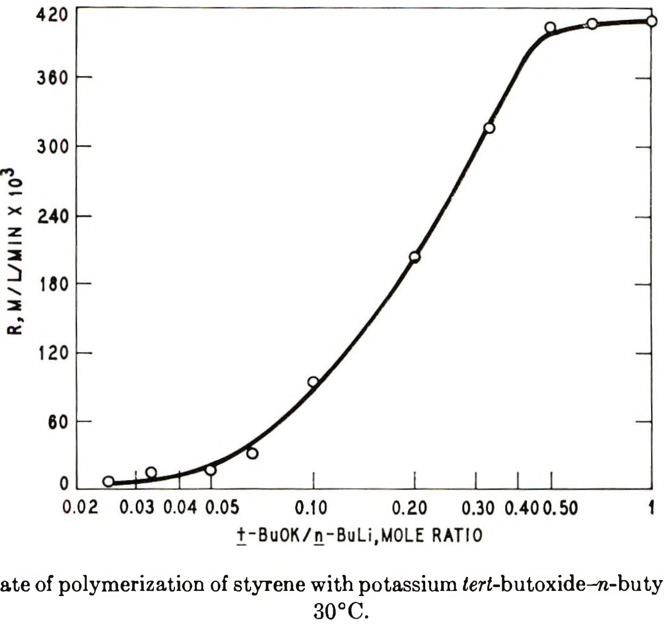


Fig. 4. Rate of polymerization of styrene with potassium *tert*-butoxide–*n*-butylllithium at 30°C.

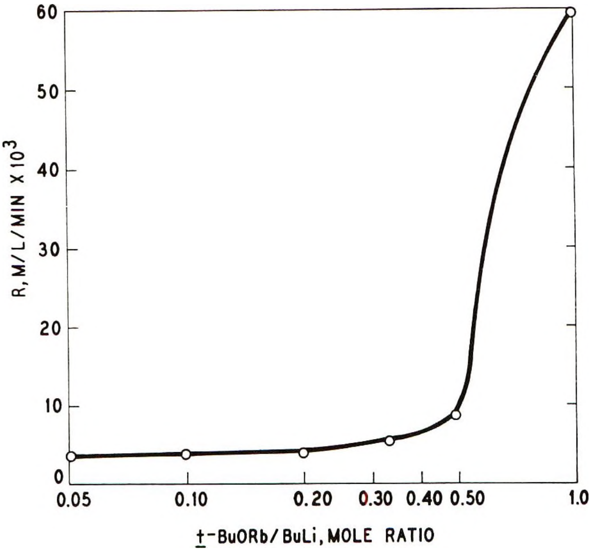


Fig. 5. Rate of polymerization of butadiene with rubidium *tert*-butoxide–*n*-butyllithium at 30°C.

amount of increases depends on the polymerization temperature, monomer, type of alkali metal, and mole ratio of butyllithium and metal *tert*-butoxide. In general, potassium salt is the most effective one. A summary of maximum increases in rate obtained with alkali-metal *tert*-butoxides is shown in Table I.

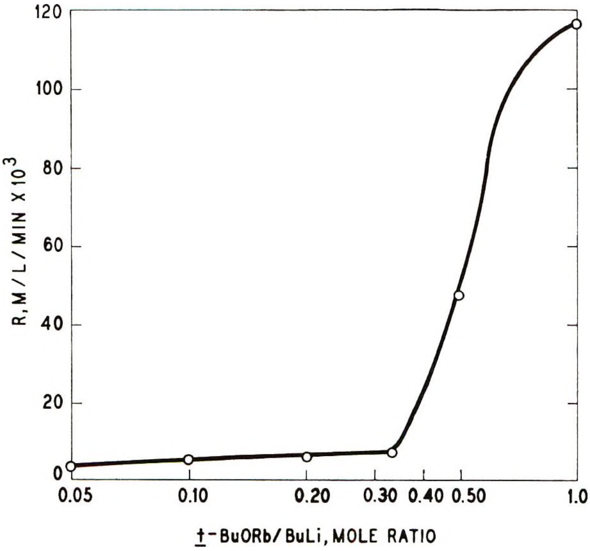


Fig. 6. Rate of polymerization of styrene with rubidium *tert*-butoxide–*n*-butyllithium at 30°C.

TABLE I
Maximum Increase in Rate of Polymerization by Association With Metal *tert*-Butoxides (*t*-BuOM)

	Maximum rate increase, for various *t*-BuOM[a]			
Monomer	Na	K	Rb	Cs
Butadiene[b]	8×	20×	20×	7×
Styrene[c]	25×	100×	30×	60×

[a] In cyclohexane at 30°C.

[b] $[Bd]_0 = 1.6$ mole/l.; $[BuLi]_0 = 1.55 \times 10^{-3}$ mole/l.

[c] $[S]_0 = 0.7$ mole/l.; $[BuLi]_0 = 1.26 \times 10^{-3}$ mole/l.

In cyclohexane, the presence of alkali metal *tert*-butoxide had a negligible effect on the intrinsic viscosity of the final product. In toluene, extensive chain transfer occurred when potassium, rubidium, or cesium salts were present.[6] Schlosser recently reported[7] the metallation of benzene with butyllithium and potassium *tert*-butoxide.

The presence of alkali metal salts had a profound effect on the microstructure of polybutadiene. Vinyl content (from 1,2-addition) varied from 6 to 67% and depended on polymerization temperature, the alkali metal *tert*-butoxide, and the ratio of butyllithium and alkoxide. This is shown in Figure 9–16. The maximum vinyl unsaturation of polybutadienes prepared with butyllithium and alkali metal *tert*-butoxide and approximately the same as those in samples prepared with the corresponding alkali metal or alkali-metal alkyl (Table II).

TABLE II
Relative Vinyl Unsaturation of Polybutadienes

	Vinyl unsaturation, %	
M	BuLi/*t*-BuOM[a]	RM or M
Li	7	6–10
Na	67	65
K	48	45
Rb	55	62[b]
Cs	53	59[b]

[a] Optimum ratio for maximum vinyl unsaturation.

[b] Literature value.[8]

DISCUSSION

The propagation center of anionic polymerization is generally agreed to be the ion-pair $(P{-}M+)_n$, where M+ is the positive alkali metal counterion. It is the ion-pair that determines the structure of the resulting polymer and the rate of propagation, as well as the cross-propagation rates in copolymerization. The nature of this ion-pair depends on the inherent ionic character of the carbon–metal bond, on the solvating ability of the solvent, and on the dielectric constant of the solvent.

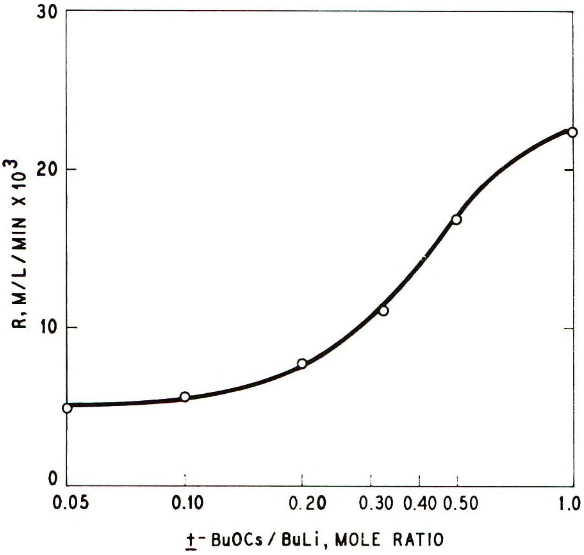


Fig. 7. Rate of polymerization of butadiene with cesium *tert*-butoxide–*n*-butyllithium at 30°C.

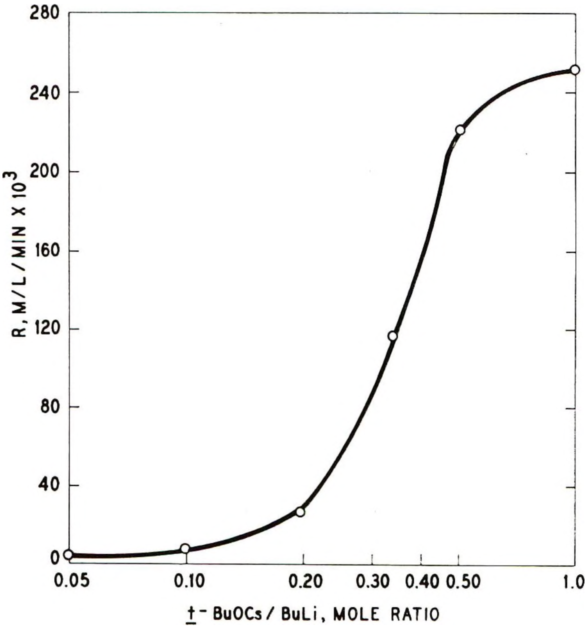


Fig. 8. Rate of polymerization of styrene with cesium *tert*-butoxide–*n*-butyllithium at 30°C.

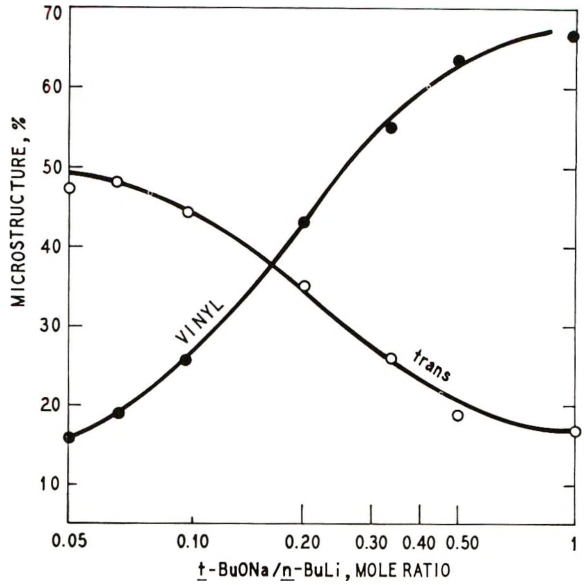


Fig. 9. Microstructure of polybutadiene obtained with sodium *tert*-butoxide–*n*-butyllithium at 30°C.

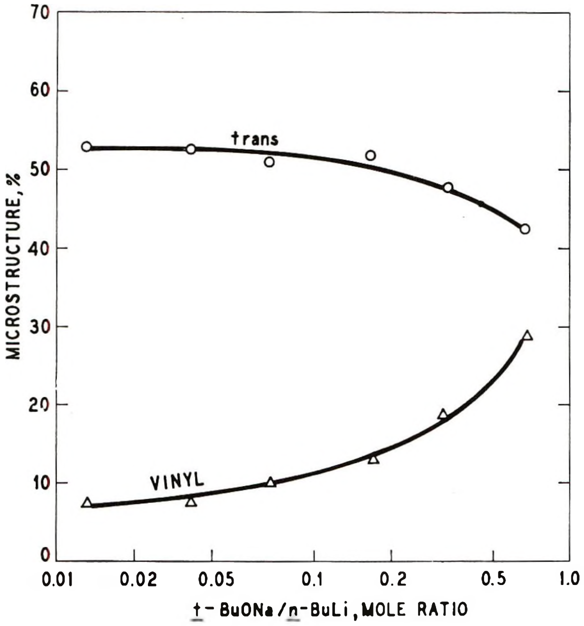


Fig. 10. Microstructure of polybutadiene obtained with sodium *tert*-butoxide-*n*-butyllithium at 50°C.

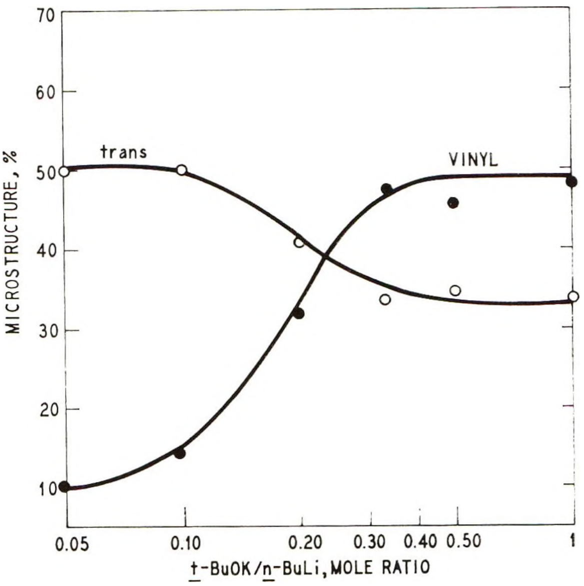


Fig. 11. Microstructure of polybutadiene obtained with potassium *tert*-butoxide–*n*-butyllithium at 30°C.

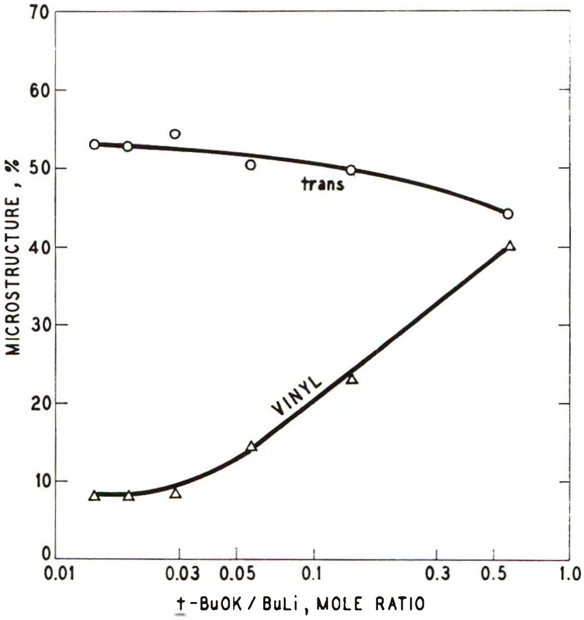


Fig. 12. Microstructure of polybutadiene obtained with potassium *tert*-butoxide–*n*-butyllithium at 50°C.

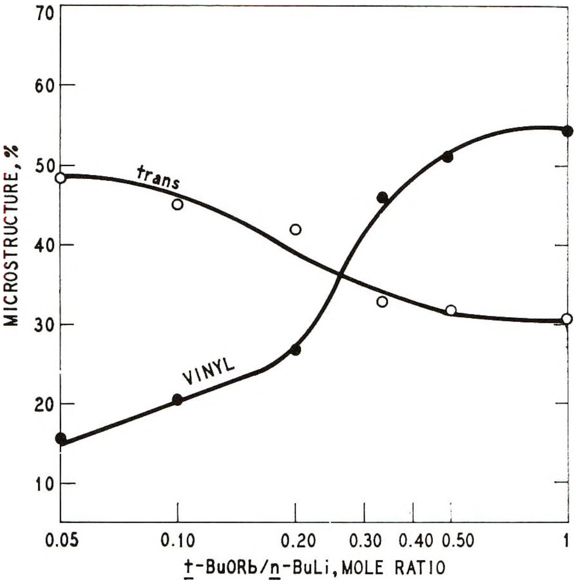


Fig. 13. Microstructure of polybutadiene obtained with rubidium *tert*-butoxide–*n*-butyllithium at 30°C.

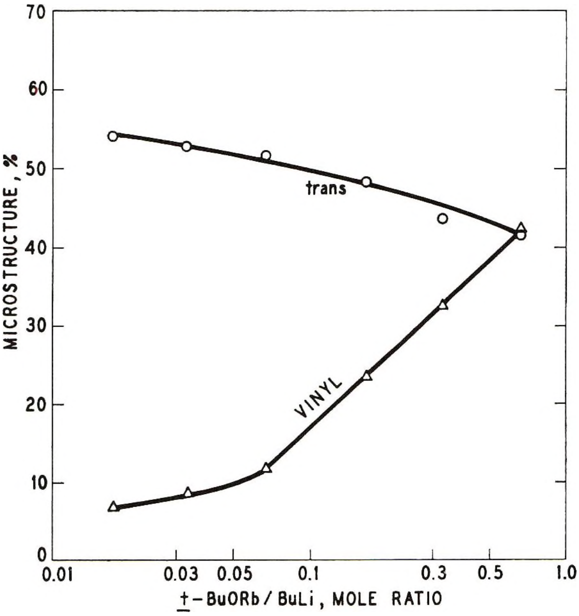


Fig. 14. Microstructure of polybutadiene obtained with rubidium *tert*-butoxide–*n*-butyllithium at 50°C.

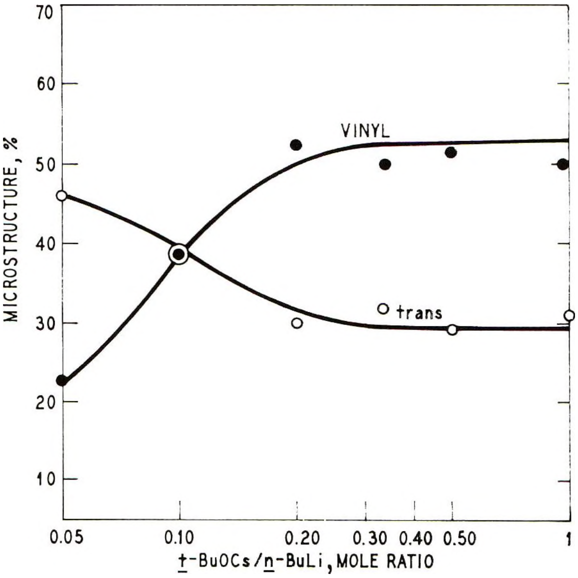


Fig. 15. Microstructure of polybutadiene obtained with cesium *tert*-butoxide–*n*-butyllithium at 30°C.

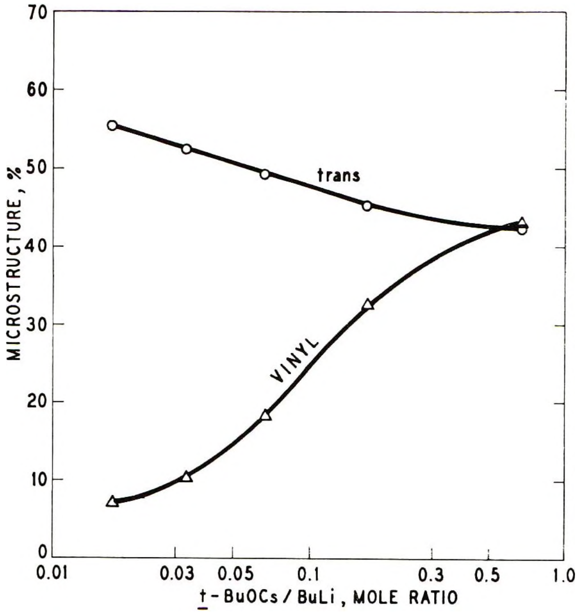
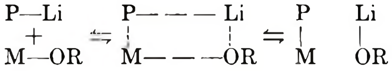


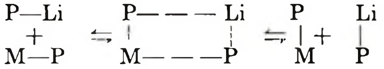
Fig. 16. Microstructure of polybutadiene obtained with cesium *tert*-butoxide–*n*-butyllithium at 50°C.

Lithium, with the lowest inherent ionic character of any of the alkali metals, gives the highest stereospecificity, lowest rate, and also is the most sensitive to changes in solvent environment. The microstructures of potassium-, rubidium-, and cesium-initiated polydienes vary little with change in type of solvent, attesting to the high inherent ionic character of the metal–carbon bond.[8]

The alkylithium compound can associate not only with itself, but also with other alkali-metal alkyls and salts such as halides and alkoxides as well as with ethers and amines. Organometallic compounds, when mixed with compounds of other metals, form associated complexes, the chemical properties of which are generally not those of a mixture of the components but of an intermediate individual type.[9–11] Polystyryllithium or polydienyllithium form associated complexes in cyclohexane in the forms of dimer for the former and trimer or tetramer for the latter. It is reasonable to expect that these polymer–lithiums also form mixed associated complexes with polymers or compounds of the same or other metals. In a polymerization initiated with combinations of alkyllithium and alkali metal alkoxides, while the exact stoichiometry, degrees of associations, and equilibria of these complexes are not known, dynamic tautomeric equilibria between carbon–metal bonds and oxygen–metal bonds must exist and would lead to quite different propagating centers than with alkyllithium alone. For the purpose of illustrating these propagating centers the reactions (1) and (2) were written. Here the monomeric P–Li (polymer-Li), P–M (polymer-metal) and RO–M (metal alkoxide) were used for the sake of simplicity, and M = Na, K, Rb, Cs.



$$\begin{array}{c} \mathrm{P{-}Li} \\ + \\ \mathrm{M{-}OR} \end{array} \rightleftharpoons \begin{array}{ccc} \mathrm{P} & \cdots & \mathrm{Li} \\ \vdots & & \vdots \\ \mathrm{M} & \cdots & \mathrm{OR} \end{array} \rightleftharpoons \begin{array}{cc} \mathrm{P} & \mathrm{Li} \\ | & | \\ \mathrm{M} & \mathrm{OR} \end{array} \qquad (1)$$



$$\begin{array}{c} \mathrm{P{-}Li} \\ + \\ \mathrm{M{-}P} \end{array} \rightleftharpoons \begin{array}{ccc} \mathrm{P} & \cdots & \mathrm{Li} \\ \vdots & & \vdots \\ \mathrm{M} & \cdots & \mathrm{P} \end{array} \rightleftharpoons \begin{array}{c} \mathrm{P} \\ | \\ \mathrm{M} \end{array} + \begin{array}{c} \mathrm{Li} \\ | \\ \mathrm{P} \end{array} \qquad (2)$$

It has been reported that organosodium and organopotassium compounds have been synthesized from reactions of organolithium with sodium and potassium alkoxides, respectively.[12] This reaction was expressed schematically by the equation

$$t\text{-BuOM} + \text{RLi} \rightarrow \text{RM} + t\text{-BuOLi} \qquad (3)$$

In the same publication, it was reported that potassium *tert*-butoxide treated with excess *n*-butyllithium in heptane formed a white-yellowish compound. Hydrolysis yielded only traces of *tert*-butyl alcohol, which means that the original product was practically free of alkoxide. The product is butyllithium–butylpotassium adduct, which is the same addition compound assumed to exist by Bryce-Smith,[9] who reacted metallic potassium with *n*-butyllithium in benzene.

The tremendous increases in polymerization rates in the presence of sodium, potassium, rubidium, and cesium alkoxides can be looked upon as resulting from shifting from alkyllithium to alkylmetals derived from the alkoxides. It is interesting to note that the relative amounts of increase in polymerization rate are much greater for styrene than for butadiene. This is expected if one considers that the polymerization rate includes both initiation and propagation. In the case of styrene with *n*-butyllithium, initiation is relatively slow with respect to propagation.[3] Only a portion of the *n*-butyllithium added actually initiates the polymerization of styrene. In the presence of metal alkoxides which give mixed complexes, the initiation can be almost instantaneous and results in a greater number of reactive species.

Another interesting point is that most of the change in both rate and microstructure occurred at mole ratios of metal alkoxides to *n*-butyllithium somewhere between 0.3 to 0.5. Beyond the ratio of 0.5, very little change was observed. This suggests that the intermediate may be P_2LiM.

CONCLUSION

In an anionic polymerization system, where the initiator is a mixture of alkyllithium and alkali metal alkoxide, the propagation center is a dynamic tautomeric equilibrium involving the two metals. The rate of polymerization as well as the stereochemistry reflect this mechanism.

The authors wish to thank Drs. J. N. Short and R. P. Zelinski for their helpful discussions.

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Copolymerization of Butadiene and Styrene by Initiation with Alkyllithium and Alkali Metal *tert*-Butoxides

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Synopsis

Combinations of the various alkali metal *tert*-butoxides with organolithium initiators give homogeneous copolymers of butadiene and styrene. The unprecedented flexibility of this initiator system allowed preparation of random copolymers with various amounts of vinyl unsaturation and various degrees of randomness. The butyllithium-potassium *tert*-butoxide initiator system was more efficient than phenylpotassium.

INTRODUCTION

Anionic copolymerizations of butadiene and styrene have drawn considerable attention in recent years because of an inversion phenomenon. When pure hydrocarbon solvents were used, only a small amount of styrene polymerized before all butadiene was consumed, then a block of polystyrene went on.[1] This block copolymer formed despite the fact that styrene homopolymerizes much faster than butadiene. In contrast to this, ether solutions of the monomer mixtures gave random copolymers with no long polymer blocks.[2,3] Even greater direction of the course of reaction occurred in the presence of alkali metal *tert*-butoxides.[4]

Effects of alkali metal *tert*-butoxides on homopolymerizations of butadiene and styrene were covered in a separate paper.[5] Here we discuss their influence on butadiene-styrene copolymerizations.

Experimental

The polymerization procedures were described in earlier publications.[5,6] The monomer ratio by weight was 75/25 butadiene to styrene.

Bound styrene analyses (Table I) were based on a modification of the method of Meehan.[7,8] Purified polymer was dissolved in chloroform, then the absorption was traced from 240 to 330 mμ with a recording spectrophotometer and measured at 262 mμ. The styrene content was determined by comparing this absorption with that of a standard polystyrene solution. Results reported in Tables II and III were determined from refractive index at 25°C. The styrene values were calculated from the difference be-

TABLE I
Effects of Varying the Alkyl Group of the Potassium *tert*-Butoxide–Alkyllithium Initiator System at Ratios of About 0.065/1

n-Butyllithium		*sec*-Butyllithium		*tert*-Butyllithium		Isopropyllithium	
Conversion, %	Bound styrene, %	Conversion, %	Bound styrene, %	Conversion, %	Bound styrene, %	Conversion, %	Bound styrene, %
0.8	24.4	7.9	21.4	2.4	15.0	2.5	11
3.2	24.7	17	26.0	5.5	19.8	5.4	19
8.8	30.0	26	27.3	9.9	24.1	11	23
18	32.3	50	28.0	20	26.4	18	26.8
45	31.3	65	27.7	46	27.4	53	27.4
61	30.2	76	27.4	62	27.4	70	27.0
71	29.0	86	26.6	71	27.0	79	26.4
84	27.4	94	25.7	83	26.7	89	25.7
93	25.8	100	25.3	96	25.8	95	25.0
100	25.0			100	25.4	100	24.9

TABLE II
Copolymerization of Butadiene/Styrene (75/25) with Potassium *tert*-Butoxide and Butyllithium (Ratio of 0.125/1) at 100°C in Cyclohexane

Conversion, %	n_D^{25}	Bound styrene, %
21.6	1.5372	25.9
44.8[a]	1.5374	26.1
60.0	1.5374	26.1
76.8	1.5374	26.1
83.8	1.5373	26.0
89.4	1.5372	25.9
94.6	1.5369	25.5
96.9	1.5367	25.2
98.4[b]	1.5365	25.0

[a] Inherent viscosity, 0.45.
[b] Inherent viscosity, 1.06.

tween the refractive indexes of copolymer of 25% bound styrene and the butadiene homopolymer made under the same reaction conditions.

Fractionation was by fractional precipitation of polymer from a 1% toluene solution with methyl alcohol.

n-Butyllithium and lithium *tert*-butoxide were purchased from Lithium Corporation of America. The *sec*- and *tert*-butyllithium and isopropyllithium were purchased from Foote Mineral Company as solutions in hexane. The alkyllithium solutions were diluted to about 0.2*M* with cyclohexane. The higher alkali metal *tert*-butoxides, alcohol-free, were purchased from MSA Research Corporation.

TABLE III
Fractionation of Butadiene/Styrene (75/25) Copolymer from Initiation with Potassium *tert*-Butoxide and Butyllithium (Ratio of 0.125/1)

Fractionations	Weight per cent	Inherent viscosity	n_D^{25}	Bound styrene, %
Original		0.99	1.5364	25.0
Fraction				
1	8.6	1.22	1.5359	24.4
2	13.0	1.14	1.5359	24.4
3	12.8	1.07	1.5359	24.4
4	12.7	1.06	1.5360	24.5
5	7.6	1.02	1.5360	24.5
6	9.5	1.00	1.5360	24.5
7	10.5	0.96	1.5365	25.1
8	9.6	0.94	1.5370	25.8
9	7.0	0.88	1.5376	26.5
10	10.8	0.57	1.5402	29.8

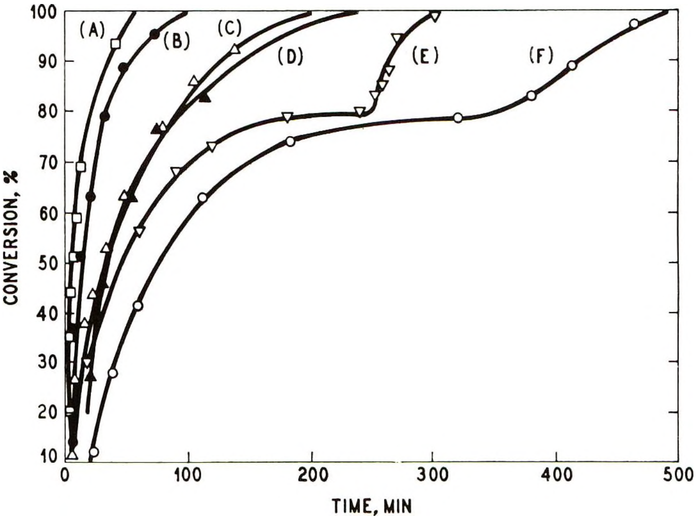


Fig. 1. Time–conversion curves for copolymerization of butadiene (75 parts) and styrene (25 parts) with equimolar mixtures of alkali metal *tert*-butoxides and *n*-butyllithium: (*A*) *t*-BuOK/BuLi at 30°C; (*B*) *t*-BuORb/BuLi at 30°C; (*C*) *t*-BuONa/BuLi at 30°C; (*D*) *t*-BuOCs/BuLi at 30°C; (*E*) BuLi control at 50°C; (*F*) *t*-BuOLi/BuLi at 50°C.

Results

Addition of alkali metal *tert*-butoxides to *n*-butyllithium-initiated copolymerizations of butadiene and styrene produced some startling results. Lithium *tert*-butoxide retarded the rate of copolymerization to a block copolymer of butadiene and styrene, while the higher alkali metal *tert*-butoxides increased the rate of copolymerization and eliminated the break in the time versus conversion curve that is characteristic of block copolymerizations (Fig. 1). From these curves we can see that potassium *tert*-

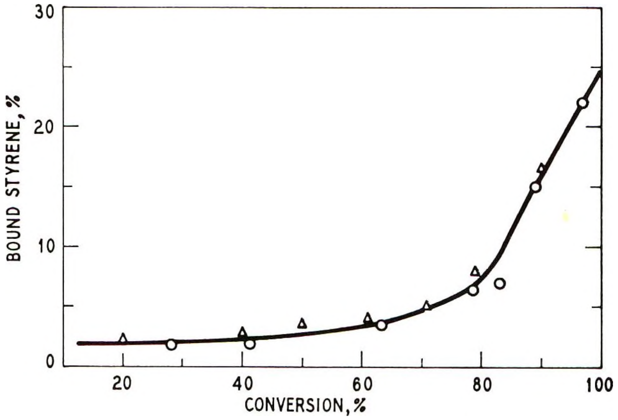


Fig. 2. Styrene (25 wt-%) incorporation with butyllithium and lithium *tert*-butoxide butyllithium at 30°C: (△) *n*-BuLi; (○) *t*-BuOLi/*n*-BuLi, 1/1.

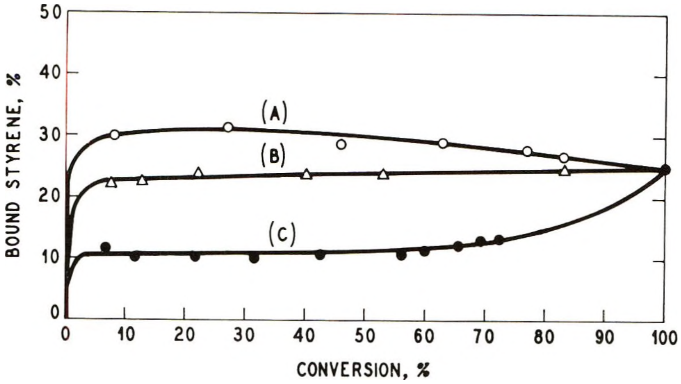


Fig. 3. Styrene (25 wt-%) incorporation with sodium *tert*-butoxide–butyllithium at 30°C at various *t*-BuONa/*n*-BuLi ratios: (*A*) 1; (*B*) 0.2; (*C*) 0.05.

butoxide gave the fastest copolymerization, with rubidium next and sodium and cesium almost equivalent.

While the lithium salt actually retarded the rate of copolymerization, there was a negligible change in the styrene inclusion profile (Fig. 2).[9] Sodium *tert*-butoxide increased the rate of styrene incorporation to such an extent that styrene was depleted before polymerization was complete when the highest level of sodium salt was used (Fig. 3). At the 0.2 sodium *tert*-butoxide to butyllithium ratio an almost uniformly random copolymer of butadiene and styrene was formed. The uniformity of the copolymer could have been improved by increasing the amount of sodium salt.

Use of equimolar amounts of potassium, rubidium and cesium *tert*-butoxides increased the relative rate of styrene incorporation to such an

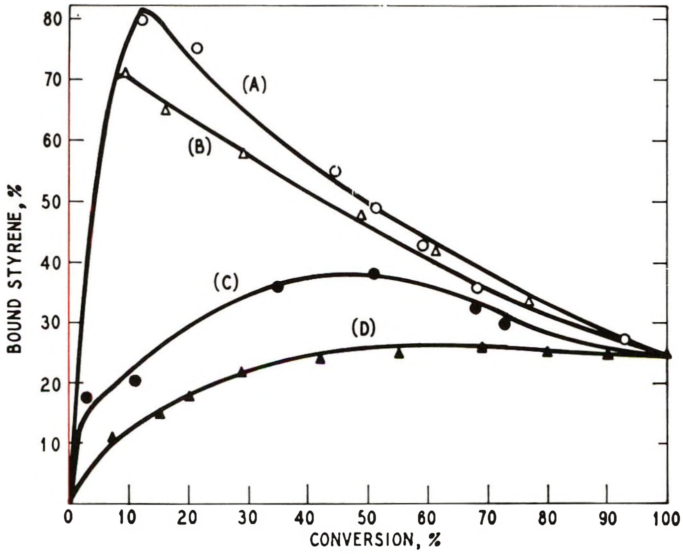


Fig. 4. Styrene (25 wt-%) incorporation with potassium *tert*-butoxide–butyllithium at 30°C at various *t*-BuOK/*n*-BuLi ratios: (*A*) 1; (*B*) 0.2; (*C*) 0.05; (*D*) 0.025.

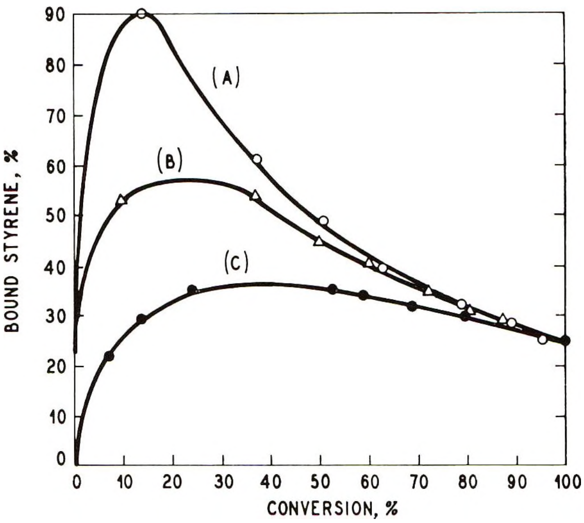


Fig. 5. Styrene (25 wt-%) incorporation with rubidium *tert*-butoxide–butyllithium at 30°C at various *t*-BuORb/*n*-BuLi ratios: (*A*) 1; (*B*) 0.2; (*C*) 0.05.

extent that the styrene had been almost completely consumed before the conversion had reached the halfway point (Figs. 4–6). Cesium *tert*-butoxide was the most efficient in accelerating styrene incorporation although the overall copolymerization, as seen from Figure 1, was slower than potassium and rubidium.

The mixed associated complex from potassium *tert*-butoxide and butyllithium was more effective than phenylpotassium with respect to rate of styrene depletion. In the early part of the polymerization the complex

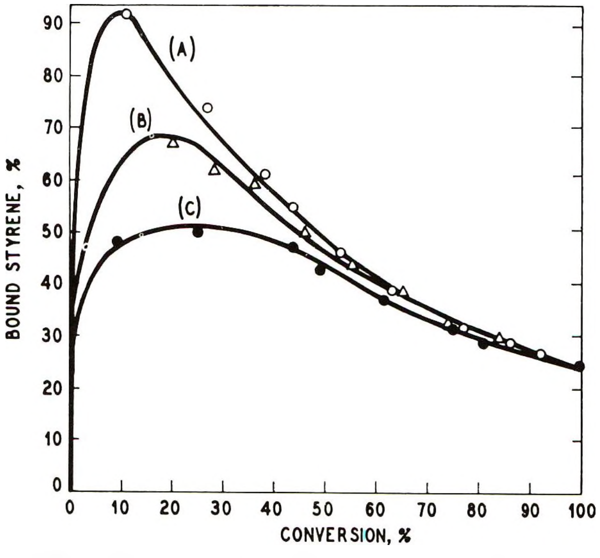


Fig. 6. Styrene (25 wt-%) incorporation with cesium *tert*-butoxide–butyllithium at 30°C at various *t*-BuOCs/*n*-BuLi ratios: (*A*) 1; (*B*) 0.2; (*C*) 0.05.

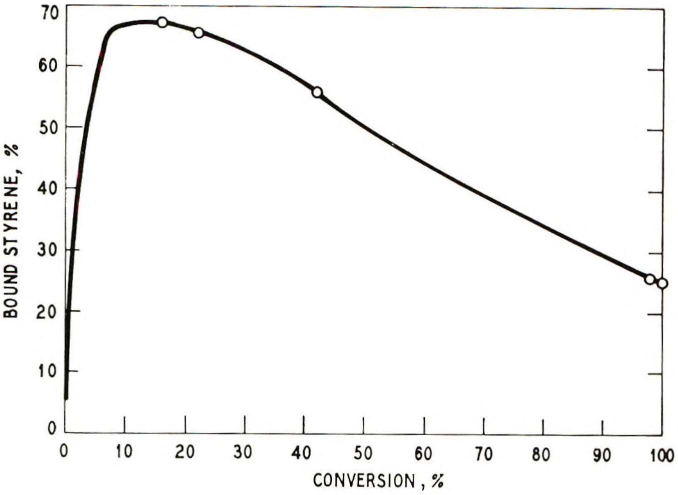


Fig. 7. Styrene (25 wt-%) incorporation with phenylpotassium at 30°C.

gave copolymer with a styrene content 10% higher than did phenylpotassium at similar conversions (Figs. 4 and 7).

The influence of temperature was determined with potassium *tert*-butoxide. Although it was more efficient at 30°C, the potassium salt gave the same effects at 50°C (Figs. 4 and 8).

The possibility that the alkyl group on the alkyllithium might influence the course of the reaction was examined, but the results show little effect (Table I). The error inherent in the method of sampling at the initiator levels used approach the limits of experimental error. *n*-Butyllithium may

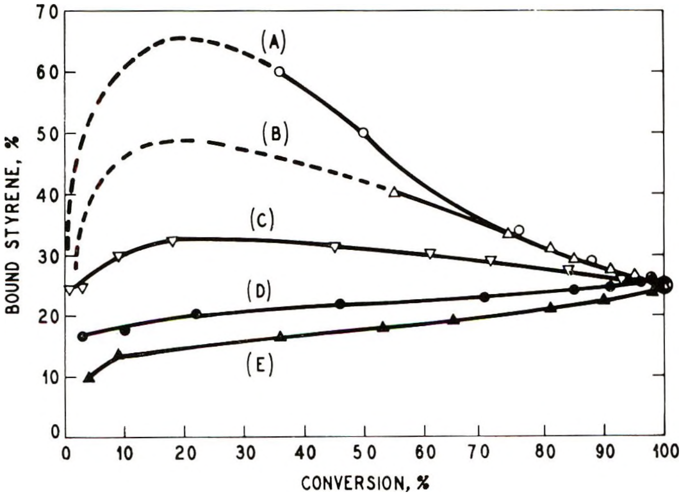


Fig. 8. Styrene (25 wt-%) incorporation with potassium *tert*-butoxide–butyllithium at 50°C at various *t*-BuOK/*n*-BuLi ratios: (*A*) 0.38; (*B*) 0.24; (*C*) 0.067; (*D*) 0.027; (*E*) 0.022.

have been a little more effective than the other alkyllithium compounds, but the difference was small.

Two kinds of homogeneity, intra- and intermolecular, are pertinent to random copolymers. Products prepared from potassium *tert*-butoxide and butyllithium can be uniform in both ways. Table II demonstrates that excellent intramolecular homogeneity is obtained. Polymer composition at all conversions is close to the butadiene-styrene charge ratio.

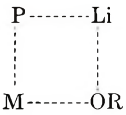
Intermolecular homogeneity is evident from the fractionation results shown in Table III. In addition to uniformity of bound styrene, the product has narrow molecular weight distribution, typical of polymers from a "living" polymerization system.

Discussion

In the alkyllithium-initiated copolymerization of butadiene and styrene in hydrocarbon solvents, the unusual "inversion" phenomenon occurs; i.e., styrene homopolymerizes faster than butadiene and yet, in a mixture, butadiene is preferentially polymerized first. The plot of conversion versus time shows the characteristic delay as the last trace of butadiene was consumed (Fig. 1, curve *E*). This seemingly anomolous behavior can be readily understood when one examines the cross-propagation rates.[1,10,11] In turn, the cross-propagation rates depend on the nature of the propagating ion-pair. Therefore, with various combinations of alkyllithium and other alkali metal compounds, copolymers with widely different comonomer distributions are produced.

The configuration of the diene portion of the copolymer was strongly influenced by the counterion introduced through *tert*-butoxide salt addition.[5] The nature of the propagating center shifted toward "limiting anionic behavior" as more alkali metal *tert*-butoxide was added to the system. We have, then, two counterions within the propagating center that can tautomerize to give copolymer chains with microsegments characteristic of each of the counterions.

The propagating center can be envisioned as a dynamic equilibrium of the species that can give the observed homogeneity to the resulting copolymers. The transition intermediate for one form of the mixed associated complex can be roughly illustrated by the structure I



I

where P is the growing polymer chain and M is the higher alkali metal atom. The dynamic equilibrium between the constituents of the propagating center and the polymerlithium moiety gives not only homogeneity of the resulting copolymers but serves also to solubilize the higher organoalkali metal compound and gives a more efficient system.

Clearly, then, just as there was a continuous range of possible microstructures in butadiene homopolymers, there is a continuous range of possible levels of styrene inclusion in the copolymers obtainable by adjusting the ratio of the additive alkali metal to lithium and the concentration of the styrene.[5] Thus, by selecting proper counterion combinations, a wide range of copolymers can be prepared in which the relative rate of styrene inclusion is varied at a constant level of 1,2-addition in the diene portion.

The nature of the propagating center in these copolymerizations allows a flexibility heretofore unknown.

Conclusion

Small amounts of alkali metal *tert*-butoxides profoundly affected organolithium-initiated copolymerizations of butadiene and styrene. When the ions of the other alkali metals were present, styrene entered the copolymer chains early in the polymerizations. The order of effectiveness was Na $< K \cong Rb <$ Cs. Lithium *tert*-butoxide retarded polymerization and had little, if any, effect on the inclusion of styrene. The alkyl group on the organolithium had little effect on the course of the polymerizations.

Uniformly random copolymers of butadiene and styrene could be prepared with any of the other alkali metal *tert*-butoxides by adjusting the ratios of butoxide to butyllithium. When higher levels of potassium *tert*-butoxide were used along with *n*-butyllithium, the amount of styrene in the copolymer during early stages of polymerization exceeded the amount obtained when phenylpotassium was used alone. Temperature also had an effect in that the influence of the alkali metal salts was less at higher temperatures.

Overall, initiation with the alkali metal *tert*-butoxide–organolithium combination initiator system gave a wide range of butadiene–styrene copolymers with unusual and sometimes unique characteristics.

We wish to thank Drs. J. N. Short and R. P. Zelinski for their encouragement and support of this work.

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Reactivity Ratios for Copolymerization of Vinyl Chloride with 2-Methylpentyl Vinyl Brassylate by Computerized Linearization*

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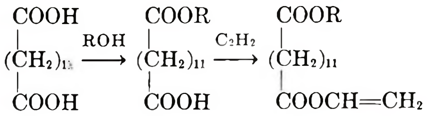
Synopsis

A computerized version of the Fineman-Ross linearization procedure was used to determine reactivity ratios for copolymerization of vinyl chloride (monomer 1) and 2-methylpentyl vinyl brassylate (monomer 2). From differential refractometry data for the products of low-conversion copolymerization, the procedure gave $r_1 = 1.06$ and $r_2 = 0.234$. The ratios computed from chlorine contents of the same products were $r_1 = 1.10$ and $r_2 = 0.239$. The polarity factor (e_2) and general monomer reactivity (Q_2) calculated for monomer 2 from these ratios were, respectively, -0.95 to -0.98 and 0.032–0.033. The interquartile range for the copolymerization of a mixture of 60% monomer 1 and 40% monomer 2 was 1.4%. These values suggest that from suitable proportions of reactants, sufficiently homogeneous distribution of monomers can be achieved in copolymers of vinyl chloride and 2-methylpentyl vinyl brassylate to offer the possibility of effective internal plasticization.

Introduction

Alkyl vinyl brassylates (AVB) have been prepared from brassylic (tridecanedioic) acid by half-esterification followed by vinylation as shown in the following reaction sequence.[1]



$$\begin{array}{c}\mathrm{COOH}\\|\\(\mathrm{CH_2})_{11}\\|\\\mathrm{COOH}\end{array}\xrightarrow{\mathrm{ROH}}\begin{array}{c}\mathrm{COOR}\\|\\(\mathrm{CH_2})_{11}\\|\\\mathrm{COOH}\end{array}\xrightarrow{\mathrm{C_2H_2}}\begin{array}{l}\mathrm{COOR}\\|\\(\mathrm{CH_2})_{11}\\|\\\mathrm{COOCH{=}CH_2}\end{array}$$

Three such mixed esters (R = ethyl, 2-methylpentyl, or nonyl) were synthesized as potential internal plasticizers in copolymers with vinyl chloride (VC), and the 2-methylpentyl vinyl brassylate (MVB) has already been tested for this purpose.[2]

The distribution of comonomers in the VC–AVB copolymers, which can be predicted from reactivity ratios (r_1, r_2),[3] is expected markedly to affect

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the internal plasticization. The determination of r_1 and r_2 for the VC–MVB system is reported in this paper. Also, the convenience of differential refractometry for finding copolymer composition and a computerized version of the Fineman-Ross linearization procedure to calculate reactivity ratios are illustrated.

Experimental

MVB was purified by two passes through an ASCO 50 Rota-Film molecular still to remove all of the lower boiling divinyl ester and part of the high boiling, inert dialkyl ester. The purity was 92.3% MVB, as determined by gas–liquid chromatography, with absence of polymer being verified by thin-layer chromatography (TLC).[1] Benzoyl peroxide (Matheson), tetrahydrofuran (Mallinckrodt, analytical reagent), and VC (Matheson) were used as received. Benzene was distilled before use.

Copolymerizations of monomer mixtures in 5.0 ml of benzene in the presence of 0.03 g of benzoyl peroxide were carried out in capped, glass pressure tubes. These were mechanically tumbled in a water bath at 60°C for 3 hr to give conversions to copolymer of 8% or less. The reactions were stopped by immersing the tubes in Dry Ice–acetone. The Teflon-gasketed caps were removed, and unreacted VC evaporated as the contents of the tubes slowly warmed to room temperature. The benzene was removed in a rotary evaporator, and the unreacted MVB was removed by 10 washings with methanol. After the last washing, complete removal of monomers was verified by TLC,[1] and residual methanol was evaporated under vacuum at 38°C for 57 hr. Homopolymers of VC and MVB were prepared in the same manner except the reaction time was 336 hr.

Refractometric measurements were taken at 20°C with a Waters Model 43 differential refractometer equipped with a 10-in. Honeywell recorder. The reference and sample cells were filled and a baseline was established before the solvent in the sample cell was replaced with polymer solution in tetrahydrofuran. Pen displacement from the baseline was directly proportional to the concentration of the solution and was determined for several concentrations ranging from 3 to 12 mg/ml for each sample investigated. The displacement per unit concentration used in subsequent calculations was the average result of the several measurements for each sample.

Chlorine analyses were performed by the method of White.[4]

Calculations

The specific refractive increment for a binary copolymer is given by the equation:[5]

$$\nu_{12} = x_1\nu_1 + (1 - x_1)\nu_2 \tag{1}$$

where ν_1, ν_2, and ν_{12} are the refractive increments of, respectively, the homopolymer from monomer 1, the homopolymer from monomer 2, and the copolymer. The quantity x_1 is the weight fraction of the monomer 1 in the copolymer. The Waters differential refractometer gives a recorder pen displacement proportional to the differential refractive index, and the values calculated by dividing the pen displacements (in inches) by concentration (in milligrams per milliliter) can be used in eq. (1). The value so obtained for poly(vinyl chloride) (PVC) was 7.90 from an average of results for three samples: 7.93 for the benzoyl peroxide-initiated homopolymer prepared as described above, 7.89 for a PVC sample prepared by 0.3% potassium persulfate-initiated polymerization,[2] and 7.89 for B. F. Goodrich Geon 101. Averaging results (4.38 and 4.35) of two sets of measurements for MVB homopolymer gave 4.37. Substituting in eq. (1) and rearranging we may write:

$$x_1 = (D_{12} - 4.37)/(7.90 - 4.37) \tag{2}$$

where D_{12} is the differential refractometer recorder pen displacement per unit concentration for the copolymer.

From the Mayo-Lewis copolymerization equation,[6] Fineman and Ross[7] derived a pair of linear equations:

$$(F/f)(f - 1) = r_1(F^2/f) - r_2 \tag{3}$$

$$(f - 1)/F = -r_2(f/F^2) + r_1 \tag{4}$$

F is the molar ratio of monomer 1 to monomer 2 in the original mixture, and f is the analogous ratio in the corresponding copolymer. Our computer program, which utilizes eqs. (3) and (4), accepts as input either weights of monomers in the initial mixture and compositional data on the copolymers produced or molar ratios calculated from such data. The quantities F and f are first computed from the input. Then the lines which fit eqs. (3) and (4) best are determined by the linear least-squares treatment[8] of the experimental data. Reactivity ratios determined from the slope and intercept of each of the two equations are shown on the printout, but values of r_1 reported here as calculated by the linear least-squares method were determined from eq. (3), and the corresponding values of r_2 were determined from eq. (4). The program also includes instruction cards necessary for calculation of the polarity factor (e_2) and general monomer reactivity (Q_2) for monomer 2. Copies of the program, which is written in Fortran IV language for an IBM 1130 computer and comprises approximately 100 cards, are available upon request.

The quantities e_2 and Q_2 for MVB were calculated from eqs. (5) and (6).[9] To substitute for the corresponding VC constants in the equations,

$$e_2 = e_1 \pm (-\ln r_1 r_2)^{1/2} \tag{5}$$

$$Q_2 = (Q_1/r_1) \exp \{-e_1(e_1 - e_2)\} \tag{6}$$

we selected the averaged values reported by Young;[10] namely, $e_1 = 0.20$ and $Q_1 = 0.044$.

The relationship between instantaneous copolymer composition and percentage conversion was determined either by graphic solution of the

Skeist equation[11] or by substitution of reactivity ratios into the Meyer-Lowry[12] solution. The values of r_1 and r_2 used for this purpose were averages of the two values computed, respectively, from differential refractometry and chlorine analysis data.

Results and Discussion

The determination of composition of copolymers by differential refractometry was first reported by Kinsinger et al.[5] and later by Urwin and Stearne[13] and was discussed by Huglin.[14] The general availability of differential refractometers as quantitative detectors on gel-permeation chromatographic units makes this technique very attractive. The results we obtained by this technique were checked by the conventional chlorine analysis. Reactivity ratios computed by the linear least-squares method from data obtained by the two different analytical methods (Table I) are given in Table II. Even though the agreement is quite good, the difference between r_1 values being less than 4% and that between r_2 values only about 2%, we investigated one probable cause contributing to these differences. When several artificial mixtures of PVC and poly(MVB) were analyzed by the method used to provide the data in the last column of Table I, the results in Table III were obtained. The arithmetic average of deviations of the found from the calculated chlorine contents, ignoring sign, was 1.6%. If all the data in the last column of Table I were lower by 1.6%, the com-

TABLE I
Copolymerization of Vinyl Chloride (VC) with 2-Methylpentyl Vinyl Brassylate (MVB)

Charge[a]			VC in copolymer, wt-%	
VC, g	MVB, g	Conversion, %	Differential refractometry	Chlorine analysis
0.1013	9.8966	2.0	2.97	3.10
0.1433	9.8432	3.5	5.79	5.52
1.1361	8.8626	4.5	21.62	21.38
5.1211	4.8721	5.8	55.82	54.95
6.3987	3.6001	7.3	66.56	66.95
7.9121	2.1131	8.4	80.41	81.07

[a] With 0.03 g of benzoyl peroxide as initiator and 5 ml of benzene as solvent.

TABLE II
Reactivity Ratios and e and Q Values for the Copolymerization of Vinyl Chloride (Monomer 1) and 2-Methylpentyl Vinyl Brassylate (Monomer 2)[a]

Method	r_1	r_2	e_2	Q_2
Differential refractometry	1.06	0.234	−0.98	0.033
Chlorine analysis	1.10	0.239	−0.95	0.032

[a] Corresponding values for VC are taken from Young[10] as $e_1 = 0.20$ and $Q_1 = 0.044$.

TABLE III
Chlorine Analysis of Artificial Mixtures of Vinyl Chloride and 2-Methylpentyl Vinyl Brassylate Homopolymers

PVC in mixture[a]					
Wt-%	Mole fraction	Cl calcd, %	Cl found, %	PVC found, wt-%	Deviation, %
1.95	0.10	1.11	1.11	1.95	0
5.41	0.24	3.07	3.16	5.57	+2.93
13.56	0.47	7.69	7.97	14.05	+3.64
28.91	0.70	16.40	16.49	29.07	+0.55
46.52	0.83	26.39	26.71	47.08	+1.21
100.00	1.00	56.73	56.02	98.76	−1.25

[a] PVC, poly(vinyl chloride).

puted reactivity ratios in the last row of Table II would be $r_1 = 1.02$ and $r_2 = 0.243$. Similarly, if all the chlorine analyses were 1.6% higher, we would then have $r_1 = 1.20$ and $r_2 = 0.235$. The resulting spread of values of r_1 and r_2 arising from analytical errors is greater than the corresponding spread in Table II. Admittedly, it is unlikely that all experimental errors will be in the same direction, but four out of six analytical results listed in Table III are high and only one is low. A similarly unsymmetrical distribution of errors in chlorine contents determined for the copolymers in Table I could readily account for the difference in r_1 and r_2 values in Table II.

We did not perform the experiment for differential refractometry analogous to the investigation of chlorine analysis represented in Table III. However, it is reasonable to assume that experimental error in this method also contributed to differences in reactivity ratios computed from the two sources of data.

Table IV shows a comparison of results given by the computerized linear least-squares method for calculating reactivity ratios with results derived from the same experimental data by other mathematical procedures. Differences are of the same order of magnitude as those which may arise from experimental deviations such as shown in Table III. Moreover, even greater experimental errors may result from the fractionation (i.e., loss of relatively small polymeric molecules) associated with isolation of copolymer samples for analysis. We believe, therefore, that the simple and convenient computerized linear least squares method gives r_1 and r_2 with as much mathematical accuracy as is warranted in view of uncertainties inherent in the experimental data.

With regard to prediction of the comonomer distribution resulting from VC–MVB copolymerizations, r_1 is near unity, so a polymer chain with a VC radical at the growing end is apt to react equally with VC or MVB. On the other hand, when an MVB radical occupies the growing end the likelihood of reaction with VC is much greater than with MVB according to the r_2 value of 0.234–0.239. The relatively large difference between e_1 (±0.20)

TABLE IV
Comparison of Different Methods for Calculating Reactivity Ratios

Monomer 1	Monomer 2	Method[a]	r_1	r_2	Source of data
Unidentified	Unidentified	A	0.18	0.49	Ref. 15
		B	0.18	0.49	
VC	Methyl acrylate	A	0.0908495	10.065542	Ref. 16
		B	0.083	8.93	
Acrylonitrile	Styrene	A	0.067	0.37	Ref. 17
		B	0.064	0.34	
VC	MVB	A	1.23998	0.218459	Table I
		B	1.06	0.234	
VC	Vinyl levulinate	C	1.40	0.419	Ref. 18
		B	1.40	0.418	
VC	Vinyl pelargonate	C	1.16	0.282	Ref. 18
		B	1.12	0.293	
VC	Vinyl pinonate	C	1.46	0.446	Ref. 18
		B	1.41	0.411	
Methyl acrylate	Acrylonitrile	D	0.71	0.50	Ref. 19
		B	0.76	0.51	

[a] Method A = computerized nonlinear least-squares method of Tidwell and Mortimer. Values of r_1 and r_2 by method A for the unidentified and for the acrylonitrile–styrene systems were taken from graphs.[15] Dr. Mortimer graciously provided the ratios computed by method A from our differential refractometry data. Method B = computerized linear least-squares method with r_1 given by slope of eq. (3) and r_2 given by slope of eq. (4). Method C = intersection method (graphic).[6] Method D = intersection method (algebraic).[19]

and e_2 (-0.95 to -0.98) favors monomer alternation,[20] so formation is unlikely of blocks of monomers that would probably limit internal plasticization and otherwise adversely affect copolymer properties. Finally, the so-called "compositional drift" was calculated from the copolymer containing 60% VC by weight, the composition which produced plasticized products with the most promising mechanical properties of the several VC–MVB copolymer samples investigated.[2] The interquartile range found was 1.3% by graphic solution or 1.4% by the Meyer-Lowry solution to the Skeist equation, indicating that the plasticizing groups of the MVB will be homogeneously dispersed throughout the product.

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Isolation and Identification of the Linear and Cyclic Oligomers of Poly(ethylene Terephthalate) and the Mechanism of Cyclic Oligomer Formation

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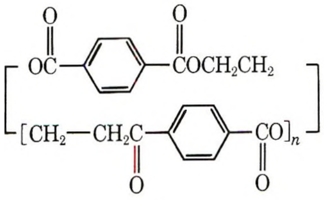
Synopsis

Chromatographic techniques are described which can be used to isolate and identify the linear and the cyclic oligomers of poly(ethylene terephthalate). Extraction of the oligomers from high molecular weight polymer produces at least eight different cyclic species, some of which are isolated and identified.

The cyclic dimer, the cyclic trimer, and the cyclic tetramer of poly(ethylene terephthalate) have also been prepared by acid chloride esterification and transesterification. Similar materials can be isolated from the ethylene glycol distillate obtained from the polymer melt. The mechanism of cyclic oligomer formation has been studied by determining the rate of formation of the cyclic oligomers during polymerization and during melt extrusion of polyesters which did not initially contain cyclic oligomers. The rate of formation depends upon the concentration of hydroxyl groups; hence, the cyclic oligomers are formed by transesterification from the chain ends or cyclodepolymerization. Therefore oligomers are inevitably produced during polymerization.

INTRODUCTION

Goodman and Nesbitt[1] have described the isolation of four cyclic oligomeric species from fibers or chip prepared from poly(ethylene terephthalate). They identified the species as the cyclic trimer, tetramer, and pentamer (I, $n = 2, 3, 4$), and a compound containing two terephthalate residues, an ethylene glycol residue, and a diethylene glycol residue (II).



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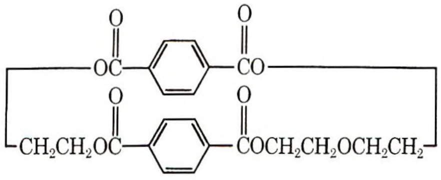


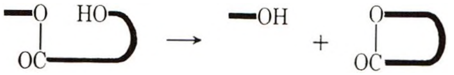
II

Because these materials appear in rather large concentration, 1.3–1.7 wt-%, we wished to confirm their identification, and to see if variations in oligomer concentration or distribution could be detected. Further, no mention is made by Goodman and Nesbitt[1] concerning the presence of linear oligomers. On the basis of the Flory distribution[2] for the weight fraction of material of size r

$$W(r) = (1 - p)^2 r p^{r-1} \tag{1}$$

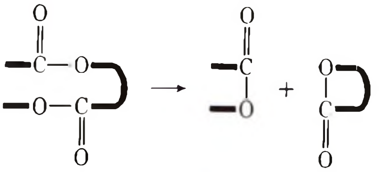
where p is the extent of conversion and $1/(1 - p) = \bar{r}_n$, the number-average degree of polymerization, we would expect very little linear oligomer to be present in high molecular weight yarn [for $\bar{r}_n = 80$, $w(r) \cong 2 \times 10^{-4}\, r$ for $r = 1\text{–}4$]. However, during the course of polymerization, either from dimethyl terephthalate or from terephthalic acid, the linear oligomers are first formed and then should decrease in relative proportion as the molecular weight increases. To determine the type and concentration of oligomers in a partially polymerized system, means were needed to readily distinguish between the linear and cyclic species.

Goodman and Nesbitt also describe three separate mechanisms for cyclic oligomer formation: (*1*) by the cyclization of the short chain linear oligomers; (*2*) by a process of cyclodepolymerization proceeding from the chain ends, or "back-biting":

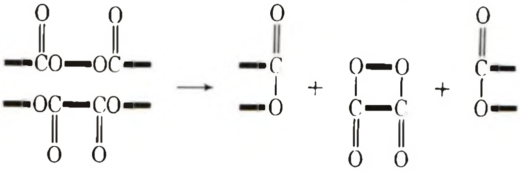


(2)

(*3*) by exchange-elimination reactions occurring randomly within or between polymer chain ester groups, or "pinch-out":



(3a)



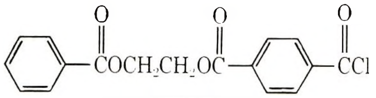
(3b)

In order to characterize further the oligomeric species of PET, it is necessary to separate and identify the various linear and cyclic components present. Thin-layer and column chromatography provided the necessary analytical techniques. In addition, several approaches were taken to provide evidence concerning the mechanism of cyclic oligomer formation in the polymerizing melt.

RESULTS AND DISCUSSION

Linear Oligomers

Linear oligomers were prepared by the recipes given by Zahn and coworkers.[3–5] The earlier papers describe the formation of the linear dimer, trimer, and tetramer by melt condensation of the monomer, bis-β-hydroxyethyl terephthalate, followed by purification utilizing fractional solubility in water, dichloroethane and tetrachloroethane. Later publications describe the preparation of these same compounds by more elaborate techniques involving reaction of purified monomer, dimer, etc., with mono-(β-hydroxyethyl benzoate) terephthaloyl chloride (III),



III

followed by selective removal of the benzoyl group by hydrogenolysis. The various techniques of preparation yielded materials with identical physical properties, so we chose to use the simpler preparative techniques.

Bis-β-hydroxyethyl terephthalate (BHET), a linear monomer of poly(ethylene terephthalate), was prepared by the action of ethylene oxide on terephthalic acid and recrystallized many times from water.

The "linear dimer" was prepared by melt condensation of BHET, followed by the recrystallization procedure of Zahn and Krzikalla.[3]

The "linear trimer" was prepared by either the melt condensation technique or by reacting one mole of terephthaloyl chloride with two moles of BHET. The product was recrystallized by the procedure of Zahn and Krzikalla.[3]

These materials were used to develop the technique of thin-layer chromatography (details in the Experimental section). When developed with chloroform–ethanol (90:10) the linear monomer (BHET) moved the least distance from the origin, while other materials moved further along the path of development. Analysis of the products described above gave a chromatogram similar to that shown in Figure 1. Most "pure monomers"

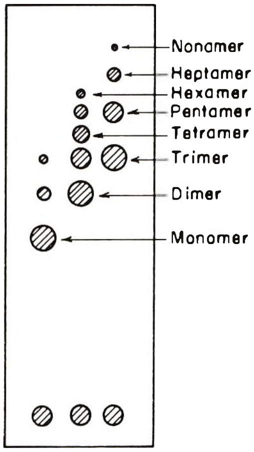


Fig. 1. Schematic chromatogram of linear oligomers, from left: monomer, dimer by melt condensation, and trimer by terephthaloyl chloride reaction. Developed with 10% ethanol in chloroform on silica gel G.F.

examined have usually contained smaller amounts of material with higher R_f values. These correspond exactly to the spots in the chromatogram of "linear dimer." Thus, we can tentatively number the spots in ascending order as monomer, dimer, trimer, tetramer, etc. Upon examination of the "linear trimer" obtained from terephthaloyl chloride by thin-layer chromatography and comparison with "linear dimer" and "linear trimer" prepared by melt condensation, we find that some of the spots of the terephthaloyl chloride preparation correspond exactly to spots in the melt condensation preparation, but the even numbered oligomers are missing from the terephthaloyl chloride preparation. It contains only trimer, pentamer, heptamer, etc.

Case[6] gives a formula for the frequency distribution of a polymer made from monomers of type AA and BB. If type BB is in excess and all groups of type A have reacted completely, the formula reduces to

$$F(r) = (1 - \beta)\beta^{(r-1)/2} \qquad r = 1, 3, 5 \text{ etc.}$$

where $\beta = [\mathrm{AA}]_0/[\mathrm{BB}]_0 < 1$. For our case, r is the number of terephthalate residues per molecule. Thus, if $\beta = {}^1/_2$, by Zahn's recipe, one should find the proportion of monomer, trimer, pentamer, heptamer to be in the series of $({}^1/_2)$, $({}^1/_2)^2$, $({}^1/_2)^3$, $({}^1/_2)^4$, etc., and this is approximately what is observed by thin-layer chromatography. The absence of the even numbered oligomers confirm the assignments of the linear oligomers. On the other hand, when terephthaloyl chloride dissolved in 1-methyl-2-pyrrolidinone was added dropwise to an eightfold molar excess of BHET in 1-methyl-2-pyrrolidinone at 70°C, a major product and a minor product were formed.

The major product melted at 179–183°C. This compares well with the 186°C melting point determined by Binder for linear trimer[7] (although it differs considerably from the 200–205°C range determined by Zahn[3–5]).

The minor product, based on evidence from thin-layer chromatography, appears to be the linear heptamer of ethylene terephthalate. The oligomer which is statistically most favored to form after the trimer is not heptamer, however, but the pentamer; for if a trimer reacts with terephthaloyl chloride, the tetrameric acid chloride formed is most likely to react with a BHET molecule (the most numerous species in the reaction mixture) and the linear pentamer would thus be formed:

$$\mathrm{GAGAGAG + ClACl \rightarrow [GA]_4Cl} \tag{4a}$$

$$\mathrm{[GA]_4Cl + GAG \rightarrow [GA]_5G} \tag{4b}$$

where G = glycol, A = terephthalic acid, and GA written together contains an ester linkage.

The fact that this does not seem to occur, and that the heptamer is instead formed, seems to indicate that perhaps the following reactions occur:

$$\mathrm{GAGAGAG + ClACl \rightarrow [GA]_4Cl} \tag{5a}$$

$$\mathrm{[GA]_4Cl + GAGAGAG \rightarrow [GA]_7G} \tag{5b}$$

The acid chloride tetramer may have a greater reactivity with the linear trimer rather than with BHET. If this is the case, the mechanism suggested parallels the work of Challa.[8] His work shows that long-chain polyesters prefer to transesterify more readily with other long chain polyesters rather than with the linear monomer, BHET.

As mentioned above, the physical properties of Zahn's oligomers are identical, regardless of the method of preparation. Thus, we question whether his physical measurements were actually made on pure compounds. No attempt was made to isolate the pure linear oligomers other than the linear trimer. Column chromatography based on the procedure given in the Experimental Section could produce quantities of the pure individual oligomers.

Cyclic Oligomers Obtained by Extraction

Polyester yarn which did not contain the manufacturer's spin finish, or polyester chip ground to at least 10 mesh was extracted by boiling solvents in a Pramuk-Friedlander extractor (Fig. 2).*

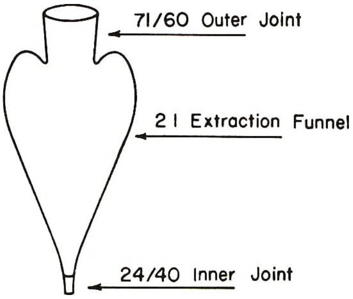


Fig. 2. Pramuk-Friedlander extractor.

The extracts obtained in this manner comprised 2.0 to 3.8 wt-% of the whole polymer. Vapor pressure osmometry measurements showed that these materials are low molecular weight fractions. Carbon, hydrogen, and oxygen analyses were consistent with ethylene terephthalate. The materials are not linear oligomers for the following reasons: (*a*) they have a high rate of movement when the thin-layer chromatogram is developed with 10% ethanol in chloroform whereas the linear oligomers do not; (*b*) infrared spectra taken from Nujol mulls do not show the presence of hydroxyl or carboxyl groups; (*c*) NMR spectra taken in tetrachloroethane or in hexafluoroacetone trideuterate do not show the presence of hydroxyl or carboxyl groups; (*d*) the compounds are neutral, and hence they must be cyclic oligomers of poly(ethylene terephthalate).

Seven components can be isolated from the origin by development with 10% ether in chloroform (Fig. 3). They are denoted as α, β, . . . , η, with α having the largest R_f value. The material remaining at the origin is called θ; it can be resolved into two additional components by means of 10% dioxane or 10% acetic acid in chloroform. The identity of the cyclic components is discussed below.

* We are indebted to Dr. H. N. Friedlander for suggesting this design.

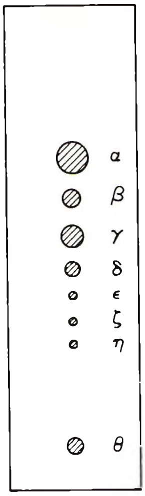


Fig. 3. Schematic chromatogram of a xylene extract of a polyester yarn. Developed with 10% ether in chloroform on silica gel G.F.

The amount of material extracted by xylene varied with the extraction time. Approximately 90 and 99% of the available material was obtained by extracting for one and two weeks, respectively. Thin-layer chromatograms of the material collected after the first and second week show that the same components are present in both extracts, but the relative concentration of oligomers varied with extraction time. There is more of the high R_f material collected during the first week of extraction. This indicates that the process of extraction may involve the diffusion of cyclic materials to the polymer surface where they are dissolved away by the solvent. The rate of extraction, then, would depend upon the rate of diffusion to the polymer surface and the solubility in the solvent.

Examination of a number of undrawn yarns showed variations in the oligomer content from 2.0–3.8%, somewhat higher than the values reported by Goodman and Nesbitt (1.3–1.7%). No correlation could be made between oligomer content and the molecular weight of the polymer. According to the Jacobson-Stockmayer theory,[9] there should be a very slow increase in oligomer content with increasing molecular weight, but the calculated increase is small and within the precision of the experiment.

Goodman and Nesbitt have given an elaborate scheme for isolating the individual components from the dioxane extracts. We used this scheme with minor modifications. The results of each fractionation were determined by thin-layer chromatography, which indicated that the efficiency of fractional extraction or fractional crystallization was very poor. Careful differential crystallization from dimethylformamide (DMF) resulted in no fractionation at all. We were able to obtain Goodman's compound A (our compound α) in reasonable purity. Otherwise, at best, we could only selectively concentrate the other components without really obtaining pure materials. The same result was observed upon fractionation of the linear oligomers; therefore one must conclude that the properties of the oligomers are too similar to permit easy isolation. Preparative chromatography of the cyclic oligomers provided reasonably large amounts of materials in high purity.

Table I gives the identity and physical properties of the cyclic oligomers so far determined. The evidence for each species is discussed separately.

TABLE I

Cyclic Oligomers of Poly(ethylene Terephthalate)

Compound	R_f value[a]	Identification	Mp, °C	Molecular weight		DEG/TA ratio	
				Found	Theory	Found	Theory
α	0.65	Cyclic trimer	319	600	576.5	0.00	0.00
β	0.56	Cyclic tetramer	326		768.7	0.00	0.00
γ	0.48	Cyclic pentamer with DEG	190			0.20	0.2
δ	0.40	Cyclic pentamer	256	900	960.9	0.00	0.00
ϵ	0.34		304			0.08	
ζ	0.28					0.18	
η	0.23		185	1730		0.11	
θ	0.00		185–190[b]	1590		0.16	
	0.77	Cyclic dimer	175,224[c]	420	384	0.00	0.00

[a] R_f value with 90:10 chloroform–ether as developer.

[b] No sharp melting point, just a broad endotherm with an exotherm starting at 200°C.

[c] Two sharp melting points indicated by DTA.

Compound α, the cyclic trimer, occurs in the extracts in the largest amount. It is easily purified by repeated fractional crystallization. The molecular weight was determined by vapor-phase osmometry with *o*-chlorophenol as solvent, and linear monomer, BHET as the standard. As only very small amounts of the other pure oligomers were available, we assumed that the other oligomers had the same concentration dependence as the compound α and only ran a single point molecular weight determination of the other oligomers. The x-ray patterns of α agreed with those described by Binns et al.[10] Differential thermal analysis showed an endotherm at 195°C similar to that described by Binns et al. which they ascribe as a transformation of crystal form.

Compound β was very difficultly soluble after isolation from the preparative chromatography experiment; it was not soluble in *o*-chlorophenol. The major evidence for identifying it as the cyclic tetramer is given below where direct synthesis of the cyclic tetramer is described. Differential thermal analysis showed an endotherm at 288°C, which may indicate a change in crystal form, and a sharp melting point at 326°C. Goodman and Nesbitt describe the cyclic tetramer as having a melting point of 225–229°C, whereas Zahn and Kusch[11] give a value of 327–329°C.

Compound γ also was not soluble in *o*-chlorophenol. NMR spectroscopy shows proton area ratios of 14/12/6 for the terephthalate acid (TA)–ethylene glycol–diethyleneglycol (DEG) moieties. This is interpreted to mean that the DEG/TA molar ratio is 1/5. A similar result is obtained by transesterification with ethanol followed by gas chromatography following the procedure of Janssen et al.:[12] DEG/TA = 0.196. The rather low melting point, 190°C is consistent with this result. Thin-layer chromatography demonstrated that the sample was not a mixture of components. Hence, we identify compound γ as a cyclic pentamer containing one DEG unit.

Compound δ is identified as the cyclic pentamer of poly(ethylene terephthalate) based on molecular weight measurements and the absence of DEG units, mp 256°C. Goodman and Nesbitt give a value of 247–250°C, whereas Zahn and Kusch report 362°C.

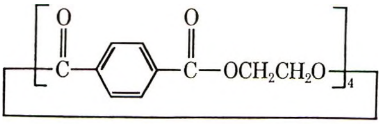
Compounds ϵ, ζ, and η have not been sufficiently characterized to permit identification.

Compound θ does not move from the origin when a chromatogram is developed with 90/10 chloroform–ethanol or 90/10 chloroform–ether. It will separate into at least two species when developed with 90/10 chloroform–dioxane or 90/10 chloroform–acetic acid. It is very difficultly soluble in most solvents, being the residue after repeated extraction with dioxane, acetone, or xylene. It does contain DEG units. The cyclic dimer that contains one DEG unit, described by Goodman and Nesbitt, may be one of the components.

Cyclic Oligomers Obtained by Direct Synthesis

In order to verify whether or not compound β is the cyclic tetramer of PET, this oligomer was prepared by a two-step process from readily available materials.

In the first step, a large excess of monomer (BHET) is reacted with terephthaloyl chloride to yield the linear trimer; then, in the second step, the linear trimer is reacted with more terephthaloyl chloride at high dilution to produce the cyclic tetramer III:

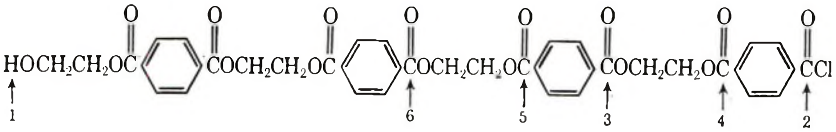


III

The procedure of Meraskentis and Zahn[13] who describe the synthesis of the cyclic trimer, was followed. The critical experimental features of their technique include (a) a reaction temperature of 150°C, (b) *N*,*N*-dimethylaniline as an acid acceptor, (c) hexamethylphosphoramide in an apparently catalytic role, (d) *o*-dichlorobenzene as solvent, as attempts to effect the reaction at lower temperature in 1-methyl-2-pyrrolidinone or dioxane did not work. Three major products appeared in the thin-layer chromatographic analysis of the reaction mixture: Two of these products are identical respectively with the cyclic trimer and the cyclic tetramer found in the xylene extract of polyester yarns. The third product is a new compound with a R_f value greater than that of the cyclic trimer (0.77 compared with 0.65); it is the cyclic dimer of PET.

Similar materials are isolated from the ethylene glycol distillates obtained from the finishing step in polyester polymerization by precipitation with salt water. Thin-layer chromatography shows that they are the cyclic dimer, cyclic trimer, and cyclic tetramer.

Since the cyclic trimer was not expected to be a product of the synthesis employed here, the following mechanism is devised to explain its formation and also that of the cyclic dimer: If a terephthaloyl chloride molecule reacts with one end of the linear trimer, the tetrameric chloride IV will be formed.



IV

If the free hydroxyl end (1) of this molecule esterifies with the acid chloride end (2), then the reaction will produce the desired product, i.e., the cyclic tetramer. If, however, the free hydroxyl end (1) undergoes transesterification at site (3), the cyclic trimer will be formed. A number of other reactions are possible. The free hydroxyl at (1) could undergo transesterification at either site (4) or (5); both of these reactions would simply rearrange the above chain into the same compound again. Transesterification could occur at site (6), which would form the cyclic dimer; this compound has never been reported in work with PET oligomers, but it can be "synthesized" without strain from molecular models.

Sufficient quantities of the cyclic dimer were isolated by preparative thin-layer chromatography for characterization. Infrared and NMR spectroscopy indicate that hydroxyl end groups are absent from the neutral compound. Both spectra show bands or band shifts characteristic of a transannular type of compound.[14] The infrared spectra shows a strong band at 1145 cm^{-1} absent from the homologs, and four medium bands at 783, 746, 720, and 705 cm^{-1} instead of the single medium band at 730–725 cm^{-1} characteristic of the higher cyclic homologs; similarly the aromatic proton band in the NMR spectrum is shifted from 8.12 ppm for the cyclic homologs to 7.63 ppm for the cyclic dimer. Vapor pressure osmometry in *o*-chlorophenol gives a molecular weight of 420 (theory for dimer 384); C, 62.75%; H, 4.82%; O, 31.22% (theory: C, 62.40%; H, 4.20%; O, 33.30%). The compound has a double melting point; DTA shows two sharp endotherms at 175 and 224°C. The material does not contain DEG units.

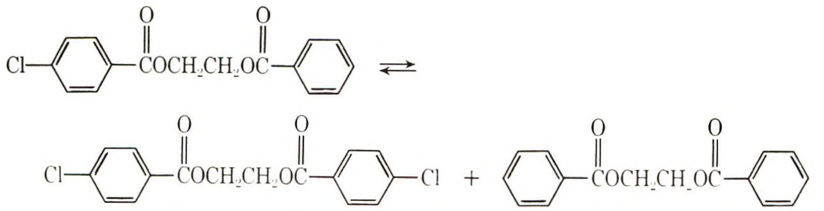
The formation of the cyclic trimer could be suppressed by omitting the *N*,*N*-dimethylaniline and lowering the temperature to 70°C. The relative proportions of cyclic dimer and cyclic tetramer were essentially unchanged.

Production of the cyclic tetramer by direct synthesis confirms the assignment given to the compound β.

Mechanism of Cyclic Oligomer Formation

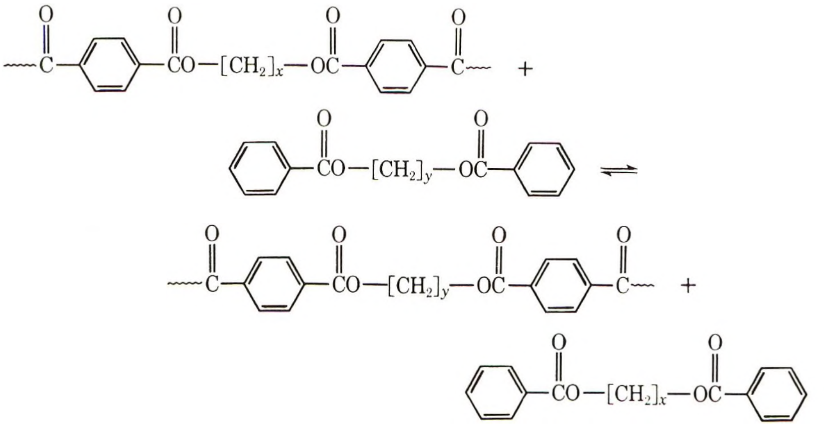
Review of Goodman and Nesbitt's Arguments. Three mechanisms are presented in the Introduction as possible means of cyclic oligomer formation in a polymerizing system. Because extracted yarns (which do not contain linear oligomers in detectable amounts) will re-form cyclic oligomers upon melting, the first reaction cannot be the mechanism. Goodman and Nesbitt dismiss mechanism (2) on the basis that insufficient hydroxyl groups are present. In support of this, they cite the fact that extracted chip can be held for 160 hr at a temperature just below the melting point without cyclic oligomer formation. Further, the work of Zahn and Krzikalla[3] and Zahn and Seidel[4] leads to the conclusion that heat treatment of the linear oligomers will not produce the cyclic oligomers.

In support of mechanism (3), Goodman and Nesbitt show that if 2-*p*-chlorobenzoyloxyethyl benzoate alone and a mixture of 1,2-dibenzoyloxyethane with 1,2-di-*p*-chlorobenzoyloxyethane were heated at about 225–245°C, both products contained all three substances, proving the occurrence of reaction (6):



(6)

Further, the reesterification of poly(ethylene terephthalate) and 1,4-dibenzoyloxybutane and of poly(tetramethylene terephthalate) and 1,2-dibenzoyloxyethane with catalytic amounts of metal salts [eq. (7)] is also



(7)

cited as evidence for the "pinch-out" mechanism.

However, we feel that Goodman and Nesbitt's work can have a different interpretation. They note that extensively dried cyclic trimer will not polymerize to high molecular weight polymer unless a small amount of an additional initiating substance is present. Presumably, the additional initiating substance is water or other hydroxyl-containing compounds which would convert the ring into a linear chain. Polymerization of the linear chain would produce ethylene glycol which could also break the ring. If the model systems described above contained small amounts of hydroxyl-containing materials, we speculate that they could also catalyze the exchange reactions. Concerning the lack of cyclic oligomer formation at high temperature in the solid phase, Coover et al.[15] have shown that polymers of high molecular weight can be prepared by solid-state polymerization. Thus, if cyclic oligomers are formed by transesterification they should form as easily in the solid state as in the melt. This line of reasoning lead us to feel that reaction (2) was the more likely reaction in the polymerizing system.

Perhaps one of the reasons why cyclic oligomers were not detected in the earlier work of Zahn and of Goodman and Nesbitt is that sensitive tests for cyclic oligomers were not available to them. However, we have available the technique of thin-layer chromatography which can identify small amounts of cyclic oligomers in the presence of large amounts of linear oligomers or high molecular weight polymer.

To collect evidence concerning the mechanism, several approaches were taken: re-examination of the extraction procedure; solid-state polymerization of linear oligomers; melt spinning of extracted chip at two levels of molecular weight and at several extrusion speeds; and examination of the compositional distribution of extracts obtained from the yarns produced from extracted chip, by column chromatography.

The results and discussion of these approaches will be treated separately. They all lead to the same conclusion: that cyclic oligomer formation occurs by the "back-biting" mechanism of cyclic depolymerization.

Re-examination of the Extraction Procedure. We have confirmed Goodman and Nesbitt's finding that the extracts of chip or yarn do not contain linear oligomers in detectable amounts. Perhaps the linear oligomers were present in the yarn initially but the process of extraction (a week at 135°C) caused the linear oligomers to disappear by polymerization. To test this effect, linear monomer, without catalyst, was refluxed for a week in *m*-xylene, the extraction solvent. No change in the monomer was detected. The process stream from the esterification reactor where terephthalic acid is reacted with ethylene glycol ("reactor tails") contains all of the additives present in high molecular weight polymer but consists primarily of the linear oligomers and no cyclic oligomers. The main change in the oligomer distribution upon refluxing for a week was the formation of small amounts of cyclic trimer. The concentrations of the low oligomers (monomer through pentamer) were not altered, but the higher oligomers appeared to have decreased somewhat in concentration, based on comparison of the intensity of the spots in the thin-layer chromatograms. Although such comparisons are only qualitative judgments, they are sufficient for the present purpose. Thus, because essentially no change in the linear oligomer concentration occurred upon refluxing, we concluded that the concentration of linear oligomers in high molecular weight polymer is below the detectable limit.

Solid-State Polymerization of Linear Oligomers. Cyclic trimer can be formed in solution by "back-biting" or cyclodepolymerization of low molecular weight oligomers as described above. Further, above we suggest a similar mechanism for the formation of the cyclic trimer while attempting to form the cyclic tetramer from the linear trimer. In order to determine if the mechanism was operative in the solid state, the reactor tails used above were heated in a tubular furnace at 200°C under a stream of nitrogen. Samples were withdrawn from the furnace at various times. The system was quite similar to that described by Coover et al.[15] The product was rather difficult to dissolve, requiring long times at higher temperatures than is normal for poly(ethylene terephthalate). This indicated that the product had formed a densely crystalline mass, rather than the somewhat amorphous undrawn polyester. After extraction with dioxane to remove the oligomers from high molecular weight polymer, then extracting the oligomers with water to remove excess linear monomer, the residue was subjected to thin-layer chromatography. The cyclic trimer was formed in increasing concentration as polymerization proceeded, based on qualitative comparison of the chromatograms. The lack of cyclic trimer formation in extracted chip held just below the melting point may be due either to the lack of mobility of the chain ends or to a lack of catalyst, rather than an inability to form the transition state structure as suggested by Goodman and Nesbitt.

Melt Spinning of Extracted Chip at Two Levels of Molecular Weight and at Several Extrusion Speeds. If the formation of cyclic oligomer in the melt is due to the backbiting reaction, i.e., mechanism (2), then the rate of cyclic oligomer formation should be proportional to the concentration of hydroxyl endgroups; if mechanism (3) is the primary mechanism, the rate should be independent of the endgroup concentration. To obtain rate data, polymers at two levels of molecular weight, $[\eta] = 0.420$ and 0.666 in 2:1 phenol–trichlorophenol at 25°C, were formed into fiber by a 1-in. screw extruder. In this apparatus, polyester chip is continuously fed to a heated zone (290°C), melted, and extruded. The volume of the melted zone is not known with certainty, because the screw of the extruder is designed to allow some backward slippage of molten polymer, hence the volume of melted polymer may vary slightly as the screw speed is altered. As a first approximation, however, the extrusion rate of the polymer, in grams per minute, is inversely proportional to the amount of time that the polymer is in the molten state. Yarns were prepared at four different extrusion rates and extracted with *m*-xylene.

The composition of the oligomer extracts has been determined by column

TABLE II

Melt Spinning of Extracted Chip

Sample	Extrusion rate, g/min	Oligomers extracted, %[a]	Compound θ, %[b]	Corrected % oligomers extracted[c]	$[\eta]$ of yarn[d]	$\bar{M}_n \times 10^{-3}$[e]	Specific rate constant, g/min[f]
H1	6.85	1.38	7.3	1.28	0.524	13.7	
H2	16.0	1.10	10.5	0.98	0.612	17.0	
H3	24.5	1.04	9.8	0.94	0.623	17.4	3.35×10^2
H4	38.0	0.91	19.3	0.73	0.660	18.8	
L1	6.70	2.91	23.3	2.23	0.406	9.77	
L2	16.5	3.54	56.4	1.55	0.440	10.76	
L3	24.5	3.32	63.1	1.22	0.441	10.83	
L4	38.0	2.29	39.9	1.38	0.443	10.90	4.11×10^2

[a] % oligomers extracted in 7 days. Approximately 88% of total oligomer content.

[b] Determined by column chromatography.

[c] % oligomers extracted corrected for the content of compound θ.

[d] Calculated from η_{sp} measured in 2/1 phenol–trichlorophenol at 25°C by means of the formula $[\eta] = (\sqrt{2/C})(\eta_{sp} - \ln \eta_{rel})^{1/2}$.

[e] $\bar{M}_n$ calculated from the formula given by Ringwald.[16]

[f] Slope of Figure 1 divided by the average hydroxyl concentration, $2/\bar{M}_n$.

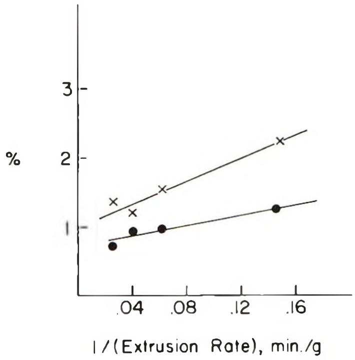


Fig. 4. Variation of oligomer content obtained by extracting fiber for 7 days, corrected for θ content, as a function of time in the melt: (×) low molecular weight polymer; (●) high molecular weight polymer.

chromatography and is described below. The compound θ an unknown mixture of ethylene terephthalate oligomers, is present in the extracts of the low molecular weight fiber in a far greater concentration than in the high molecular weight fiber; further, the composition varies erratically as the extrusion rate varies. When the concentration of the compound θ is eliminated from the total weight of extract (Table II), the oligomer content increases linearly with the reciprocal of the extrusion rate (Fig. 4). The intrinsic viscosity of the extruded yarn, before extraction, is also given in Table II, from which one can calculate a number-average molecular weight, $\bar{M}_n$. Figure 5 shows that the reciprocal of $\bar{M}_n$, and therefore, the hydroxyl concentration, increases as the time in the melt increases. The gradual degradation of polyesters in the melt is well known; great care is taken to minimize the degradation. Some of the degradation observed here is due to re-formation of the low molecular weight oligomers, the rest is due to hydrolytic and thermal degradation.

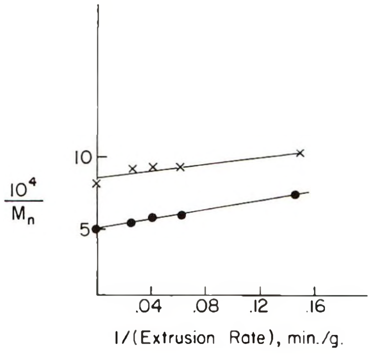


Fig. 5. Variation of hydroxyl ends with time in the melt: (×) low molecular weight polymer; (●) high molecular weight polymer. The point on the $10^4/\bar{M}_n$ axis is for chip before extrusion.

If the rate of oligomer formation is dependent upon the hydroxyl content, then the rate, calculated from Figure 4, times the average molecular weight (Fig. 5), should be a constant. The specific rate constants are listed in Table II. In view of the inaccuracies involved in determining both the time in the melt and the molecular weight, the agreement is excellent. This demonstrates that the rate of oligomer formation is dependent on the molecular weight. Hence, the mechanism of oligomer formation must be predominantly by the backbiting mechanism, (2) and not by the pinch-out mechanism, (3).

Composition Distribution of Oligomer Extracts. The thin-layer chromatograms of the oligomer extracts indicated that the compositional distribution of the oligomers was varying from sample to sample. To obtain more quantitative results and also to obtain sufficient quantities for identification, several extracts were examined by column chromatography. The experimental details are given below. The concentration by weight of each component is given in Table III. The content of cyclic trimer, determined by multiplying the weight fraction given in Table III by the total oligomer extracts, Table II, also varies with extrusion rate (Fig. 6) in a fashion similar to the total oligomer extracts corrected for θ content. The specific rate constants for cyclic trimer formation are 222 and 295 g/min for the high and low molecular weight polymers, respectively. The apparent content of the other oligomers varies erratically, probably because of experimental error in the measurement. The curvature shown in the low molecular weight polymer must be caused by an approach to equilibrium of the cyclic trimer content.

TABLE III
Composition Distribution of Oligomer Extracts[a]

	Composition, %							
Sample	α	β	γ	δ	ε	ζ	η	θ
H1	35.0	10.7	5.7	7.5	9.3	4.6	19.9	7.2
H2	22.7	15.6	6.6	10.8	8.9	5.8	12.8	16.6
H3	19.5	22.8	10.1	10.5	7.7	4.0	15.6	9.8
H4	16.3	17.2	6.7	8.0	10.6	4.6	17.4	19.3
Avg.	23.4	16.6	7.3	9.2	9.1	4.8	16.4	13.2
L1	22.0	7.9	6.0	3.3	9.4	3.6	24.5	23.3
L2	14.2	7.7	1.9	2.3	4.6	1.3	11.7	56.4
L3	11.5	6.2	2.4	2.9	4.4	2.3	7.2	63.1
L4	13.6	11.2	5.8	3.4	8.1	6.0	11.9	39.9
Avg.	15.3	8.3	4.0	3.0	6.6	3.3	13.8	45.7

[a] Values of Goodman and Nesbitt: cyclic trimer, 87%; cyclic tetramer, 7%; cyclic pentamer, 2%; cyclic dimer containing 1 DEG, 4%.

The distribution of the oligomers given in Table III is significantly different from that given by Goodman and Nesbitt for their four components, primarily because different extraction procedures were used.

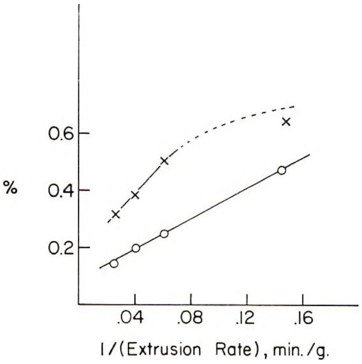


Fig. 6. Variation in the cyclic trimer content of fibers as a function of time in the melt: (×) low molecular weight polymer; (O) high molecular weight polymer.

Analysis of the compositional distribution of chip extracted with xylene for one week shows that the cyclic trimer is present in the extracts in higher concentration, the larger the chip size, which is consistent with the statements above.

EXPERIMENTAL DETAILS

Extraction

Undrawn yarns, spun without finish, were placed in Pramuk-Friedlander extractors (Fig. 2) made from a 2-liter pear-shaped separatory funnel. Fiber (150 g) or polymer chip (500 g) was held in place by fluted filter paper. Rising vapor of mixed xylene or dioxane kept the entire contents warm, whereas the descending liquids extracted the oligomers and returned them to a 1-liter tared stillpot. A gentle stream of nitrogen swept over the top of the condenser. This style of extractor is more efficient than a Soxhlet extraction because (1) extraction occurs at the boiling point of the solvent and (2) the material being extracted is not subjected to cyclic temperature variations and the attendant "breathing" of the apparatus which occurs when a Soxhlet extractor alternately fills and empties. After extraction, the bulk of the solvent was removed by distillation, the remaining solvent was removed by rotary evaporation, then the stillpot plus residues was dried overnight at 100°C. The amount of extracted material was determined by the flask weight increase. Essentially no oxidation of dioxane occurs with this procedure.

On the other hand, the apparatus did have some disadvantages. Freshly prepared polymer tended to polymerize during extraction, whereas aged polymers tended to depolymerize if they were not carefully dried. Also, the amount of material extracted from drawn fiber was significantly lower than that obtained from undrawn fiber. Dissolution of the fibers in boiling dimethylformamide, followed by cooling to room temperature to precipitate the bulk of the polymer, and isolating the soluble material did not show these disadvantages. Drawn yarn had the same oligomer content as undrawn yarn.

Thin-Layer Chromatography

The 5% solutions were prepared in phenol or phenol–tetrachloroethane; 2μl quantities were spotted onto an Analtech silica gel GF plate, dried at 100°C until no phenol odor remained, cooled, developed with 10% ethanol–90% chloroform for linear esters or 10% ether–90% chloroform for the cyclic oligomers, and the chromatograms were visualized by the hydroxamic acid reaction,[17] which gave brown spots on a white background. The hydroxamic acid reaction requires the following solutions: (1) aqueous 10% hydroxylamine hydrochloride, (2) 20% aqueous sodium hydroxide, (3) 40 g ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] dissolved in 600 ml distilled water and 400 ml acetic acid, and (4) concentrated hydrochloric acid. The plates were sprayed with a mixture of equal volumes of solutions 1 and 2 until evenly moistened. They were then heated at 110°C for 10 min, cooled, and sprayed with a mixture of 45 ml of solution 3 and 6 ml of solution 4. The solutions must be mixed immediately before use.

Column Chromatography

A 5-ft stainless steel $^5/_8$ in. ID column was filled with silica gel H. The ends of the column were closed with tight fitting piston heads with a nickel felt filter. Teflon tape was used as packing material. Various solvents were pumped through a solenoid valving system arranged as a series of T joints. The valves were activated by a preselected program set into a controller so that after a given volume of the first eluting solvent passed through the column, the second eluting solvent was introduced. In this manner the material on the column was chromatographed and the column reconditioned for the next run automatically. The column effluent passed through a 1-mm continuous-flow cell inserted in a Beckman DB spectrophotometer, thence to a syphon-activated fraction collector. As the fraction collector indexed, an electrical impulse was sent to the controller which kept count of the number of tubes collected by means of stepping switches; hence the volume of solvent that had passed through the column. The spectrophotometer was set at a wave-length of 287 mμ, the less intense peak of the terephthalate ester absorption band. A recorder produced a record of absorption versus time; as the fraction collector indexed, an index mark was produced on the record. The identity and purity of each fraction tube was determined by thin-layer chromatography. The average absorption of each tube of eluent collected was summed to obtain the total absorption. The fraction of each species present was calculated based on the recorder traces and the composition based on thin-layer chromatography.

Oligomer samples were prepared for column chromatography by dissolving 0.1 g of sample in approximately 5 ml of tetrachloroethane (TCE) and adding 1 g of the silica gel H. The TCE was then evaporated with care and the gel dried overnight at 100°C. The sample-coated gels were stored in a desiccator until used. To place the sample on the column the gel was slurried in chloroform and transferred quantitatively to the column.

A typical solvent system for eluting the sample is as follows: 1250 ml $CHCl_3$–CCl_4 (50:50); 500 ml $CHCl_3$–CCl_4 (75:25); 10 ml 10% ethanol in $CHCl_3$–CCl_4 (75:25); 500 ml $CHCl_3$–CCl_4 (75:25); 100 ml 10% ethanol in $CHCl_3$–CCl_4 (75:25); 500 ml $CHCl_3$–CCl_4 (50:50). The volume of the fractions collected was 10 ml. The purpose of the CCl_4 is to reduce the ethanol content of the $CHCl_3$, which is normally added as preservative.

We are indebted to Mr. R. B. Coffey for interpretation of infrared spectra, Dr. J. C. Randall for interpretation of the NMR spectra, Mr. J. W. Meeks for design of the column controller, Mr. W. R. Hocutt for use of the melt extruder and Dr. H. N. Friedlander for many helpful discussions.

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Polymerization of Aromatic Aldehydes. II. Cationic Cyclopolymerization of Phthalaldehyde*

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Synopsis

Phthalaldehyde was found to undergo cyclopolymerization with ease by several cationic catalysts and by γ-ray irradiation. The polymer was composed entirely of the dioxyphthalan unit, as confirmed by infrared spectroscopy and ready decomposition to monomer. The enhanced polymerizability of phthalaldehyde as compared with other aromatic aldehydes was explained in terms of the intermediate-type or, preferably, concerted propagation scheme. The conversion reached a saturation value of 87% in about 1 hr in methylene chloride at −78°C, indicating an equilibrium polymerization. The ceiling temperature of the polymerization was −43°C, as estimated from the relation between the saturation yield and polymerization temperature. The enthalpy and entropy of propagation were −5.3 kcal/mole and −23.0 eu, respectively. Since the molecular weight of the polymer was proportional to conversion, the propagating chain end was considered to be "living" in this system. The rate constant for propagation was calculated to be 0.18 l/mole-sec in methylene chloride at −78°C with BF_3OEt_2 catalyst.

INTRODUCTION

Despite many studies on the polymerization of aliphatic aldehydes, there have been few reports on the polyacetal formation by the carbonyl addition of aromatic aldehydes. Recently it was shown that benzaldehyde, though not homopolymerizable, could copolymerize readily with styrene,[2–4] indene or some conjugated dienes[2] by cationic catalysts.

Some aliphatic dialdehydes such as malealdehyde[5,6] and succinaldehyde[7] polymerized spontaneously to cyclopolymers, and the driving force of the facile polymerization was considered to be the ease of cyclization. Therefore, it was expected that phthalaldehyde might have an enhanced polymerizability compared to benzaldehyde because of the possibility of the sterically favorable cyclization during propagation.

In this paper cyclopolymerization of phthalaldehyde with several cationic catalysts is reported, and the enhanced reactivity of phthalaldehyde and the thermodynamics of the polymerization are discussed.

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* A preliminary report has been published.[1]

EXPERIMENTAL

Materials

Phthalaldehyde was prepared in 69% yield from *o*-xylene by the method of Bill and Tarbell;[8] mp 54.5–55.0°C (lit. mp 55.5–56°C). 1,3-Diethoxyphthalan was prepared by refluxing an ethanol solution of phthalaldehyde in the presence of ammonium chloride according to Powell and Rexford;[9] yield 88.2%; bp 101–104°C/5 mm Hg (lit. bp 120–129°C/25 mm Hg).

ANAL. Calcd for $C_{12}H_{16}O_3$: C, 69.21%; H, 7.74%. Found: C, 69.10%; H, 7.97%.

1,3-Dimethoxyphthalan was prepared by the method of Schmitz;[10] yield 70%; bp 116–118°C/11 mm Hg. (lit. bp 113.5–115°C/11 mm Hg).

ANAL. Calcd for $C_{10}H_{12}O_3$: C, 66.65%; H, 6.71%. Found: C, 65.54%; H, 7.00%.

Triphenylmethyl fluoroborate was prepared according to the method of Dauben.[11] Solvents and other catalysts were purified by conventional methods.

Polymerization Procedures

The cationic polymerization was carried out in a Schlenk-type vessel. The monomer and solvent were placed in the vessel. After purging with dry nitrogen, the vessel was cooled to a given polymerization temperature and a precooled catalyst solution was added. After given periods, the polymerization was terminated by adding pyridine, and the white powdery polymer was obtained by pouring the reaction mixture into excess methanol or diethyl ether. The polymer was purified by reprecipitation and dried *in vacuo* at room temperature for 2 days.

The γ-ray irradiation was carried out in a similar vessel or in an ampoule. The work-up was the same as above.

Characterizations of Polymer

The number-average molecular weight of the polymer was measured in benzene at 37°C by using a vapor pressure osmometer (Mechrolab Co. Model 301A). Viscosities were obtained in benzene at 30°C with a modified Ubbelohde viscometer. The infrared spectra were obtained with a Nippon Bunko DS301 spectrometer.

RESULTS

Cationic Polymerization

As shown in Table I, phthalaldehyde polymerized readily with cationic catalysts such as Friedel-Crafts catalysts and triphenylmethyl fluoroborate. Polymerization proceeded homogeneously, and the pale yellowish-green color of the monomer solution disappeared gradually. Because of low

TABLE I
Cationic Polymerization of Phthalaldehyde at −78°C

Catalyst	Catalyst concn, mole-%	Solvent	Monomer concn, g/ml	Time, hr	Conversion, %	[η], dl/g	$\bar{M}_n \times 10^{-3}$	Softening range, °C
BF_3OEt_2	1.0	CH_2Cl_2	0.10	12.0	87.1[a]	0.31	11.70	—
"	1.3	CH_2Cl_2	0.10	1.0	88.3	0.20	11.06	129–131
"	0.6	CH_2Cl_2	0.10	1.0	90.0	0.25	16.68	—
"	1.3[b]	CH_2Cl_2	0.063	5.0	90.4	0.14	6.30	—
"	5.0	Toluene	0.017	16.5	94.5	—	—	108–109
$SnCl_4$	1.0	CH_2Cl_2	0.10	24.0	87.6	—	—	110–112
$TiCl_4$	1.0	CH_2Cl_2	0.093	21.6	80.0	0.13	—	120–122
$(C_6H_5)_3C^+BF_4^-$	0.5	CH_2Cl_2	0.10	24.0	86.7	0.11	8.59	125–127

[a] Anal. Calcd. for $C_8H_6O_2$, C, 71.63%; H, 4.51%. Found: C, 70.54%; H, 4.77%.

[b] Polymerization temperature: −90°C.

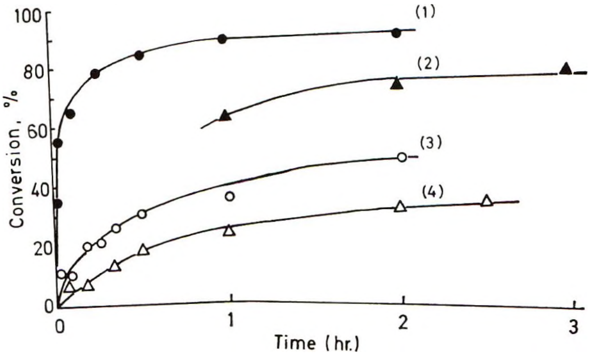


Fig. 1. Time–conversion curves at (*1*) −78°C; (*2*) −70°C; (*3*) −60°C; (*4*) −50°C. Solvent, CH_2Cl_2; $[M]_0 = 0.746$ mole/l.; $BF_3OEt_2 = 1.34$ mole-%.

solubility of the monomer, polymerization in toluene was carried out with low monomer concentrations. All the polymers were white powdery solids, which softened at 110–130°C. They were soluble in benzene and chloroform but insoluble in carbon tetrachloride, diethyl ether, and cyclohexane. A film could be cast from a benzene solution.

Figure 1 shows time–conversion curves at four temperatures with BF_3OEt_2 catalyst in methylene chloride. The polymerization was quite fast at −78°C, and the conversion reached a saturation value of 87% in about 1 hr. The saturation yield decreased with increase in the polymerization temperature, and no polymer was obtainable at −40°C. The saturation yield did not seem to be affected by the amount and the kind of the catalyst used, as is apparent from Table I. These data suggested that the ceiling temperature of the polymerization system was at about −40°C.

TABLE II
Effects of Temperature Changes during Polymerization on Conversion and Molecular Weight[a]

No.	Time, hr at T_1, °C	Time, hr at T_2, °C	Time, hr at T_3, °C	Conversion, %	$[\eta]$, dl/g	$\bar{M}_n \times 10^{-3}$
1	1, −78	—	—	89.3	0.195	11.1
2	2, −50	—	—	29.8	0.077	2.3[b]
3	1, −78	4, −50	—	29.9	0.090	3.4
4	1, −50	1, −78	—	67.7	0.268	18.8[b]
5	2, −50	1, −78	—	72.6	0.280	16.5
6	1, −78	1, −20	1, −78	76.7	0.315	14.2

[a] $[M]_0 = 0.678$ mole/l.; $BF_3OEt_2 = 1.34$ mole-%.
[b] Values calculated from eq. (3).

That saturation of the maximum yield was due to the ceiling temperature and not due to other factors is further illustrated by the data of Table II. When the reaction mixture was kept first at −78°C for 1 hr, then at −50°C for 4 hr (expt. 3), the conversion (29.9%) was very close to that of expt. 2 (polymerization for 2 hr at −50°C), and much lower than 89% of expt. 1 (polymerization for 1 hr at −78°C). When the polymerization temperature was lowered from −50°C to −78°C (expts. 4 and 5), the final conversion was close to that of −78°C. The last experiment of Table II shows that, in spite of the complete depolymerization at −20°C, the final yield was close to that typical of −78°C. Some lowering in the conversion of expts. 4, 5, and 6 as compared with that of expt. 1 might be due to side reactions.

These experiments strongly indicated that the conversion was determined by the final polymerization temperature and that monomer and polymer were in equilibrium in this polymerization system.

As already described,[12] there is the following relationship between the equilibrium concentration of the monomer ($[\mathrm{M}]_e$) and the polymerization temperature

$$\ln[\mathrm{M}]_e = \frac{\Delta H_p}{R}\left(\frac{1}{T}\right) - \frac{\Delta S_p^\circ}{\mathrm{R}} \tag{1}$$

$$T_c = \frac{\Delta H_p}{\Delta S_p^\circ + R\ln[\mathrm{M}]_e} \tag{2}$$

where ΔH_p and ΔS_p° denote the enthalpy of propagation and entropy of propagation at the monomer concentration of 1 mole/l., $[\mathrm{M}]_e$ is the equilibrium monomer concentration and T_c is the ceiling temperature (°K).

Figure 2 shows the plot of $\ln[\mathrm{M}]_e$ and $1/T$. A straight line was obtained in the temperature range of −50 to −90°C. From the slope and the intercept, the following values were obtained: $\Delta H_p = -5.3$ kcal/mole; $\Delta S_p^\circ = -23.0$ cal/deg mole; and $\Delta F^\circ_{195^\circ\mathrm{K}} = -0.82$ kcal/mole. The ceiling temperature calculated from eq. (2) was −43°C at 1 mole/1.

Figure 3 gives the relationship between conversion and molecular weight. Within each series the molecular weight was approximately proportional to the conversion. The dotted line is a theoretical line obtained by assuming that initiation was much faster than propagation, i.e., 100% catalyst efficiency. The disagreement between the theoretical and experimental lines might be attributed to the presence of impurities and/or to the incomplete initiation. In Figure 4 is shown the relation between the equilibrium conversion and the molecular weight at several temperatures. Apparently the molecular weight was proportional to the equilibrium conversion.

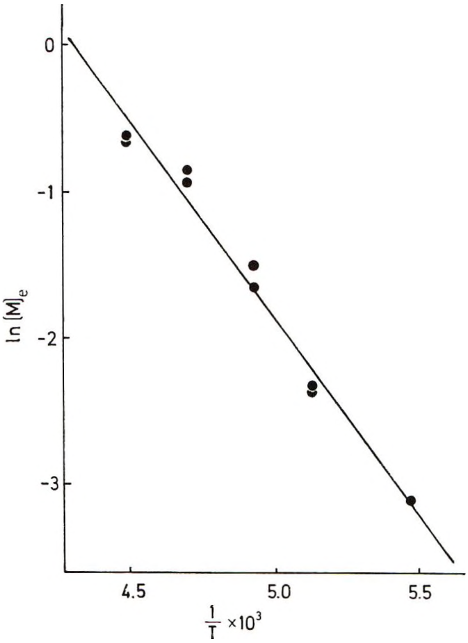


Fig. 2. Arrhenius plots of equilibrium monomer concentration.

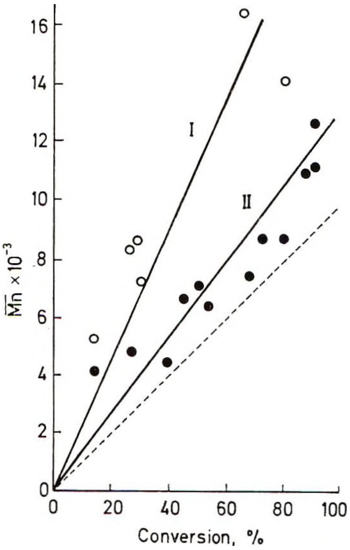


Fig. 3. Relationship between conversion and molecular weight at −78°C. $[M]_0$ = 0.746 mole/l.; BF_3OEt_2 = 1.34 mole-%. Monomers in series I and II were prepared separately.

γ-Ray-Initiated Polymerization

Table III gives the results of the γ-ray-initiated polymerization of phthalaldehyde. When a methylene chloride solution was irradiated, a suspension was obtained. The work-up of the reaction mixture gave white powders which contained some benzene-insoluble fraction. This fraction, however, was soluble in dimethyl sulfoxide and showed a softening point and infrared spectrum (see below) similar to those of the cationic polymer. Irradiation of the solid monomer at −78°C yielded no polymer.

TABLE III
^{60}Co γ-Ray Irradiation Polymerization of Phthalaldehyde in CH_2Cl_2 at −78°C[a]

Monomer concn, g/ml	Time, hr	Conversion, %	Benzene-insolubles %	[η], dl/g	Softening range, °C
0.10	115	24	—	0.06[b,c]	130–132
0.10	49	72.8	9.9	0.03[b]	—
0.09	46.3	62	—	—	—
solid	49.2	0	—	—	—

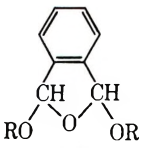
[a] Dose rate = 1.89 × 10^6 r/hr.

[b] Benzene-soluble fraction.

[c] Elemental analysis: Calcd for $C_8H_6O_2$, C, 71.63%; H, 4.51%. Found: C, 70.18%; H, 4.89%.

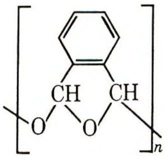
Infrared Spectra of the Polymer

Figure 5 shows the infrared spectra of monomer, polymer, and 1,3-dimethoxy- and 1,3-diethoxyphthalans (I). The monomer spectrum has a sharp carbonyl peak at 1700 cm^{-1} and formyl C—H bands at 2760 and 858 cm^{-1}. In the polymer spectrum, these peaks disappear almost completely, and new peaks indicative of the presence of the acetal linkage appear at 850–1180 cm^{-1}. In addition, the polymer spectrum resembles the spectra of 1,3-dialkoxyphthalans, especially in the acetal region of 850–1150 cm^{-1}. These results strongly supports the premise that the polymer possesses predominantly the 1,3-dioxyphthalan repeat unit, as shown by II.



R; CH_3, C_2H_5

I



II

Degradation of the Polymer

The polymer softened with decomposition at 110–130°C. When heated at 180°C for 30 min in an evacuated ampoule, the polymer decomposed to give a yellowish solid in about 70 wt-% yield. Yellowish green crystals obtained upon recrystallization of the decomposition product were identified to be phthalaldehyde from the melting point, the infrared spectrum, and elemental analysis.

Treatment of a benzene–ethanol solution of the polymer with an ethanol solution of 2,4-dinitrophenylhydrazine produced the bis-hydrazone of phthalaldehyde almost quantitatively (crude yield: 98.8%). The recrystallized hydrazone agreed with the hydrazone of the pure monomer in decomposition point, infrared spectrum, and elemental analysis.

ANAL. Calcd for $C_{20}H_{14}N_8O_8$: C, 48.59%; H, 2.85%; N, 22.66%. Found: C, 48.40%; H, 3.45%; N, 22.21%.

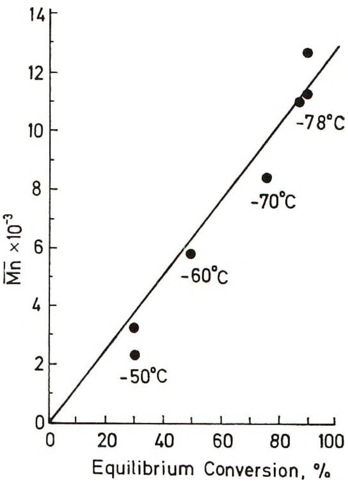


Fig. 4. Relationship between equilibrium conversion and molecular weight at several temperatures. $[M]_0 = 0.746$ mole/l.; $BF_3OEt_2 = 1.34$ mole-%.

All these results are consistent with the conclusion that the polymer chain is predominantly composed of the acetal linkage which decomposes easily to monomer by heating or by hydrolysis, just like polyacetals obtained from aliphatic aldehydes. Formation of the ester and other linkages by other than simple carbonyl addition seems negligible.

Attempted Polymerization of Some Aromatic Aldehydes

Polymerizations of benzaldehyde, isophthalaldehyde, and terephthalaldehyde were attempted in methylene chloride at −78°C with BF_3OEt_2 or 1:1 BF_3OEt_2–epichlorohydrin as catalyst. In spite of long polymerization periods (100–170 hr), no polymer was obtained.

Viscosity-Molecular Weight Relationship

A plot of log $[\eta]$ versus the number-average molecular weight for polyphthalaldehyde obtained by cationic catalysts is given in Figure 6. The relationship obtained by the least-square method is expressed by eq. (3).

$$[\eta] = 7.8 \times 10^{-4}\bar{M}_n^{0.59} \tag{3}$$

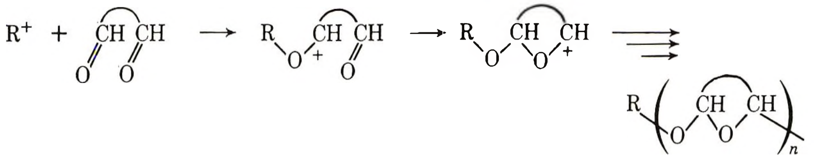
DISCUSSION

Propagation Schemes of Dialdehydes

Phthalaldehyde polymerized quite readily to give a polyacetal at low temperature by Friedel-Crafts catalysts or by γ-ray irradiation from a ^{60}Co source, while benzaldehyde, its derivatives, isophthalaldehyde, and terephthalaldehyde, resisted polymerization under similar conditions. Thus facile homopolymerization of phthalaldehyde may be attributed to the unique reactivity of an aldehyde group influenced by the adjacent aldehyde group or to the capacity of intramolecular cyclization of two aldehyde groups, or to both.

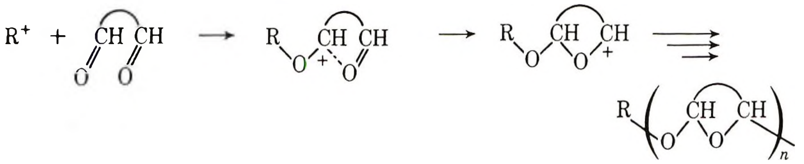
The cationic propagation of dialdehydes may be represented by either of the following three mechanisms:

Stepwise addition:



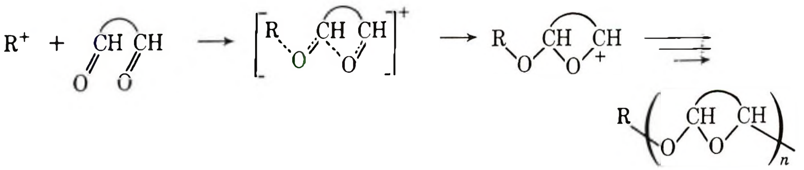
(4)

Intermediate-type addition:



(5)

Concerted addition:



(6)

The corresponding potential energy profiles are shown in Figure 7. In the stepwise addition, two carbonyl additions occur as separate elementary processes with similar activation energies. In the concerted addition, two aldehyde groups simultaneously undergo the double bond opening. Since two separate steps in eq. (4) merge into one in eq. (6) the energy released in the concerted addition should be the same as the sum of the energies released in the stepwise processes, i.e., ΔH in eq. (6) is equal to ΔH_1 plus ΔH_2 in eq. (4). As the enthalpy change in the concerted scheme is greater than that in one of the stepwise processes, the activation energy for the concerted addition is expected to be lower than that in each of the stepwise processes according to Evans-Polanyi's principle.[13] In the intermediate-type addition, the initially-formed carbonium ion is stabilized by interaction with the second aldehyde group, and the intermediate corresponds to the minimum in the potential energy profile.

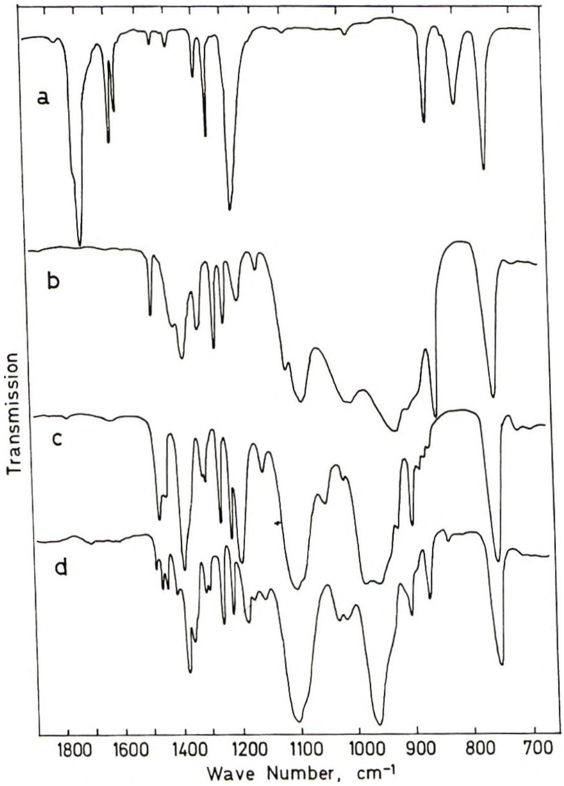


Fig. 5. Infrared spectra of (*a*) monomer (in benzene); (*b*) polymer film; (*c*) 1,3-dimethoxyphthalan (liquid film); (*d*) 1,3-diethoxyphthalan (liquid film).

Enhanced reactivity of phthalaldehyde over benzaldehyde and complete cyclization of polyphthalaldehyde strongly suggest that the cationic propagation of phthalaldehyde proceeds by scheme (5) or (6). The reactivity of bifunctional monomers should be enhanced by the favorable steric arrangement of two functional groups. Thus, malealdehyde, which has the *cis* configuration, underwent spontaneous polymerization much more readily than succinaldehyde, and the reactivity of some aliphatic dialdehydes paralleled their cyclization tendency.[6] The fixed *cis* arrangement of the two aldehyde groups must also be an important factor in increasing the reactivity of phthalaldehyde.

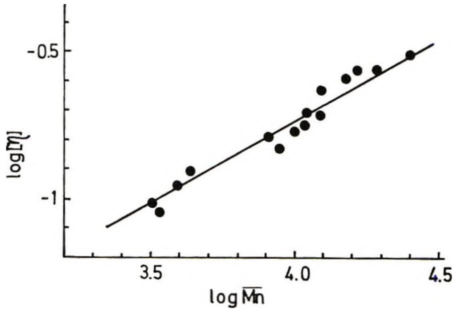


Fig. 6. Viscosity-molecular weight relationship.

Thermodynamic Constants

The thermodynamic constants obtained for polymerization of phthalaldehyde from Figure 2 are compared in Table IV with the corresponding

TABLE IV
Thermodynamic Constants of Polymerization of Aldehydes

Aldehydes	ΔH_p, kcal/mole	ΔS_p°, cal/mole-deg	T_c, °C	Polymerization conditions	
				Catalyst	Solvent
Phthalaldehyde	−5.3	−23.0	−43	BF_3OEt_2	Methylene dichloride
n-Butyraldehyde[a]	−6.8	−27.5	−18	Potassium triphenyl methoxide	Pentane
α-Chlorobutyraldehyde[b]	−4.7	−21.6	−54	Sodium naphthalene	Tetrahydrofuran

[a] Data of Vogl et al.,[15,16]

[b] Data of Mita, et al.[14]

values for a few aliphatic monaldehydes. If the values for *n*-butylaldehyde and α-chloroisobutylaldehyde can be considered typical of aliphatic monoaldehydes, phthalaldehyde shows enthalpic and entropic changes similar to those for aliphatic monoaldehydes. Since ΔH_p for phthalaldehyde corresponds to the addition of two carbonyl groups, ΔH for aromatic monoaldehyde would be approximated to be $^1/_2\ \Delta H_p$ or -2.6 kcal/mole, which is about one half of the value for aliphatic aldehydes. It is interesting that the entropic change for phthalaldehyde is similar to those for aliphatic monoaldehydes. This result may suggest that the intramolecular cyclization of the second aldehyde group does not contribute much to the overall entropic change for propagation.

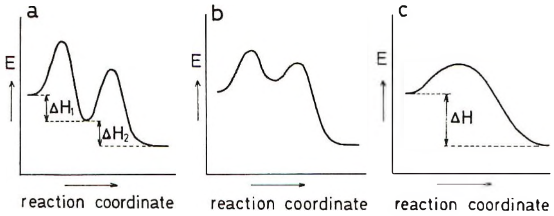


Fig. 7. Potential energy profiles for propagation of dialdehydes: (*a*) stepwise addition; (*b*) intermediate-type addition; (*c*) concerted addition

The ceiling temperature found for polymerization of phthalaldehyde was -43°C. In calculating the ceiling temperature from eq. (2), it is implicitly assumed that incorporation of a monomer molecule into a polymer chain proceeds in the concerted way. If, on the contrary, the propagation is considered to occur in a stepwise manner, there will exist more than one ceiling temperature. Since the entropy change for the intermolecular propagation is expected to be greater than that for the intramolecular cyclization, the lower ceiling temperature will be observed for the intermolecular propagation. Then the ceiling temperature for phthalaldheyde in the stepwise scheme would not be very different from those for aromatic monoaldehydes, because the first step in the stepwise addition is similar to the propagation of monoaldehydes.

Therefore, enhanced reactivity of phthalaldehyde over benzaldehyde is difficult to explain in terms of the stepwise addition. On adopting scheme (6) for propagation of phthalaldehyde, this difference in reactivity can be explained by assuming that the propagation of phthalaldehyde has a lower activation energy than that of benzaldehyde and/or that the ceiling temperature for benzaldehyde is lower than the polymerization temperature used. Actually, these two explanations are interrelated when the Evans-Polanyi's principle is applied: the activation energy of propagation for phthalaldehyde will be lower than that for benzaldehyde, as the former reaction is more exothermic ($\Delta H \approx 2\Delta H_1$ in Fig. 7) and has a correspondingly higher ceiling temperature.

On assuming that ΔH_p is −2.6 kcal/mole as discussed above and ΔS_p° is the same as that for phthalaldehyde, the ceiling temperature for polymerization of benzaldehyde can be calculated to be −160°C from eq. (2). Thus polymerization of benzaldehyde is being investigated in order to test the validity of the above discussion.

Living Polymerization

Living polymerizations of some aliphatic aldehydes with sodium-naphthalene and of *n*-butylaldehyde with potassium triphenylmethoxide were suggested by Mita et al.[14] and Vogl et al,[15] respectively. The data in Figure 3 and 4 show that molecular weight is proportional to conversion. These linear relations suggest that there was no termination process involved in the polymerization, i.e., the living growing end existed. The data of Table II also do not contradict the presence of the living end, since the molecular weight of the polymer varied reversibly with the polymerization temperature (or rather with the conversion), being about 3000 at −50°C and 11000–18000 at −78°C. That the molecular weight of polymer was determined essentially by the final conversion can be reasonably interpreted in terms of the reversible propagation of the living end.

In a typical living polymerization, the degree of polymerization is equal to the molar ratio of monomer to the growing end.[17] The data of Figure 3 indicate that the molecular weight was greater than that expected for a typical living polymerization. The deviation from the theoretical value is probably due to the fact that the concentration of the growing end was not the same as the initial catalyst concentration, which may be caused by the insufficient utilization of BF_3OEt_2 or by destruction of the living end by impurities, or by both. That the slope of the linear relation in Figure 3 was dependent of the monomer preparation used(different lots of the monomer were used for each series), appears to indicate the effect of impurities on the concentration of the living end.

Since the concentration of the living end seems to be constant as apparent from the linear relation between molecular weight and conversion, the relation of eq. (7) should hold, as already described for the living polymerization of tetrahydrofuran:[18]

$$k_p[P^*]t = \ln\{([M]_0 - [M]_e)/([M]_t - [M]_e)\} \tag{7}$$

where k_p denotes the rate constant for propagation, $[P^*]$ is the concentration of the living growing end, $[M]_0$ is the initial monomer concentration, and $[M]_t$ is the monomer concentration at time *t*.

Figure 8 gives the first-order plot of time versus conversion, which corresponds to the data (series II) of Figure 3. The linear relation obtained indicates that the concentration of the living chain end is kept constant.

As [P*] is equal to the number of polymer molecules, it can be calculated from the relation between conversion and molecular weight given in Figure 3. Thus [P*] was 7.5×10^{-3} mole/l. for series II, and it is shown that 75% of the catalyst molecules were converted to the living growing end. Then k_p can be calculated to be 0.18 l./mole-sec by dividing the slope of the line of Figure 8 by [P*].

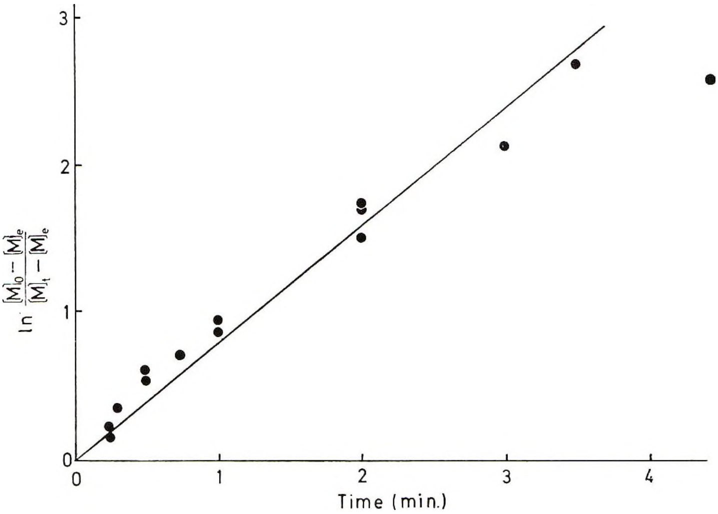


Fig.8. First-order plots of the rate of polymerization at −78°C. $[M]_0$ = 0.746 mole/l.; BF_3OEt_2 = 0.01 mole/l.

There are a few rate constants of propagation determined in similar polymerization systems. For example, k_p for tetrahydrofuran was 4.8 $\times 10^{-3}$ l./mole-sec (Et_3OBF_4 catalyst, 0°C, dichloroethane solvent)[19] and k_p for 1,3-dioxolane was 4.3×10^{-2} l./mole-sec (Et_3OBF_4 catalyst, 30°C, methylene chloride solvent).[20] The greater k_p value for phthalaldehyde observed at −78°C compared to these examples is interesting.

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γ-Ray-Induced Copolymerization of Ethylene and Vinyl Chloride in Liquid Carbon Dioxide

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Synopsis

The γ-ray-induced copolymerization of ethylene and vinyl chloride with the use of liquid carbon dioxide as a solvent was studied under a total pressure of 400 kg/cm^2, with a dose rate of 2.5×10^4 rad/hr at 30°C. A rubberlike, sticky polymer is obtained when the molar concentration of vinyl chloride is less than 30% in the monomer mixture, and the polymer is a white powder at higher concentrations of vinyl chloride. Infrared, x-ray, and differential thermal analyses confirm that the polymerization products are noncrystalline, true random copolymers. The rate of copolymerization decreases markedly when a small amount of vinyl chloride is added to ethylene monomer. In the range of vinyl chloride concentration higher than 5%, however, the rate and the molecular weight of copolymer increase with increasing concentration of vinyl chloride. It has been concluded from kinetic considerations based on these results that the rate of initiation increases proportionally with the concentration of vinyl chloride. Further, the growing chain radicals are shown to be deactivated by the cross-termination reaction between the radicals with terminal unit of ethylene and vinyl chloride, and no transfer reaction occurs.

INTRODUCTION

Copolymerization reactions of ethylene with α-olefins, unsaturated carboxylic acids and their esters, and some halogenated monomers have been extensively investigated. The free radical copolymerization of ethylene and vinyl chloride have been studied in some detail with the use of azobisisobutyronitrile (AIBN),[1,2] Ti(O-n-Bu)$_4$–AlEtCl$_2$,[3] Ti(O-n-Bu)$_4$–AlEtCl$_2$–donor,[4] and trialkylboron–peroxide[5] catalyst systems. However, no details on the radiation-induced copolymerization of ethylene and vinyl chloride have been reported.

The present paper is concerned with the γ-ray induced copolymerization of ethylene and vinyl chloride in liquid carbon dioxide solvent. The effects of the monomer composition on the rate of copolymerization and molecular weight were investigated, and the copolymerization mechanism is discussed from the point of kinetics. The variation of the structure of the copolymer produced with its composition is also reported.

EXPERIMENTAL

The copolymerization reaction was carried out in a stainless steel autoclave of 100 ml capacity. Ethylene was 99.9% pure, containing less than 5 ppm O_2, and polymerization grade vinyl chloride (VCl) (Gunma Kagaku Co.) was used as obtained. Liquid carbon dioxide which was used as a solvent for the monomers and as a precipitant for the resulting copolymer was 99.99% pure, and its major impurities were H_2O (37 ppm), CH_4 (20 ppm), and O_2 (2 ppm).

After the autoclave was repeatedly swept out by VCl, a definite amount of VCl and liquid carbon dioxide were charged and ethylene was then fed to a pressure of 400 kg/cm^2 by an oilless type compressor at reaction temperature of 30°C. During the reaction, the temperature was maintained constant to within ± 1°C by using an automatic controller. The γ-radiation was from a ^{60}Co source, and the dose rate was 2.5×10^4 rad/hr. The copolymer yield was determined by direct weighing and the number-average molecular weight of the copolymer was obtained from osmotic pressure measurements of solutions of the copolymer in cyclohexanone at 70°C with the use of a Hewlett-Packard osmometer, Model 502. Analyses of chlorine in copolymers were carried out by a combustion method in oxygen. The x-ray diffraction diagrams were obtained with a powder camera in a Rigaku Denki diffractometer, Model D-6C. Ni-filtered Cu$K\alpha$ radiation was used. Infrared absorption spectra were recorded with a Perkin-Elmer spectrometer, Model-521, in the range of 500–800 cm^{-1}. The specimens were studied in the shape of films made of ca. 2% solution in tetrahydrofuran by evaporating the solvent at room temperature in a Petri dish. Differential thermal analyses were carried out by an AGNE Research Center thermal spectrometer.

RESULTS AND DISCUSSION

Polymer Yield and Molecular Weight

The results of the copolymerization reaction carried out under various conditions are summarized in Table I. Rubberlike, sticky polymers were formed in the range of concentration less than 30 mole-% of VCl in monomer mixture, and at 30–60 mole-% VCl, somewhat elastic, solid polymers were obtained. The elasticity of the polymers became less with increasing concentration of VCl in the monomer mixture, the products obtained in higher range of VCl concentrations being white powders.

As shown in Figure 1, the copolymerization rate first decreases with the addition of VCl, passes through minimum at a concentration of ca. 2 mole-% VCl, and thereafter increases rapidly with increasing concentration of VCl. It should be noted that in the range less than 15 mole-% VCl, only trace amounts of polymer are formed, and there is observed a pronounced inhibiting effect of a very small amount of VCl upon the copolymerization. The number-average molecular weight of the resulting

TABLE I

Copolymerization Reaction of Ethylene and Vinyl Chloride Induced by γ-Radiation[a]

Run no.	Concentration of monomers, mole/l C_2H_4	Concentration of monomers, mole/l C_2H_3Cl	Reaction time, hr	Copolymer yield, g/100 ml	Molecular weight $\times 10^{-4}$	Molar fraction of C_2H_3Cl in copolymer	Rate of copoly-merization, g/l − hr	Rate of formation of copolymer chain $\times 10^4$, mole/l − hr
1	13.82	0	3	1.13		0	3.77	
2	11.71	0.77	3	0.16			0.53	
3	12.50	1.60	3	0.20	1.14	0.401	0.67	0.59
4	11.43	3.60	3	0.52	1.76	0.627	1.73	0.98
5	9.63	4.88	3	0.85	2.77		2.83	1.03
6	8.73	6.24	1.5	0.80	4.02	0.822	5.33	1.33
7	6.07	9.60	1.5	2.08	6.27	0.896	13.9	2.22
8	3.75	11.28	1	2.00	7.70		20.0	2.60
9	2.50	12.48	1.5	4.04	7.95	0.964	26.9	3.38
10	1.43	13.60	1	2.46		0.991	24.6	
11	0	14.00	1	3.75	9.86	1.000	37.5	3.80
12[b]	14.11	0	8	1.55		0	1.94	
13[b]	13.64	1.60	8	0.24		0.342	0.30	
14[b]	2.86	9.60	6	1.32		0.894	2.20	
15[b]	0	13.25	4	1.49		1.000	3.73	

[a] Reaction conditions: pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 2.5×10^4 rad/hr; concentration of carbon dioxide, 4.0 mole/l; reactor volume, 100 ml.

[b] AIBN-initiated copolymerization: pressure, 400 kg/cm^2; temperature, 45°C; AIBN, 4.3 mmole/l; reactor volume, 100 ml.

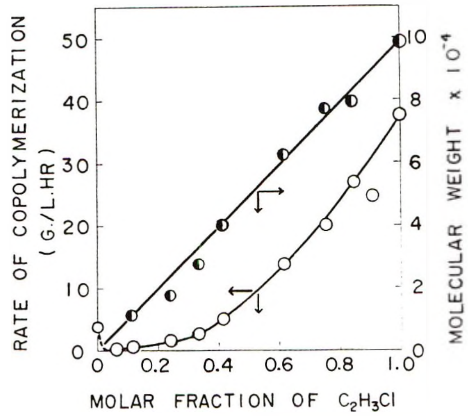

Fig. 1. Plots of (○) rate of copolymerization and (◐) molecular weight vs. molar fraction of vinyl chloride in monomers. Reaction pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 2.5 × 10^4 rad/hr.

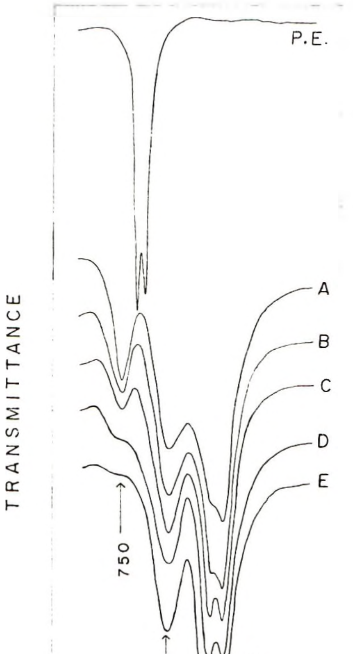

Fig. 2. Infrared spectra of vinyl chloride–polyethylene (PE) copolymers with the molar fraction of vinyl chloride: 0.000 (polyethylene); (*A*) 0.822; (*B*) 0.896; (*C*) 0.964; (*D*) 0.991; (*E*) 1.000.

polymers which is also shown in Figure 1 increases linearly with the concentration of VCl in the range higher than 10 mole-%.

Infrared Spectra of the Copolymers

Figure 2 shows the infrared spectra of the copolymers. Four characteristic absorption bands are observed in the range of far infrared. The band at 750 cm^{-1} is assigned to the —CHCl—CH_2—CH_2—CH_2—CHCl— structure in the copolymer chain;[5] this absorption band disappears gradually with increase in the percentage of VCl in the copolymer. Although it has not been clearly shown, the small inflection observed near 750 cm^{-1} in the spectrum of the 100% poly(vinyl chloride) may be assigned to the head-to-head —CHCl—CH_2—CH_2—CHCl— structure in the polymer chain. Also observed are bands at 635 cm^{-1} (C—Cl stretching vibration, syndiotactic crystalline part) (this becomes stronger with increasing VCl content); 690 cm^{-1} (C—Cl stretching vibration, disordered part), and 610 cm^{-1} (C—Cl stretching vibration, syndiotactic amorphous part). The last two bands show little change among the various spectra.

X-Ray Diffraction of the Copolymers

As shown in Figure 3, x-ray diffraction diagrams of the copolymers do not show crystallinity. Only the haloes are observed in the neighborhood of $2\theta = 17°$ and $2\theta = 24°$. These haloes disappear as the percentage of VCl in the copolymers decreases. This corresponds to the variation of the absorption bands at 750 and 635 cm^{-1} of the infrared spectra given in Figure 2.

Thermograms of the Copolymers

Figure 4 shows the thermograms of the copolymers. No peaks due to melting or crystalline–crystalline transitions are observed in the temperature range from 30 to 200°C, and only a shift of the baseline due to the glass transition is observed. The glass transition temperature increases with increasing percentage of VCl in the copolymer, which is very consistent with the change in the appearance of the copolymer.

Monomer Reactivity Ratio

The copolymer composition curve is shown in Figure 5. The molar fraction of ethylene in copolymers is always smaller than that in monomer mixture.

Some authors have previously reported that the propagation rate is proportional to the second power of the ethylene fugacity and to the first power of the concentration of VCl in the γ-ray induced homopolymerization of ethylene[6] and VCl,[7] respectively, in liquid carbon dioxide. In the calculation of the monomer reactivity ratios, a similar relationship is assumed to be realized in the propagation step of the copolymerization, i.e., the rate of addition of ethylene to the propagating radicals is assumed to be proportional to the second power of the ethylene fugacity and that of

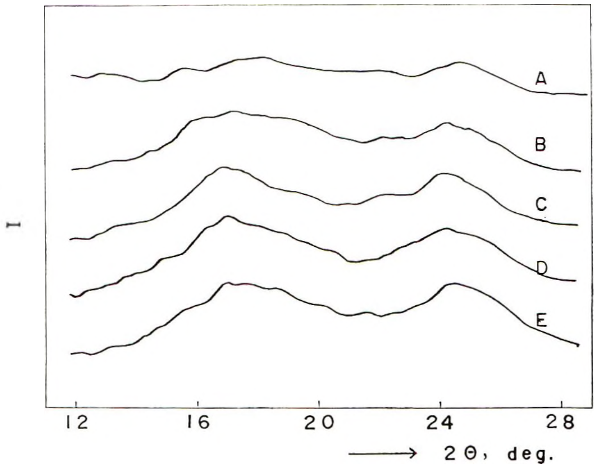

Fig. 3. X-ray diffraction diagrams of copolymers. Symbols same as in Fig. 2.

VCl is proportional to the first power of the VCl fugacity under high pressure. The monomer reactivity ratios calculated by the method of Lewis and Mayo[8] are $r_1 = (0.30 \pm 0.05) \times 10^{-3}$ and $r_2 = (2.0 \pm 0.60) \times 10^3$ (M_1 = ethylene, M_2 = VCl). The reactivity ratio products (r_1r_2) is ca. 0.60 ± 0.31. This shows that the copolymerization tends to be ideal and that truly random copolymers, with little alternating tendency, are obtained. The monomer reactivity ratios obtained by the authors are greatly different from those of Burkhart, et al.[1] ($r_1 = 0.24$, $r_2 = 3.60$), Erussalimsky et al.[2] ($r_1 = 0.20$, $r_2 = 1.85$) obtained from the copolymerization studies at higher pressure, and Misono et al.[5] ($r_1 = 0.05$, $r_2 = 4.16$) at lower pressure. It should be noted that the values of these three groups of authors are calculated by assuming that all reactions of four propagation

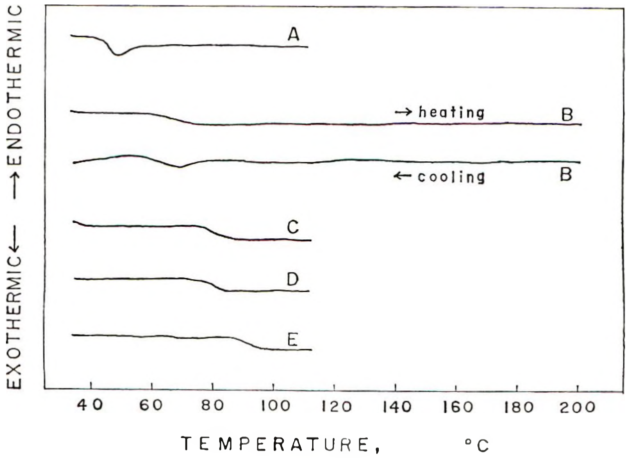

Fig. 4. Thermograms of copolymer for α-alumina in ambient air at a heating rate of 2.5°C/min. Symbols same as shown in Fig. 2.

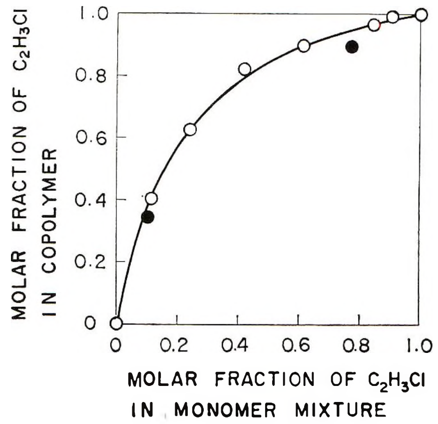

Fig. 5. Copolymer composition vs. monomer composition: (○) γ-ray-induced copolymerization (the reaction conditions are the same as shown in Fig. 1); (●) AIBN-initiated copolymerization: reaction pressure, 400 kg/cm^2; temperature, 45°C; AIBN, 4.3 mmole/l.

steps of the copolymerization are first-order with respect to the concentration of each monomer. When the above assumption for the propagation is adapted, the values of r_1 and r_2 calculated from the data given in Figure 5 are 0.18 ± 0.02 and 5.3 ± 0.14, respectively.

Kinetical Consideration of the Copolymerization

Previous studies on the copolymerization of ethylene and VCl initiated by AIBN, Ti(O-n-Bu)$_4$–AlEtCl$_2$–(donor), and trialkylboron–peroxide catalyst systems indicated that the reaction could proceed by a free-radical mechanism. It appeared that the copolymerization induced by radiation could also be interpreted in terms of a general mechanism developed for free radical-initiated copolymerization reactions. However, it must be pointed

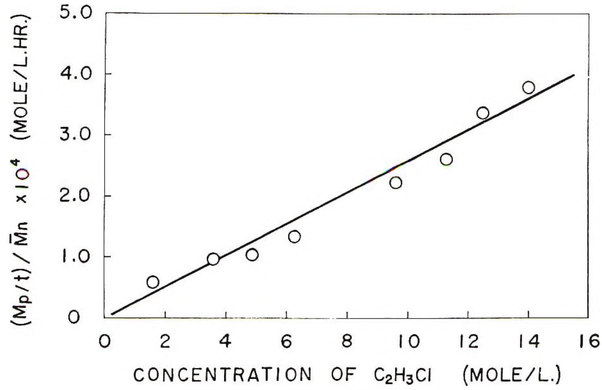

Fig. 6. Rate of formation of polymer chain, $(M_p/t)/\bar{M}_n$, vs. initial concentration of vinyl chloride in monomers. Reaction conditions are the same as shown in Fig. 1.

out that both monomers and the solvent can contribute to the initiation in the radiation-induced copolymerization, since no chemical substance is inert when subjected to ionizing radiations.

The straight line in Figure 6 shows plots of the rate of formation of the polymer molecule, defined as the ratio of the amount of monomer polymerized per unit time to the molecular weight of the copolymer, $(M_p/t)/\bar{M}_n$, as a function of the concentration of VCl. Since, as reported in previous papers on the homopolymerizations of ethylene[6] and VCl[7] in liquid carbon dioxide solvent, transfer to the monomer or to the solvent has been found not to occur, it is reasonable to consider that the transfer reactions are also absent in the ternary mixture of the monomers and liquid carbon dioxide. Therefore, the straight line obtained indicates that the rate of initiation is accelerated by the addition of VCl and increases proportionally with its concentration. Various types of primary radicals may also be produced by the absorption of the radiation energy by the monomers and the solvent in this copolymerization system. However, the number of radicals from ethylene and carbon dioxide is thought to be negligibly small in comparison with that from VCl, and the copolymerization is exclusively initiated by the radicals generated from the radiolysis of VCl.

Denoting E and V as ethylene and VCl monomer, respectively, E· and V· as the growing chain radicals having a terminal unit of ethylene and VCl, respectively, we propose reactions (1)–(6) and the corresponding rate equations (7)–(9) are proposed for the copolymerization.

Initiation:

$$\mathrm{E,\ V,\ CO_2} \overset{k_i}{\rightsquigarrow} \mathrm{R\cdot} \tag{1}$$

Propagation:

$$\mathrm{E\cdot} + 2\mathrm{E} \xrightarrow{k_{p1}} \mathrm{E\cdot} \tag{2}$$

$$\mathrm{E\cdot} + \mathrm{V} \xrightarrow{k_{p2}} \mathrm{V\cdot} \tag{3}$$

$$\mathrm{V\cdot} + 2\mathrm{E} \xrightarrow{k_{p3}} \mathrm{E\cdot} \tag{4}$$

$$\mathrm{V\cdot} + \mathrm{V} \xrightarrow{k_{p4}} \mathrm{V\cdot} \tag{5}$$

Termination:
$$\mathrm{E\cdot} + \mathrm{V\cdot} \xrightarrow{k_t} \text{polymer} \tag{6}$$

$$R_i = k_i \rho_V I \tag{7}$$

$$R_p = k_{p1}[\mathrm{E\cdot}]f_E{}^2 + k_{p2}[\mathrm{E\cdot}]f_V + k_{p3}[\mathrm{V\cdot}]f_E{}^2 + k_{p4}[\mathrm{V\cdot}]f_V \tag{8}$$

$$R_t = k_t[\mathrm{E\cdot}][\mathrm{V\cdot}] \tag{9}$$

In the rate equations, the k's are the reaction rate constants, and the concentrations (in brackets) are expressed in the usual molar concentration of reactant per unit volume. f_E and f_V are the fugacity of ethylene and VCl, respectively; ρ_V, the concentration of VCl, and I, the dose rate. Further, in considering a kinetic scheme of the type given, the following assumptions are made on the basis of the results obtained from the homopolymerization

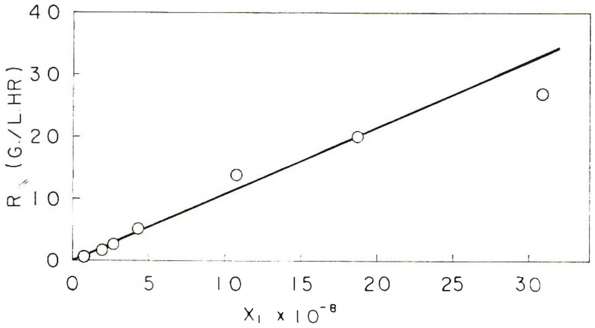

Fig. 7. Rate of copolymerization R vs. X_1. Reaction conditions are the same as shown in Fig. 1.

studies of each monomer:[6,7] (*1*) the addition of ethylene to the propagating radicals is a second-order reaction with respect to ethylene fugacity, and that of VCl is first-order with respect to the fugacity, and that of VCl is first-order with respect to the fugacity of VCl under high pressure; (*2*) the growing chain radicals are deactivated only by the cross termination reaction between the radicals ending in ethylene and VCl unit since the termination reaction has been found to be almost absent in the homopolymerization of each monomer at room temperature.

With the steady-state hypothesis the above scheme gives the following equations:

$$k_{p2}[\mathrm{E}\cdot]f_{\mathrm{V}} = k_{p3}[\mathrm{V}\cdot]f_{\mathrm{E}}^2 \tag{10}$$

$$R_i = k_i\rho_{\mathrm{V}}I = k_t[\mathrm{E}\cdot][\mathrm{V}\cdot] = R_t \tag{11}$$

From eqs. (10) and (11), the concentrations of the growing chain radicals are obtained in terms of the measurable quantities and the constants as follows:

$$[\mathrm{E}\cdot] = (K_ik_{p3}/k_tk_{p2})^{1/2}(\rho_{\mathrm{V}}f_{\mathrm{E}}^2/f_{\mathrm{V}})^{1/2} \tag{12}$$

$$[\mathrm{V}\cdot] = (K_ik_{p2}/k_tk_{p3})^{1/2}\cdot(\rho_{\mathrm{V}}f_{\mathrm{V}}/f_{\mathrm{E}}^2)^{1/2}$$

where $k_iI = K_i$. In eq. (12), k_iI is replaced by a newly defined constant K_i, since all experiments were carried out under a constant dose rate.

The overall rate of the copolymerization R is approximately equal to the rate of the propagation; accordingly, it becomes:

$$R = -d(\mathrm{E} + \mathrm{V})/dt \simeq R_p = k_p(K_ik_{p3}/k_tk_{p2})X_1 \tag{13}$$

where

$$X_1 = f_{\mathrm{E}}^3\{28(\rho_{\mathrm{V}}/f_{\mathrm{V}})^{1/2} + (90.5/r_1)\cdot(\rho_{\mathrm{V}}f_{\mathrm{V}})^{1/2}/f_{\mathrm{E}}^2 + 62.5(r_2/r_1)f_{\mathrm{V}}(\rho_{\mathrm{V}}f_{\mathrm{V}})^{1/2}/f_{\mathrm{E}}^4\} \tag{14}$$

The number-average molecular weight of the copolymer, $\bar{M}_n$, is given as the total amount of the copolymer divided by the total copolymer chains:

$$\bar{M}_n = \frac{\int R_p dt}{\int R_i dt - {}^1/_2\int R_t dt} \tag{15}$$

TABLE II
Calculation of X_1, and X_2 in Equations (13) and (16)[a]

Run no.	C_2H_3Cl concentration, mole/l.	Fugacity, kg/cm²		$X_1 \times 10^{-8}$	$X_2 \times 10^{-7}$
		C_2H_4	C_2H_3Cl		
3	1.60	85.4	1.87	0.77	4.68
4	3.60	80.5	4.28	1.97	5.46
5	4.88	68.3	5.15	2.72	5.56
6	6.24	60.7	6.69	4.25	6.92
7	9.60	41.0	9.51	10.72	11.57
8	11.28	29.2	11.05	18.78	16.35
9	12.48	19.3	12.38	30.86	27.48

[a] $r_1 = 0.30 \times 10^{-3}$, $r_2 = 2.0 \times 10^3$, $X_1 = f_E{}^3\{28(\rho_V/f_V)^{1/2} + (90.5/r_1)\cdot(\rho_V f_V)^{1/2}/f_E{}^2 + 62.5(r_2/r_1)f_v(\rho_V f_V)^{1/2}/f_E{}^4\}$, $X_2 = f_E\{28f_E{}^2(f_V\rho_V)^{1/2} + (90.5/r_1)\cdot(f_V/\rho_V)^{1/2} + 62.5(r_2/r_1)\cdot(f_V/f_E{}^2)\cdot(f_V/\rho_V)^{1/2}\}$.

Substitution of eqs. (7), (8) and (9) into R_i, R_p, and R_t gives, after integration,

$$\bar{M}_n = 2k_{p1}(k_{p3}/K_ik_tk_{p2})^{1/2}X_2 \tag{16}$$

where

$$X_2 = f_E\{28f_E{}^2/(f_V\rho_V)^{1/2} + (90.5/r_1)\cdot(f_V/\rho_V)^{1/2} + 62.5(r_2/r_1)(f_V/f_E{}^2)(f_V/\rho_V)^{1/2}\} \tag{17}$$

The numerical values of X_1 and X_2 are listed in Table II. The rate of copolymerization is plotted in Figure 7 against X_1, and the molecular weight is plotted in Figure 8 against X_2 according to eqs. (13) and (16), respectively. In view of the fact that straight lines practically passing through origin are obtained in both Figures 7 and 8, the proposed scheme and the assumptions that the growing chain radicals are mainly deactivated by the cross-termination reaction and that there is no transfer reaction may be accepted. The pronounced inhibition by a small amount of VCl which was pointed out above may be satisfactorily interpreted in terms of the effective cross-termination.

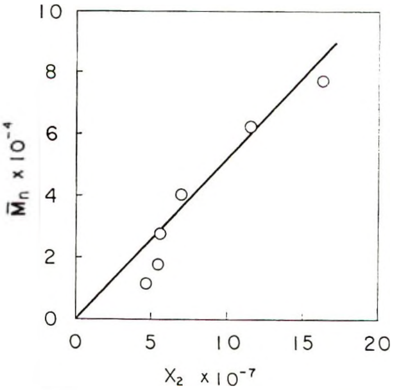

Fig. 8. Molecular weight $\bar{M}_n$ vs. X_2. Reaction conditions are the same as shown in Fig. 1.

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Epoxide Polymers: Synthesis, Stereochemistry, Structure, and Mechanism*

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Synopsis

Epoxide polymerization studies have yielded technically important catalysts and polymers. The polymers were studied by cleaving them with Group IA organometallics to monomer, dimer, and trimer glycol fragments. The identification of these glycol fragments has established that the crystalline polymers from the *cis*- and *trans*-2,3-epoxybutanes are respectively racemic and meso-diisotactic and that the amorphous polymer from the *cis*-oxide is disyndiotactic. These studies also showed that the amorphous fraction from propylene oxide polymerization with coordination catalysts contains substantial head-to-head and tail-to-tail segments. This work has led to a much better understanding of the mechanism of epoxide polymerization. These facts were established: (1) epoxides polymerize with inversion of configuration of the ring-opening carbon atom; (2) monosubstituted epoxides polymerize largely by attack on the primary carbon with a coordination catalyst; and (3) two or more metal atoms must be involved in the coordination polymerization of epoxides.

INTRODUCTION

General

Low molecular weight polymers of epoxides are readily prepared with ordinary acid and base catalysts and have been known for many years. Only in the last decade, however, have great advances been made in the preparation of high molecular weight polymers from epoxides. This recent progress has resulted from the discovery of new catalyst systems. The purpose of this paper is to discuss our work in this area, with particular emphasis on our studies related to the stereochemistry and structure of epoxide polymers. This work, previously reported in part in communication form,[1-3] has changed and broadened our understanding of the mechanism of epoxide polymerization.

Early Polymerization Work

The first high molecular weight polyepoxide, poly(ethylene oxide), was reported by Staudinger in 1933.[4] This interesting, water-soluble, crystal-

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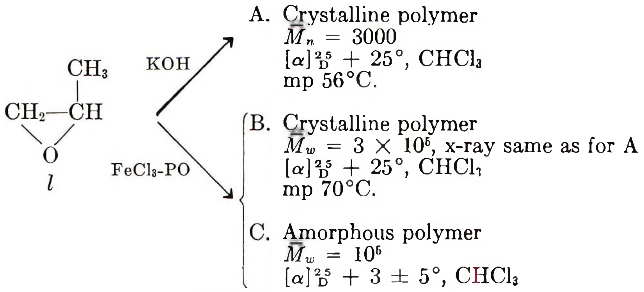
line thermoplastic was commercialized in 1957 by the Union Carbide Corporation after Hill and co-workers developed some new catalyst systems consisting of specially prepared carbonates and amides of calcium.[5,6] Another important development occurred in 1955, when Pruitt and Baggett of the Dow Chemical Company developed a new catalyst consisting of the reaction product of ferric chloride and propylene oxide.[7,8] This catalyst, which will be referred to as the iron catalyst or as $FeCl_3$-PO, polymerized propylene oxide to a new crystalline polymer of high molecular weight as well as to an amorphous rubber.

Early Mechanism Studies

The first work on the stereochemistry and mechanism of epoxide polymerization was reported by Price and Osgan,[9] who polymerized a pure enantiomorph of propylene oxide [eqs. (1)].

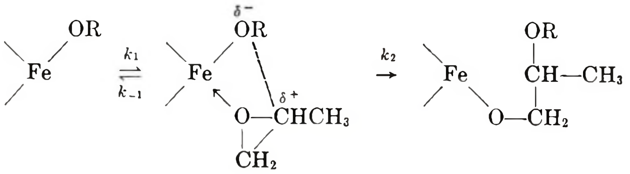


(1)

With an ordinary base catalyst, potassium hydroxide, the *l*-monomer gave a low molecular weight, optically active crystalline polymer, as compared with the liquid, low molecular weight polymer obtained under comparable conditions with racemic monomer. This crystalline polymer from *l*-monomer was obviously a stereoregular, isotactic polymer, and the liquid poly(propylene oxide) from racemic monomer was evidently a stereorandom polymer. Since Gee[10,11] had shown that nucleophilic attack on epoxides occurs preponderantly (>97%) at primary rather than secondary carbon, the asymmetric carbon in the optically active crystalline polymer was presumed to have the same configuration as in the optically active monomer.

With the iron catalyst and *l*-propylene oxide, Price obtained two different high molecular weight poly(propylene oxides), one an optically active crystalline polymer and the other a largely racemized amorphous polymer [eq. (1)]. The optically active crystalline polymer made with the iron catalyst was identical, except for molecular weight, to the optically active crystalline polymer made with the potassium hydroxide catalyst in both its x-ray pattern and its sign and magnitude of optical rotation. The fact that the crystalline polymer made from racemic monomer with the iron catalyst also had the same x-ray pattern very elegantly showed that the crystalline polymer from the iron catalyst was isotactic and that the asymmetric carbon atoms in this polymer had the same configuration as in the monomer from which it was derived, i.e., the propylene oxide polymerized with retention of configuration of its asymmetric carbon atom.

As a result of these findings, Price[9] proposed a mechanism for the action of the iron catalyst [eq. (2)]. This



(2)

mechanism had several important features: first, coordination of the epoxide and growth of the polymer on one metal atom; second, ring opening at the secondary carbon atom of the epoxide; third, retention of configuration of this ring opening asymmetric carbon atom because of a front-side attack; fourth, a possible racemization of the asymmetric carbon atom during ring opening due to free carbonium ion formation under some conditions to explain the amorphous optically inactive fraction. The author's studies,[1,2] reported here in detail, have shown that most of these features are incorrect.

EXPERIMENTAL

Reagents

n-Heptane was Phillips pure grade, used as received. Other solvents (C.P. grade) were dried by passing through a molecular sieve column.

The trialkylaluminums were the commercial products of Texas Alkyls, Inc. Amylsodium was a commercial sample in *n*-heptane from Orgmet. By analysis this material contained about equal amounts of Na ($0.33M$) and amylsodium ($0.28M$). It was used on an amylsodium basis. *n*-Butyllithium was obtained from Foote Mineral in *n*-hexane ($1.6M$).

Preparation and Properties of Polyepoxides

The general procedures used for the preparation of alkyl-aluminum-water type catalysts and the use of these catalysts in preparing polyepoxides is described below for the polymers derived from the 2,3-epoxybutanes, cyclohexene oxide and phenyl glycidyl ether. Catalyst preparations and polymerizations were run in capped pressure vessels under nitrogen using the self-sealing liner and hypodermic techniques previously described.[12] Polymers were dried for 16 hr at 80°C/0.4 mm. Inherent viscosities were run at 0.1% in $CHCl_3$ at 25°C for the *trans*-oxide and cyclohexene oxide polymers; 0.1% in tetrachloroethane at 100°C for the *cis*-oxide polymers; and 0.1% in chloronaphthalene at 135°C for poly(phenyl glycidyl ether). Differential thermal analysis (DTA) was used to measure the melting behavior of the crystalline polymers. The melting point is taken as the temperature at which the last crystallinity disappears. Qualitative crystallinity levels are based on x-ray diffraction examination.

Catalysts

Catalysts are described by the molar ratio of their components, listed in the order in which they were added. Similar procedures were used for preparing other organometallic catalysts used in this work.

i-Bu_3Al–0.5 H_2O in *n*-Heptane. A 0.5M solution of i-Bu_3Al in n-heptane was prepared under nitrogen, cooled to 0°C, and water (0.5 mole/mole i-Bu_3Al) added dropwise over a 15-min interval while stirring with a Teflon-coated magnetic bar. After stirring 1 hr at 0°C, the temperature was allowed to rise spontaneously to room temperature and stirring was continued overnight. The catalyst was a clear, colorless solution and was stable on storage at room temperature, provided that air was properly excluded.

Et_3Al–0.6 H_2O in Ether. A 25% solution of Et_3Al in n-heptane was diluted with absolute ether to 0.5M concentration in a stirred flask under nitrogen. The water (0.6 mole/mole Et_3Al) was added dropwise over 2 hr while stirring at reflux. After two additional hours of refluxing, the clear catalyst solution was transferred to capped pressure bottles and stored at room temperature. This catalyst was stable, provided that air was properly excluded.

Et_3Al–0.5 H_2O–0.5 Acetyl Acetone (Chelate Catalyst). A 25% solution of Et_3Al in n-heptane was diluted with absolute ether to 0.5M, cooled to 0°C, and then water (0.5 mole/mole Et_3Al) was added dropwise over 15 min while stirring with a Teflon coated magnetic bar. Acetyl acetone (0.5 mole/mole Et_3Al) was added dropwise, stirring at 0°C continued for 15 min; this was followed by stirring overnight at room temperature. This catalyst was a clear, light-yellow solution and was stable on storage at room temperature, provided that air was properly excluded. Effective catalysts can also be made by reversing the order of addition of the water and acetyl acetone.

Et_3Al–0.5 H_2O–0.5 Acetyl Acetone–1.0 Cyclohexanol (Modified Chelate Catalyst). The Et_3Al–0.5 H_2O–0.5 acetyl acetone catalyst was modified by adding cyclohexanol (1 mole/mole Et_3Al) dropwise at 0°C, with agitation, followed by stirring overnight at room temperature and heat treatment for 4 hr at 65°C. The catalyst was a clear, yellow solution.

Poly-(*trans*-2,3-epoxybutane)

The *trans*-2,3-epoxybutane (10 g) was polymerized at −78°C in n-heptane diluent (75 ml) with the i-Bu_3Al–0.5 H_2O catalyst in heptane (4 mmole i-Bu_3Al). The polymerization is essentially instantaneous, with the polymer precipitating out. After 2 hr at −78°C, anhydrous ethanol shortstop (5 ml) is added. The product was diluted with n-heptane at room temperature, stirred twice for 15 min with 3% aqueous HCl, and

TABLE I

Polymerization of 2,3-Epoxybutanes with Various Catalysts[a]

	Catalyst		Conditions		Isolated polymer			
Monomer	Type	Amt, mmole	Time, hr	Temp, °C	Conversion, %	η_{inh}[b]	X-ray crystallinity	Mp, °C
trans-Oxide	Et_2Zn–1.0 H_2O[c]	4	19	0	86	1.8	High	91
	BF_3 etherate[d]	2	19	−78	86	0.15	High	94
	Et_2AlCl[e]	4	19	−78	37	0.25	Moderate	89
	$Al(Oi\text{-}Pr)_3$[e]	0.4	40	100	43	0.20	High	91
	$FeCl_3$–PO[f]	1.2	115	80	9.8	0.07	Low	—
cis-oxide	Et_2Zn–1.0 H_2O[c]	4	19	0	93	1.1	None	—
	BF_3 etherate[d]	2	19	−78	91	0.15	None	—
	$Al(Oi\text{-}Pr)_3$[e]	0.4	40	100	75	0.10	None	—
	$FeCl_3$–PO[f]	1.2	115	80	6.5[g]	1.7	Moderate	147
					44	0.21	None	

[a] A 10-g portion of monomer polymerized without added diluent except for that in catalyst. Ether added during isolation and the ether-soluble recovered. Unless otherwise noted, there was little, if any, ether-insoluble.

[b] 0.1% $CHCl_3$, 25°C, for the *trans*-oxide polymers and 0.1% tetrachloroethane, 100°C, for the *cis*-oxide polymers.

[c] Prepared at 0.25*M* concentration in n-heptane and reacted four hours at 0°C.

[d] 1*M* solution in benzene.

[e] 1.35*M* solution in *n*-heptane.

[f] Prepared as described by Price and Osgan;[9] used as 1.2*M* ($FeCl_3$ basis) dispersion in diethyl ether.

[g] Ether-insoluble fraction.

washed neutral with water. The heptane-insoluble was collected, washed twice with *n*-heptane, once with *n*-heptane containing 0.1% Santonox antioxidant, and dried to give 96% conversion of highly crystalline polymer, η_{inh} 3.9, mp 105°C. The heptane-soluble polymer was recovered by stripping off the solvent after adding 0.5% Santonox based on the polymer and then dried to give 4% conversion of moderately crystalline product, η_{inh} 0.4.

Other polymerizations of this monomer were run in a similar fashion using other conditions as noted. Inherent viscosity of this polymer varies inversely with temperature; thus at 5°C η_{inh} of the heptane-insoluble (90%) is 1.2. Diethyl ether is a very effective chain transfer agent in this system and must be excluded to obtain the highest molecular weights. Studies with other catalysts are summarized in Table I. Typical mechanical properties of poly-(*trans*-2,3-epoxybutane) are given in Table II.

TABLE II
Mechanical Properties of Crystalline Polymers from Symmetrical Disubstituted Epoxides[a]

		Poly-(*cis*-2,3-epoxybutane) from chelate catalyst		
Property	Poly-(*trans*-2,3-epoxybutane)	Unmodified[b]	Modified with cyclohexanol	Poly-(cyclohexene oxide)[c]
Tensile strength × 10^{-3}, psi	3.3	2.3	3.2	5.6
Ultimate elongation, %	400	360	250	1.5
Tensile modulus × 10^{-3}, psi	48.0	2.8	18.0	410.0
Yield stress, psi	2,000	—	—	none
Yield strain, %	14	—	—	none
Density (25°C), g/cc	1.016	—	1.041	1.067

[a] Compression-molded at 175°C and then cooled to room temperature under pressure.

[b] Molded film was of low crystallinity.

[c] Molded film was amorphous.

Poly-(*cis*-2,3-epoxybutane)

i-Bu$_3$Al–H$_2$O Catalyst. The *cis*-oxide was polymerized with the i-Bu$_3$Al–0.5 H$_2$O catalyst by the procedure described above for the *trans*-oxide to give a 98% conversion of heptane-soluble amorphous polymer, η_{inh} 1.7. Under these conditions no heptane-insoluble polymer was formed.

Chelate Catalyst. The *cis*-oxide (10 g) was polymerized in *n*-heptane (94 ml) with the Et$_3$Al–0.5 H$_2$O–0.5 acetyl acetone catalyst (8 mmoles Et$_3$Al) for 19 hr at 65°C. After shortstopping with 5 ml anhydrous ethanol, ether was added to give a handleable slurry which was washed by stirring twice for 1 hr with 10% aqueous HCl. After washing neutral with water, the ether-insoluble was collected, washed several times with ether and once with ether containing 0.05% Santonox. The dried ether-insoluble represented 79% conversion to a highly crystalline tough solid; η_{inh} 10.1 and mp 135°C. DTA examination showed that on heating this polymer to 175°C and cooling to room temperature it did not recrystallize. Mechanical properties are given in Table II. The ether-soluble plus 0.5% Santonox (based on solids) was recovered by stripping off the solvent and drying to give 21% conversion of a tacky rubber; η_{inh} 1.5, amorphous by x-ray.

Modified Chelate Catalyst. The *cis*-oxide (10 g) was polymerized with the Et_3Al–0.5 H_2O–0.5 acetyl acetone–1.0 cyclohexanol catalyst by replacing the unmodified chelate catalyst in the procedure described above. The ether-insoluble represented 36% conversion, η_{inh} 4.2. By DTA, this sample gave a melt range of 88–157°C, and, on cooling from 175°C, it recrystallized at 90°C. Mechanical properties are given in Table II. The ether-soluble amorphous fraction represented 41% conversion, η_{inh} 0.42. The ether-insoluble (3.0 g) was purified for the cleavage studies by dissolving in $CHCl_3$ (140 ml) at 94°C and then filtering through Celite at room temperature. The polymer was precipitated with 3 liters of CH_3OH, collected, washed with CH_3OH, and dried. This polymer was then dissolved in 280 ml of *n*-heptane at 120°C and then recrystallized at 60°C (did not crystallize at 80°C) for 2 hr. The temperature was raised to 80°C, and the insoluble collected by centrifuging, resuspended in hot *n*-heptane, heated overnight at 80°C, and the insoluble again collected. The latter process was repeated three more times and then the insoluble was washed with anhydrous ethanol containing 0.1% Santonox and dried. The product (0.84 g, η_{inh} 5.4) had a melt range of 110–149°C.

Poly(cyclohexene oxide)

i-Bu_3Al–0.5 H_2O Catalyst. Cyclohexene oxide was polymerized with the i-Bu_3Al–0.5 H_2O catalyst by the procedure described for the *trans*-oxide to give a 99% conversion of heptane-soluble, amorphous polymer, η_{inh} 1.5.

Chelate Catalyst. Cyclohexene oxide (10 g) was polymerized in *n*-heptane (42 ml) with the Et_3Al–0.5 H_2O–0.5 acetyl acetone catalyst (4 mmole Et_3Al) for 19 hr at 65°C. The product was isolated by the procedure described for the *cis*-oxide with the same catalyst. The ether-insoluble represented 9.4% conversion, η_{inh} 3.8, low crystallinity, and mp 76°C. After melting, this polymer did not recrystallize on cooling. The ether-soluble was obtained in 84% conversion, η_{inh} 0.21, amorphous.

Modified Chelate Catalyst. Cyclohexene oxide (10 g) was polymerized in *n*-heptane (84 ml) with the Et_3Al–0.5 H_2O–0.5 acetyl acetone–1.0 cyclohexanol catalyst (8 mmole Et_3Al) for 42 hr at 65°C. The product was isolated by the procedure described for the *cis*-oxide with this catalyst. The ether-insoluble represented 0.3% conversion, η_{inh} 3.6, high crystallinity with the same x-ray pattern as with the unmodified catalyst. The major lattice spacings (and relative intensity) were: 6.2 Å (10), 4.7Å (10), 3.85Å (2), 3.04Å (3), 2.82Å (1), 2.65Å (3), and 2.06Å (3). DTA showed two melt ranges, one at 61–88°C and the other at 108–126°C. The ether-soluble material was obtained in 53% conversion, η_{inh} 0.3, amorphous.

Copolymerization of *cis*- and *trans*-2,3-epoxybutanes

i-Bu_3Al–0.5 H_2O Catalyst. A 50:50 mixture of the *cis*- and *trans*-oxides was polymerized with the i-Bu_3Al–0.5 H_2O catalyst by the procedure described above for the *trans*-oxide, except that the polymerization was shortstopped after 40 sec. There was no heptane-insoluble polymer, and the heptane-soluble polymer was a tacky, amorphous rubber, 61% conversion, η_{inh} 2.3. This product was analyzed by the cleavage method of Table III after correcting for the instability of the *meso* diol in this test, and found to be derived 60% from the *cis*-oxide and 40% from the *trans*-oxide. These data indicate the reactivity ratios of the *cis*- and *trans*-oxides to be, respectively, 1.95 and 0.51, assuming $r_1r_2 = 1$. Thus, this copolymerization is a relatively favorable one with the *cis*-oxide entering the copolymer at about twice the rate of the *trans*-oxide.

Chelate Catalyst. A 50:50 mixture of the *cis*- and *trans*-oxides was polymerized with the Et_3Al–0.5 H_2O–0.5 acetyl acetone catalyst by the method described for the *cis*-oxide with this catalyst. The ether-insoluble polymer was obtained in 36% conversion, η_{inh} 9.1 (0.1%, tetrachloroethane, 100°C), was moderately crystalline with the typical *cis*-oxide polymer x-ray pattern along with some of the *trans*-oxide polymer pattern (low crystallinity) and gave two distinct melting points at 72 and 128°C. Cleavage by the method of Table III (corrected for the instability of the *meso* diol) indicated that this fraction was derived 90% from the *cis*-oxide and 10% from the *trans*-oxide. Thus, the crystalline fraction forms in a very unfavorable copolymerization with the *cis*-oxide entering the copolymer at least 20-fold faster than the *trans*-oxide and probably even less favorably than this, since x-ray shows that *trans*-oxide homopolymer is in this fraction. The ether-soluble polymer was obtained in 20% conversion as a tacky, amorphous rubber, η_{inh} 3.3. Cleavage by the method of Table III (corrected) indicated that this product was derived 87% from the *cis*-oxide and 13% from the *trans*-oxide. Thus, this amorphous fraction is also formed in an unfavorable copolymerization with the *cis*-oxide entering the copolymer at least tenfold faster than the *trans*-oxide.

Isotactic Poly(phenyl glycidyl ether)

Phenyl glycidyl ether (40 g, Shell Chemical Corp.) was polymerized in absolute diethyl ether (80 ml) with the Et_3Al–0.6 H_2O catalyst (16 mmole Et_3Al) for 19 hr at 30°C. The ether-insoluble, crystalline polymer was isolated by the same general procedure described above for poly-(*cis*-2,3-epoxybutane) with the chelate catalyst and was obtained in 84% conversion and 92% yield; η_{inh} 2.2, mp 203°C. This product was 97% insoluble in benzene at room temperature.

TABLE III

Nature of Monomer Diol from Cleavage of 2,3-Epoxybutane Polymers[a,b]

Catalyst[c]	Polymerization temp, °C	Polymer form	Monomer diol[d]		
			Conversion, %	*dl*	*meso*
trans-oxide					
i-Bu$_3$Al-0.5H$_2$O	−78	Crystalline	23	<0.5	>99.5
Et$_2$Zn-1.0 H$_2$O	0	"	21	<4	>96
BF$_3$ etherate	−78	"	25	<8	>92
Et$_2$AlCl	−78	"	20	<10	>90
Al(Oi-Pr)$_3$	100	"	34	<3	>97
FeCl$_3$-PO	80	"	22	<2	>98
cis-oxide					
Et$_3$Al-0.5 H$_2$O-0.5 acetylacetone-1.0 cyclohexanol	65	Crystalline	21	99.5	0.5[e]
FeCl$_3$-PO	80	"	25	>99	<1
FeCl$_3$-PO	80	Amorphous	16[f]	>99.5	<0.5
Et$_2$Zn-1.0 H$_2$O	0	"	23	>99	<1
BF$_3$ etherate	−78	"	32	>93	<6

[a] Conditions: 2.2 mmole C_4H_8O; 5–10 mmole amylsodium; 18–30 ml *n*-heptane; 22 hr, 90°C.

[b] Treating a 55-45 mixture of *dl*- and *meso*-2,3-butanediol with 9 mmole of excess amylsodium under these same conditions gave complete recovery of the *dl*-diol and a 33% loss of the *meso*-diol.

[c] See Table I for specific catalyst preparation details.

[d] Values preceded by < are limits of detection. This component was not detected.

[e] 0.2% *trans*-oxide in starting *cis*-oxide.

[f] Cleavage at 65°C.

Cleavage Method to Prepare Monomer, Dimer, and Trimer Diols

All polyether cleavages with amylsodium or butyllithium were run in capped pressure vessels under nitrogen with the use of self-sealing liner and hypodermic techniques (butyl liners with benzene) previously described.[12] Cleavages to monomer and dimer diols at 30–65°C were usually agitated on a rotating rack in a water bath or, if at room temperature, by using a wrist-action shaker. Cleavages at 90°C were run in an oil bath with periodic hand shaking.

Polyether (0.157 g) dissolved in cleavage solvent (by heating at elevated temperature if needed). The air in the reaction vessel was replaced with nitrogen and the cleaving agent added. After the indicated reaction time, the run was shortstopped with 1 ml of anhydrous ethanol and cooled to room temperature. The product was added to 90 ml of 96% ethanol which was cooled by wet ice. Using a pH meter the pH was then adjusted to the 7–9 range by adding concentrated HCl (2% aqueous NaHCO$_3$ added if pH decreased too much). If there was any insoluble material (NaCl in amyl-sodium systems, none in butyllithium systems) it was removed by centrifuging and washed once with 100 ml of anhydrous ethanol. The combined supernatant plus washes was deionized by agitating 15 min with ethanol–wet Amberlite MB-1 ion-exchange resin (30 ml/150 ml of sample), the resin removed, and then the solvent stripped off in a Kuderna-Danish evaporator fitted with a Snyder column. Benzene (100–150 ml) was added and stripping repeated to a final volume of 10–15 ml. This was then further concentrated at 5:1 reflux ratio to ca. 1 ml. The final volume, after rinsing with 1 ml of anhydrous ethanol, was measured with a 5 ml hypodermic syringe. This product was then analyzed by GC using a column consisting of Carbowax 400 on Anakrom ABS.

Preparation and Identification of Monomer, Dimer, and Trimer Diols

Butylene Glycols

2,3-Butanediols. These pure diols were obtained by fractionating commercial samples at 50 mm in an 85-plate column at an 85:1 reflux ratio. The *meso*-2,3-butanediol (from Celanese 2,3-butanediol, 85% *meso* and 15% *dl*), was 100% pure by GC (bp 111.4°C/50 mm, n_D^{30} 1.4356). The *dl*-diol (from K and K Lab 2,3-butanediol, 53% *dl* and 47% *meso*) was 98.5% *dl* and 1.5% *meso* by gas chromatography (GC) (bp 107.4°C/50 mm, n_D^{30} 1.4292). *p*-Nitrobenzoates were prepared from the *dl*- and *meso*-diols. The *dl* derivative had mp 129.6–131.5°C (lit.[13] mp = 128°C) and the *meso* derivative had mp 193–194°C (lit.[13] mp 192–193°C).

Dimers and Trimers Related to *cis*-Oxide Polymers. *dl*-2,3-Butanediol (361.4 g, 4.0 mole) was reacted at room temperature in a stirred flask under nitrogen with 180 mmole Na (6*M* dispersion in mineral oil) which was added dropwise. When the Na was completely reacted, the mixture was transferred to two 28-oz capped pressure bottles under nitrogen. A total of 200 g (2.8 mole) of *cis*-2,3-epoxybutane was added in four equal portions (at 0, 20, 26, 46 hr) while tumbling at 90°C for 62 hr. Infrared studies indicated <1% of the *cis*-oxide. Water (4 ml) was added and then, while stirring in a warm H_2O bath, Dry Ice was added (60 g over 3 hr). The insoluble material was removed by centrifuging and was washed twice with heptane. Analysis of the combined liquid phases gave the results summarized in Table IV.

TABLE IV

r	Compound	Total diols, %
1.00	*dl*-2,3-Butanediol	30
1.85	Dibutylene glycol I	32
2.96	Dibutylene glycol II	21
4.58	Tributylene glycol I	6.3
5.76	Tributylene glycol II	8.5
6.44	Tributylene glycol III	2.4

TABLE V

	BP, °C/10 mm	n_D^{30}	Purity by GC, %	Analysis		$\bar{M}_n$ (osmometry, in benzene)
				C, %	H, %	
Dimer I	109.3	1.4383	99+	—	—	—
Dimer II	117.4	1.4334	100	58.83	11.39	199
Dimer (theory for $C_8H_{18}O_3$)				59.2	11.18	162
Trimer I	136.2	1.4336	96	61.37	11.34	226
Trimer II	142.4	1.4375	99	61.10	11.28	234
Trimer (theory for $C_{12}H_{26}O_4$)				61.3	11.18	234

The crude product was fractionated at 50 mm in a 20-plate column at a 25:1 reflux ratio to remove the unreacted *dl*-2,3-butane-diol and then at 10 mm in a 100 plate column at 75:1 reflux ratio to obtain the higher diols. The main components were separated out in pure form, 23% of dibutylene glycol I and 20% of dibutylene glycol II. Trimer III was not obtained pure. The properties of the best fractions are listed in Table V.

Mass spectra on dibutylene glycols I and II were in accord with the assigned structure.

Dimers and Trimers Related to *trans*-Oxide Polymers. This dimer and trimer diol synthesis was carried out exactly as described above for the dimers and trimers related to the *cis*-oxide by using *dl*-2,3-butanediol and *trans*-2,3-epoxybutane. The main product was not miscible with heptane and therefore the inorganics were washed with toluene. GC analysis of the total product is given in Table VI. None of the dimers and trimers related to the *cis*-oxide were deteted where separation is feasible.

TABLE VI

r^a	Compound	Total diols, %
1.13	*meso*-2,3-Butanediol	37
2.76	Dibutylene glycol III	26
3.16	Dibutylene glycol IV	24
5.53[b]	Tributylene glycol IV	4.0
6.60[c]	Tributylene glycol V	6.6
8.04	Tributylene glycol VI	2.9

[a] Relative to dl-2,3-butanediol.

[b] Same retention time as tri-II.

[c] Retention time close to tri-III.

Dibutylene glycol III (24% of total diols isolated) showed BP 115.7°C/10 mm, 99% pure by GC;

ANAL. Calcd for $C_8H_{18}O_3$; C, 59.2%; H, 11.18%. Found: C, 59.5%; H, 11.43%.

Dibutylene glycol IV (23% of total diols isolated) showed bp 119.0°C/10 mm, 99% pure by GC;

ANAL. Found: C, 59.0%; H, 11.30%.

Of the tributylene glycols, only IV was isolated in fair (82%) purity, bp 142.2°C/10 mm.

The dibutylene glycols I–IV gave different infrared and near-infrared spectra. *p*-Nitrobenzoates (not recrystallized) gave the following melting points: I, 121–122°C; II, 143–144°C; III, 166–168°C; IV, 116–117°C.

Stereochemistry of Di- and Tributylene Glycols

Dibutylene Glycols I and II. Based on the synthesis method, one of these dibutylene glycols must be a racemic compound with all *d* or *l* carbon atoms and the other a *meso* compound with *dd-ll* carbon sequences. The earlier preparation of crystalline *poly-*(*cis*-2,3-epoxybutane)[2] in optically active form indicated that the main cleavage product from this polymer, dibutylene glycol I, should be the racemic glycol and thus resolvable. The general resolution scheme given below is similar to that described for 2-octanol.[14]

Dibutylene glycol I (40.5 g, 0.25 mole) was placed in a three-necked, 500-ml flask under nitrogen with 150 ml of pyridine (dried over 4 Å molecular sieve) with 74.0 g (0.5 mole) phthalic anhydride (reagent grade) and heated on steam bath at 95–97°C for 3 hr. Temperature was then increased to reflux (116–117°C) and held for 11 hr. Acid number data in H_2O and alcohol indicated that only 11% of the phthalic anhydride was unreacted. The product was added to 400 g of ice plus 175 cc of concentrated HCl and the precipitate dissolved in $CHCl_3$, water-washed until chloride-free, filtered, dried over Na_2SO_4, filtered, stripped, and dried at room temperature (0.4 mm) to give 83.8 g (acid number, 228, 230; theory for acid phthalate, 244).

The acid phthalate (82.8 g, 0.17 mole) was dissolved in 200 ml acetone and 134.7 g (0.34 mole) of brucine [E. H. Sargent, $[\alpha]_D^{25}$ −85° (2%, C_2H_5OH)] was added slowly. The mixture was refluxed and 25 ml acetone added to dissolve completely. After 4 days at 2°C, the crystals were collected, washed with cold acetone, and dried [76.3 g, $[\alpha]_D^{25}$ −18.7 (2%, C_2H_5OH)]. This product was refluxed 1 hr with 700 ml of acetone and the insoluble material collected, washed with acetone, and dried, $[\alpha]_D^{25}$ −0.5° (1%, C_2H_5OH, dissolved with heat, came out on standing) and + 9.2 (2%, CH_3OH). Two recrystallizations from anhydrous ethanol gave 15.2 g of a constant rotation product, $[\alpha]_D^{25}$ + 11.8 (2%, CH_3OH), which contained 46% brucine by ultraviolet spectroscopy (theory for monobrucine salt, 46.2; for dibrucine salt, 63.4). All of this product was dissolved in boiling CH_3OH (150 cc), cooled to room temperature, and 1.72 cc concentrated HCl (20% excess) was added, followed by 1500 ml of water. After 20 hr, the insoluble material was collected, washed neutral with water, and dried at room temperature (0.4 mm) to give 7.50 g of product (94% theory), amorphous by x-ray. Since this contained 0.9% brucine, it was purified by repeating the brucine removal procedure to give 7.15 g of a material with $[\alpha]_D^{25}$ +56.3° (2%, C_2H_5OH); ultraviolet spectra indicated 0.13% brucine with the expected acid phthalate bands at 223 mμ (36.7 a) and 273 mμ (5. 6a).

ANAL. Calcd for $C_{24}H_{26}O_9$: C, 62.9%; H, 5.72%; acid no., 244. Found: C, 62.9%; H, 5.78%; acid no, 242.

The acid phthalate of the other enantiomorph of dibutylene glycol I was also isolated from the soluble brucine salt by similar procedures and in somewhat less pure form, $[\alpha]_{\mathrm{D}}^{25}$ −42° (2% ethanol).

Dibutylene Glycols III and IV. Dibutylene glycol IV is a *meso* isomer with *dl-dl* carbon sequences, since it is obtained from the cleavage of poly-*trans*-2,3-epoxybutane, which is the known *meso*-diisotactic polymer.[1] Thus, dibutylene glycol III should be a racemic compound with *dl-ld* carbon sequences based on the synthesis method. This conclusion was confirmed by the following resolution of dibutylene glycol III.

The general resolution method is the same as described above for dibutylene glycol I, but with the use of 32.4 g (0.20 mole) of dibutylene glycol III. The reaction time in forming the acid phthalate was 3 hr at 98°C (6.9% unreacted anhydride). The brucine salt crystallized out of the initial reaction mixture at room temperature. This salt was purified by two recrystallizations from 80–20 acetone–anhydrous ethanol (25 ml/g), $[\alpha]_{\mathrm{D}}^{25}$ −26.0° and −28.4° (2%, C_2H_5OH), 57% brucine by ultraviolet (theory for dibrucine salt, 63%). Brucine was removed from this salt as before except that for complete removal it was dissolved in CH_2Cl_2, washed four times with 1% aqueous HCl, washed neutral, stripped, and dried. After two recrystallizations from toluene the acid phthalate (4 g) had $[\alpha]_{\mathrm{D}}^{25}$ +28.6 (2%, C_2H_5OH); 0.1% brucine was found by ultraviolet, with typical acid phthalate bands at 223 mμ (36.5 a) and 274 mμ (5.5a).

Anal. Calcd for $C_{24}H_{26}O_9$: C, 62.9%; H, 5.72%; acid no., 244. Found: C, 62.83%; H, 5.78%; acid no., 237.

Not all the dibutylene glycols that we have prepared are easily resolvable by GC if in the same mixture. Thus I and II, and III and IV are resolvable; however II and III, and II and IV are not resolvable if present together.

Tributylene Glycols IV, V, and VI. Dibutylene glycol IV (10.0 g, *dl-dl* carbon sequences) was reacted with *trans*-2,3-epoxybutane (5 cc) in the same way as described above for the synthesis of dibutylene glycols from 2,3-butanediols. The tributylene glycol fraction was 54% IV and 48% V by GC, no VI being detected. Tributylene glycol IV is of known structure with *dl-dl-dl* carbon sequences since it is the only trimer from the cleavage of poly-(D(+)-*trans*-2,3-epoxybutane). Thus tributylene glycol V is the *dl-dl-ld*, *ld-ld-dl* racemic pair based on this reaction synthesis.

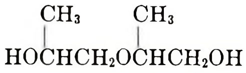
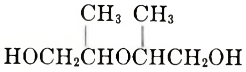
Tributylene glycol VI is the only other possible tributylene glycol from *trans*-oxide polymer cleavage, and thus is the *dl-ld-dl* (*meso*) compound.

Propylene Glycols

The 1,2-propanediol used in this work was E. K. Co. 1321. GC indicated that it was pure with no dimer detected (<1%).

Dow dipropylene glycol was the source of our dimer standards. This material was fractionated at 50 mm in a 100-plate column at 100:1 reflux ratio to yield four isomers in high purity (98–99.5%) (names based on nature of alcohol groups, Table VII).

TABLE VII
Dipropylene Glycols

Polymerization type	Structure	Type
Head-to-tail	 $HO\overset{CH_3}{C}HCH_2O\overset{CH_3}{C}HCH_2OH$	Mixed, 2 *dl* pairs
Head-to-head	 $HO\overset{CH_3}{C}HCH_2OCH_2\overset{CH_3}{C}HOH$	Disecondary, *meso* and *dl*
Tail-to-tail	 $HOCH_2\overset{CH_3}{C}HO\overset{CH_3}{C}HCH_2OH$	Diprimary, *meso* and *dl*

These were 37% disecondary (bp 146.5°C/50 mm, η_D^{30} 1.4367), 52% mixed (bp 150.9°C/50 mm, η_D^{30} 1.4379), 6% diprimary I (bp 156.5°C/50 mm, η_D^{30} 1.4346), and 5% diprimary II (bp 153.8° C/50 mm, η_D^{30} 1.4408). These products were initially identified by their infrared spectra, based on published data,[15,16] and the spectrum of a known sample of diprimary II from C. C. Price. This structure assignment was confirmed by NMR studies at Hercules and at C. C. Price's laboratory.

One problem in the dipropylene glycol analysis by GC was that the diprimary isomer II overlapped about 30% with the mixed dimer glycol. The diprimary isomers I and II did give a good separation one from the other.

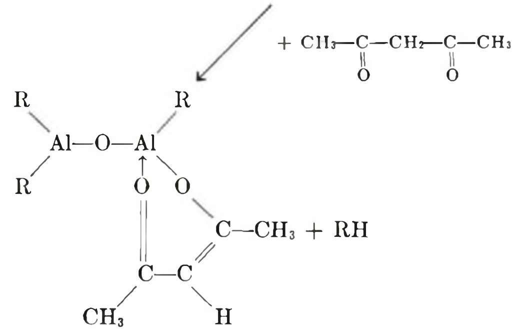
RESULTS AND DISCUSSION

Catalyst Studies

The author's success in synthesizing many new high molecular weight polyepoxides resulted from the finding of a variety of unique and highly effective organometallic catalyst systems.[3] Some of these new catalyst systems are the reaction products of aluminum,[17] zinc,[18] and magnesium,[19] organometallics with water, i.e., Et_3Al–0.5 H_2O; Et_3Al–0.5H_2O–0.5 acetylacetone; Et_2Zn–1.0H_2O; and Et_2Mg–1.0H_2O. These ratios of components generally give a very effective catalyst. However, the ratio of these ingredients can be varied over a wide range, and the best composition will depend somewhat on the conditions, the epoxide, and the type of products desired. Active catalysts were always found to contain residual organometal bonds. The diethylzinc–water catalyst was discovered independently in Japan by Professor Furukawa and his co-workers.[20] Also Colclough[21] found that trimethylaluminum must be reacted with water to give an active catalyst for propylene oxide polymerization, particularly for the preparation of crystalline polymer.

These new organometallic catalysts vary a great deal in their behavior and nature. In our work, we have found the alkyl-aluminum-based catalysts to be especially useful. The two types of ethylaluminum catalysts indicated, as will be shown later, vary considerably in their performance. Both of these ethylaluminum–water catalysts are stable and soluble in organic media. These properties are in contrast with those of the diethylzinc and diethylmagnesium catalysts which usually are not storage stable and are heterogeneous. The fundamental reactions involved and basic structures formed in making these alkylaluminum catalysts are indicated in eq. (3).

$$R_3Al + 0.5\ H_2O \rightarrow \underline{R_2Al{-}O{-}AlR_2} + RH$$



(3)

With the alkylaluminum–H$_2$O catalyst, water reacts at both of its active hydrogens to form a bis(dialkylaluminum)oxide species and liberates a hydrocarbon. This conclusion is based on measuring the residual alkylaluminum groups in the final catalyst by gas evolution on acid hydrolysis and also by using tritiated water in the initial catalyst preparation and showing that the final catalysts did not retain appreciable ($<1\%$ of initial) radioactivity. Furukawa and co-workers[22] have also used tritiated water to study the Et$_3$Al–H$_2$O reaction as it relates to the cationic polymerization of vinyl monomers and bis(chloromethyl)oxetane, but not epoxides. They used very short reaction times (1.5 hr at room temperature) and found residual active hydrogen was required for the polymerizations they studied. Thus, heat-treating destroyed the active hydrogen and the catalytic activity. These results are not in disagreement with our results since we used much longer reaction times in preparing our catalysts (ca. 24 hr at room temperature). Also, our catalysts are stable and retain their catalytic activity for epoxide polymerization after heat treatment.

In the formation of the acetylacetone-modified catalyst (referred to as the chelate catalyst) [eq. (3)], acetylacetone reacts further with the organoaluminum intermediate to liberate another mole of hydrocarbon and form what we believe to be the chelated type of species shown. This conclusion is based on infrared and ultraviolet spectra of the catalyst. In addition, alkylaluminum acetylacetonates with a chelate structure have previously been reported.[23–25] It is also of interest that organoaluminums modified with acetylacetone alone[26] are catalysts for epoxide polymerization, although not quite as versatile as the similar water modified catalysts. After our work on these catalysts was reported, Kambara and co-workers[27] described epoxide catalysts based on the combination of alkylaluminums with transition metal chelate compounds (as acetylacetonates). Since Sartori et al.[24] previously showed that Et_3Al and chromium triacetylacetonate interact to form alkylaluminum acetylacetonate-type products, it is evident that Kambara's catalysts merely offer an alternative way of preparing, in part, our alkylaluminum acetylacetonate catalysts. Actually, in these cases, adventitious water in reagents, monomer, and the reaction vessels may be yielding, in part, the preferred alkylaluminum–H_2O–chelate catalyst. In our experience, Kambara's catalyst is not as effective as our directly-prepared alkylaluminum chelate catalysts.

Our chelate catalyst can also be prepared in effective form by reversing the order of addition of water and chelating agent from that shown in eq. (3) or by using twice as much acetyl acetone, i.e., 1 mole/mole aluminum. One role of the coordinating chelating agent may be to minimize ordinary cationic polymerization by blocking the fourth coordinate position of aluminum and allowing the fifth and/or sixth coordinate positions of aluminum to function in a coordination propagation step.

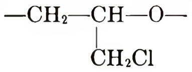
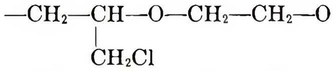
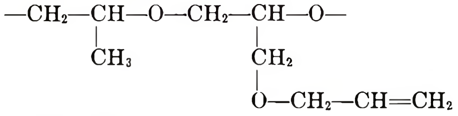
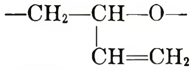
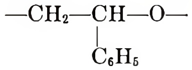
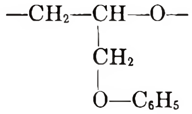
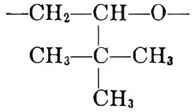
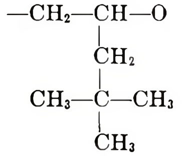
The exact nature of the catalytic species is unknown, because it is difficult to determine under the conditions necessary, that is, during a polymerization. However, it is probably built of the fundamental structural units underlined in eq. (3) by their association with themselves, by their coordination with epoxide or other donor solvents, and by the reaction of the organoaluminum groups with the epoxide. The presence of the metal–oxygen–metal grouping in the catalyst is particularly noteworthy. The zinc and magnesium catalysts also contain these groupings, as our work has shown, and the work of Furukawa[28] and others[29,30] has shown with dialkyl zinc–water catalysts. Early in our work we recognized the considerable importance of having two or more organometal groups joined together by another atom such as oxygen to obtain a good epoxide catalyst. We also found that a variety of other polyreactive additives, as polyols,[31] amines, hydrogen sulfide, carbon dioxide, diacids, diketones,[19] etc. can be utilized to join together organometal groups to form active catalysts. Useful additives vary considerably depending on the starting organometal compound. Organomagnesium compounds exhibit the most versatile behavior in this respect.[19] Water is, of course, the most widely studied polyreactive additive. Burgess and Colclough[32] reported numerous important studies on the preparation and characterization of metal alkyl–H_2O systems.

New Polyepoxides From Organometallic Catalysts

From Monosubstituted Epoxides. These new organometallic catalysts enabled us to synthesize many new high molecular weight polyepoxides, both homopolymers and copolymers.[3] A few of the more interesting monosubstituted epoxides that were polymerized to both amorphous and crystalline homopolymers are summarized in Table VIII. Some interesting amorphous copolymers are also shown. The amorphous epichlorohydrin homopolymer and its amorphous copolymer with ethylene oxide are especially interesting as oil-resistant rubbers.[33,34]

The amorphous copolymers of propylene oxide with small amounts of an unsaturated epoxide such as allyl glycidyl ether are sulfur vulcanizable rubbers with excellent low temperature properties, good dynamic properties, and good ozone resistance. These interesting products were apparently first prepared in useful form by the author[35] and have recently been described by others.[36-38]

TABLE VIII
High Polymers from Monosubstituted Epoxides

	Amorphous	Crystalline mp, °C
 $-CH_2-\underset{CH_2Cl}{\underset{\mid}{CH}}-O-$	Solvent-resistant rubbers	120
 $-CH_2-\underset{CH_2Cl}{\underset{\mid}{CH}}-O-CH_2-CH_2-O$		
 $-CH_2-\underset{CH_3}{\underset{\mid}{CH}}-O-CH_2-\underset{O-CH_2-CH=CH_2}{\underset{\mid}{\underset{CH_2}{\underset{\mid}{CH}}}}-O-$	S-vulcanizable rubber	
 $-CH_2-\underset{CH=CH_2}{\underset{\mid}{CH}}-O-$	Rubber	74
 $-CH_2-\underset{C_6H_5}{\underset{\mid}{CH}}-O-$	Like polystyrene	149
 $-CH_2-\underset{O-C_6H_5}{\underset{\mid}{\underset{CH_2}{\underset{\mid}{CH}}}}-O-$	Rubber	203
 $-CH_2-\underset{CH_3}{\underset{\mid}{\underset{CH_3-C-CH_3}{\underset{\mid}{CH}}}}-O-$	Rubber	152
 $-CH_2-\underset{CH_3}{\underset{\mid}{\underset{CH_3-C-CH_3}{\underset{\mid}{\underset{CH_2}{\underset{\mid}{CH}}}}}}-O$	Rubber	82

Butadiene monoxide is interesting because it can be polymerized to both an amorphous rubber and a low melting crystalline polymer without affecting its vinyl group. Styrene oxide has given both amorphous and crystalline, presumably isotactic, high polymers which have physical properties and behavior very much like amorphous and crystalline polystyrene. Recently some additional properties of poly(styrene oxide) have been reported by Allen and co-workers.[39–41] Other crystalline, isotactic polyepoxides with high melting points also have bulky, branched side chains, e.g., poly(phenyl glycidyl ether), first reported by Noshay and Price[31] mp 203°C, and poly(*tert*-butyl ethylene oxide), mp 152°C, reported by the author[42] and others.[43,44] Thus, side chain branching raises the melting points of isotactic polyepoxides as it does with isotactic poly(alkyl vinyl ethers) and polyolefins.[12] In general the isotactic polyepoxides with comparable side chains to the isotactic polyolefins have much lower melting points; e.g., poly(neopentyl ethylene oxide), mp[42] 82°C compares with poly-4,4-dimethylpentene-1, mp[45] >320°C. This large difference in melting behavior between isotactic polyepoxides and polyolefins is no doubt due to the flexibilizing effect of the oxygen chain atom in polyepoxides.

From Symmetrical Disubstituted Epoxides. Our studies of the polymerization of symmetrical disubstituted epoxides as exemplified by the *cis*- and *trans*-2,3-epoxybutanes are particularly important[46] (Table IX). The alkylaluminum-water catalyst polymerized both isomers essentially instantaneously at dry ice temperature. This rapid polymerization is to be contrasted with the fairly slow polymerization of propylene oxide with this catalyst even at room temperature. With this catalyst, the *cis*-oxide generally gives only an amorphous high molecular weight rubber; the *trans*-oxide gives only a crystalline, high molecular weight plastic. An equal *cis–trans* oxide mixture copolymerizes with favorable reactivity ratios to give a high molecular weight rubbery copolymer. In this copolymerization the *cis*-oxide enters the copolymer about twice as fast as the *trans*-oxide.

TABLE IX
High Polymers from *cis*- and *trans*-2,3-epoxybutanes

		Polymerization		
Oxide	Catalyst	Temp, °C	Rate	Polymer
cis	R_3Al–0.5 H_2O	−78	Instantaneous	Amorphous rubber
trans	R_3Al–0.5 H_2O	−78	Instantaneous	Crystalline polymer, mp 100°C
cis	R_3Al–0.5 H_2O–0.5 acetylacetone	65	Slow	Crystalline polymer, mp 162°C
trans	R_3Al–0.5 H_2O–0.5 acetylacetone	65	Very little	

On the other hand, the alkylaluminum–water–acetylacetone catalyst polymerizes the *cis*-oxide slowly at 65°C, and, under these conditions, the product is largely a crystalline polymer with a melting point up to 162°C. This crystalline polymer from the *cis*-oxide is totally different from the crystalline polymer obtained from the *trans*-oxide with the alkylaluminum-water catalyst, having a completely different x-ray pattern, different solubility properties and a higher melting point. This chelate catalyst, however, caused very little polymerization of the *trans*-oxide at 65°C. In addition, one can selectively polymerize the *cis*-oxide from an equal *cis*-*trans* mixture and obtain fairly pure crystalline *cis*-polymer, thus indicating very unfavorable copolymerization reactivity ratios with the chelate catalyst. Indeed, our results indicate that the *cis*-oxide enters the crystalline fraction at least twentyfold faster than the *trans*-oxide. Actually it is probable that copolymerization is even much less favorable than this at the catalyst sites which form the most stereoregular polymer. Even the amorphous fraction in this copolymerization with the chelate catalyst forms with unfavorable reactivity ratios since the *cis*-oxide enters the copolymer at least tenfold faster than the *trans*-oxide.

In general, these results indicate that the polymerization site in the acetylacetone-modified catalyst is much more hindered than that of the unmodified catalyst, since it facilitates the formation of crystalline polymer from the less hindered *cis*-oxide and does not polymerize the more hindered *trans*-oxide very well. This conclusion is also supported by the very large difference in copolymerization reactivity ratios of the *cis*- and *trans*-oxides with these two catalysts. Based on these results, the chelate catalyst was classified as a coordination catalyst.

The copolymerization results with the chelate catalyst also indicate that the polymerization site in this catalyst varies considerably, probably due to variations in steric hindrance. Thus, there are sites which give nearly pure stereoregular homopolymer and there are sites which give amorphous copolymer but with the *cis*-oxide still greatly preferred.

The mechanical properties of the crystalline *cis*-oxide polymer prepared with the chelate catalyst suggest it is a stereoblock polymer. This polymer does not recrystallize well from the melt and, after molding, has very rubbery properties but is quite strong due to crystallization on stretching (Table II). This behavior is similar to that which we observed with certain fractions of isotactic poly(vinyl methyl ether) and which we attributed to a stereoblock structure.[12] By adding cyclohexanol to the chelate catalyst, which presumably increased the steric hindrance at the polymerization site, we were able to prepare crystalline *cis*-oxide polymer which recrystallized readily from the melt to give a product without pronounced rubbery properties (Table II).

These results with the *cis*- and *trans*-oxides with the chelate catalyst indicate that stereoregularity and copolymerization are controlled largely by steric factors inherent in the catalyst at the polymerization site and not by steric hindrance inherent in the growing chain end. These conclusions are in accord with Tsuruta's recent conclusion that "catalyst site control" is involved in the formation of isotactic poly(propylene oxide)[47] with a coordination catalyst.

Cyclohexene oxide is an interesting symmetrical disubstituted epoxide related to *cis*-2,3-epoxybutane. It was previously reported that our alkylaluminum–water catalyst will polymerize this monomer to high molecular weight amorphous polymer.[26] Bacskai[48] recently reported that aluminumalkyls alone will give similar results on cyclohexene oxide* and proposed a "stereoregular" poly-*trans* structure for this polyether. Considering our prior work on the *cis*- and *trans*-2,3-epoxybutane polymers,[1,2] the poly-*trans*-structure for poly(cyclohexene oxide) would certainly be expected. However, Bacskai does not mention that each carbon atom in the main chain is asymmetric and that optical as well as geometric isomerism is possible. Thus, the *dl* carbon sequences can be ordered or random, i.e., we may have both head-to-tail and heat-to-head polymerization.

As in the case of *cis*-2,3-epoxybutane, cyclohexene oxide has been polymerized with our chelate catalyst to a crystalline polymer (mp 78°C). The cyclohexanol-modified chelate catalyst gave a crystalline fraction of higher crystallinity and of higher melting point (126°C) with the same x-ray pattern. This crystalline polymer not only has the poly-*trans*-structure but it is evidently highly stereoregular, unlike Bacskai's or our amorphous poly(cyclohexene oxide). Based on our subsequent studies with the crystalline *cis*-oxide polymer formed with the same catalyst, this crystalline poly(cyclohexene oxide) is presumably a diisotactic polymer.

Mechanism Studies Based on the 2,3-Epoxybutane Polymers

Stereochemistry. Our ability to homopolymerize the 2,3-epoxybutanes with different catalysts to different products offered us a unique opportunity to learn more about the mechanism of epoxide polymerization. Since both carbon atoms in the monomer unit are asymmetric, the stereochemistry of the monomer unit would tell us whether the ring-opening carbon atom retained or inverted configuration during polymerization. Of course, the crystalline polymers initially appeared most attractive since we would expect these to have repetitive monomer and/or dimer stereosequences.

The 2,3-epoxybutane polymers are ideal for studying stereochemistry since all the carbon atoms in the chain are chemically equivalent, thereby restricting the number of possible stereoisomeric dimer units to the four shown in Table X.† Two of the possible dimer configurations correspond

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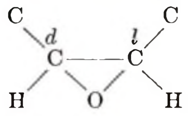
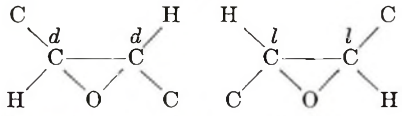
* We had also found that aluminum alkyls alone would polymerize the *cis*- and *trans*-2,3-epoxybutanes[49] as well as cyclohexene oxide.

† We omit two other stereoregular sequences listed by Barlow,[50] i.e., dimer units with *-dd-ld-* and *-dd-dl-*carbon sequences. Such stereosequences are very unlikely to result from the stereoregular homopolymerization of either the *cis*- or *trans*-oxide since a very complex, improbable polymerization mechanism would be required.

TABLE X

Stereochemistry and Polymerization Mechanism of the 2,3-Epoxybutane Polymers

Name[a]	Carbon atom configuration	Polymerization mechanism	
		cis-oxide	*trans*-oxide
			
Meso-diisotactic	*-dl-dl-*	Retention, head-to-tail	Inversion, enantiomorph selection
Racemic diisotactic	*-dd-dd-* *-ll-ll-*	Inversion, head-to-tail	Retention, enantiomorph selection
Meso$_1$-disyndiotactic	*-dl-ld-*	Retention, head-to-head	Inversion, alternation
Meso$_2$-disyndiotactic	*-dd-ll-*	Inversion, head-to-head	Retention, alternation

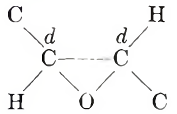
---

[a] The nomenclature used here combines that of Natta et al[51] for 1,2-disubstituted olefins with the usual nomenclature for simple compounds containing two similar asymmetric carbon atoms. Using Natta's method[51] the diisotactic polymers would be called (in the order given above); erythro-diisotactic and threo-diisotactic.

to diisotactic polymer and the other two to disyndiotactic polymer. Only one of the four stereosequences, the racemic diisotactic one, can exist in optically active form. The other three are all *meso.*

Any one of the four possible dimer configurations from the stereoregular homopolymerization of the 2,3-epoxybutanes can theoretically arise from either the *cis-* or *trans*-oxide by an appropriate mechanism, as shown in Table X. The conceivable mechanisms listed differ in two respects for each oxide. First: polymerization may be visualized to involve either inversion or retention of configuration of the ring opening carbon atom with either the *cis-* or *trans*-oxide. Second: polymerization with the *cis*-oxide, a *meso* isomer, can be either head-to-tail or head-to-head; on the other hand, polymerization with the *trans*-oxide, a racemate, can involve either enantiomorph selection or enantiomorph alternation. Since each enantiomorph of the *trans*-oxide has an identical head and tail, there is no possibility of head-to-tail or head-to-head polymerization. Whether one has retention or inversion of configuration of the ring-opening carbon atom is readily determined by examining the stereochemistry of a monomer unit in the polymer chain. On the other hand, whether a head-to-tail or head-to-head polymerization is involved with the *cis*-oxide, or an enantiomorph selection or alternation process is involved with the *trans*-oxide, can be determined only by examining the stereochemistry of a dimer unit. The stereochemistry of the dimer unit also tells us if the polymer is diisotactic or disyndiotactic.

Optically Active *Trans*-Oxide Studies. Our initial effort to determine the stereochemistry of these polymers was to take advantage of the fact that only one stereo sequence could be optically active, i.e., the racemic diisotactic one.[1] Thus, the pure *l*-isomer of the *trans*-oxide was polymerized with a triisobutylaluminum-water catalyst at Dry Ice temperature. A quantitative conversion to a crystalline, high molecular weight polymer with a melting point of 96°C was obtained [eq. (4)]. This polymer showed



$\xrightarrow[-78°\text{C}]{\text{i-Bu}_3\text{Al-0.5 H}_2\text{O}}$ 97% conversion to crystalline polymer

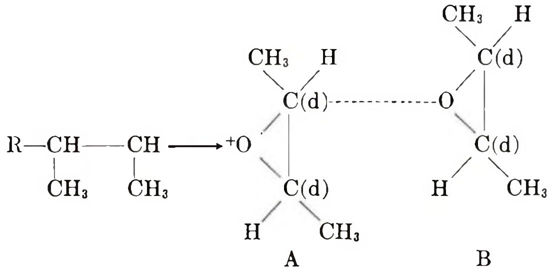
η_{inh} 1.0, mp 96°C
$[\alpha]^{25}_{D}$ 0.0 ± 1.0 (C_6H_6 or $CHCl_3$)

(4)

no optical activity even though the monomer had a high optical rotation. Compared with the polymer from racemic monomer, this polymer has a similar x-ray pattern; the same infrared pattern, both below and above its melting point; and similar solubility properties. There were some minor differences; for example, the optically active monomer product was insoluble in benzene, whereas the racemic monomer product was soluble; also slight variations were noted in the x-ray patterns. These minor differences indicate that we have some imperfections in the structure of the polymer from the racemic monomer.

On the basis of the optical inactivity of the polymer from active monomer, we concluded that the crystalline polymer from the *trans*-oxide has -*dl*-*dl*-carbon sequences and is thus the *meso*-diisotactic polymer. This conclusion meant, contrary to prior concepts, that the *trans*-oxide polymerized with inversion of configuration of the ring-opening carbon atom. It also indicates an isomer selection process in the stereoregular polymerization of the racemic *trans*-oxide.

We proposed, on the basis of the very facile polymerization, the high chain transfer activity of diethyl ether and on the stereochemistry observed with the *trans*-oxide, that it polymerizes by a cationic mechanism similar to that suggested for polymerizations with Friedel-Crafts catalysts of tetrahydrofuran,[52] of oxacyclobutanes[53] and of ethylene oxide.[54] This mechanism requires a rearward, nucleophilic attack of an epoxide molecule, B, on either equivalent carbon atom of the epoxide molecule, A, involved in the propagating oxonium ion [eq. (5)]. With racemic monomer, A and B must be the same optical isomers to obtain the stereoregular diisotactic polymer. Molecular models of the transition state, based on the likely assumption that the plane of epoxide ring B is perpendicular to the plane of epoxide ring A, indicate that steric hindrance inherent in the monomer can bring about this selection process. Thus, the stereoregularity of this polymerization appears to be controlled by the monomer rather than by the catalyst structure which often controls the stereoregularity of many other polymerizations, particularly of epoxides. This conclusion is supported by the fact that one can obtain only stereoregular polymer with quite a variety of catalysts including aluminum isopropoxide, aluminumalkyls, diethylzinc–H_2O, and ordinary cationic catalysts such as boron trifluoride etherate, aluminum chloride, and stannic chloride. An occasional failure of this isomer selection process would lead to a stereoblock structure with -*dl*-*dl*-*dl*- sequences followed by -*ld*-*ld*-*ld*- sequences of the carbon atoms. Such a stereoblock structure undoubtedly explains the somewhat different properties of the crystalline polymer prepared from the racemic monomer in comparison with that prepared from a pure enantiomorph.



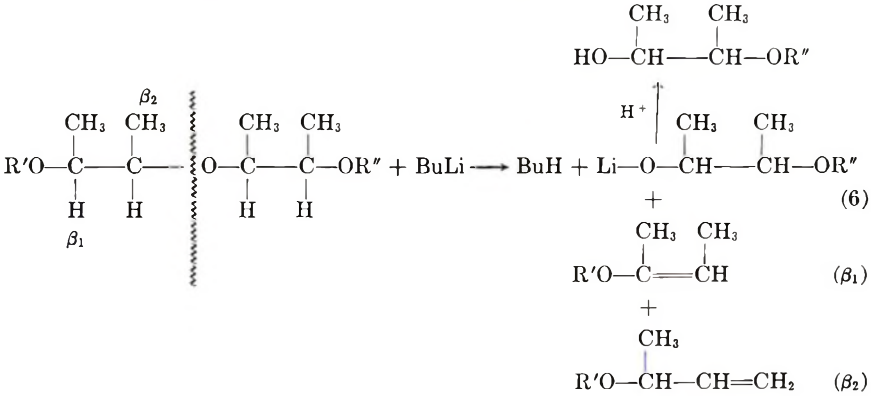
(5)

This work also indicates that alkylaluminum–water catalysis can involve just a simple cationic mechanism.[1] Furukawa and coworkers[55,56] have come to the same conclusion on the basis of other evidence for the polymerization of certain vinyl monomers, oxetanes and furanes. Since the Et_2Zn–

H_2O catalyst readily polymerizes the *trans*-oxide, this catalyst also can operate by a simple cationic mechanism. Recently Tsychiya and Tsuruta[57] reported conditions under which the $Et_2Zn–H_2O$ catalyst will give cationic polymerization of tetrahydrofurane, 3,3-bis(chloromethyl)oxetane and styrene. The $Et_2Zn–H_2O$ catalyst has usually been considered to be a coordination catalyst, particularly for propylene oxide.

Polymer Cleavage to Diol Fragments. These very unexpected results on the stereochemistry of the *trans*-oxide polymer made it highly desirable that we confirm this work by some independent method. Also, the stereochemistry of the crystalline polymer from the *cis*-oxide was needed, particularly since this polymer is formed by a different mechanism, that is, coordination polymerization. The standard x-ray structure analysis method was investigated by Samuels[58] of our laboratory, and more recently by Barlow,[50] using our samples, but an unequivocal assignment of structure was not obtained. Our own studies[2] had indicated that the crystalline *cis*-oxide polymer was the racemic diisotactic one since we had obtained it in optically active form by polymerizing the *cis*-oxide with our alkylaluminum–water–acetyl acetone catalyst modified with *l*-menthol. Here too, because of the low optical rotations, it was desirable that this result be confirmed by an independent approach. Thus a chemical method was sought by which these polyethers could be cleaved to their monomer and dimer units without affecting the stereochemistry of the carbon atoms. Our first effort in this direction led to a very facile unique, general method of cleaving polyethers.[59]

This method [eq. (6)] involves cleaving the polyethers with a Group IA organometallic such as amylsodium or butyllithium in an organic solvent



$$\mathrm{HO{-}\overset{CH_3}{CH}{-}\overset{CH_3}{CH}{-}OR''}$$

$$\mathrm{R'O{-}\underset{\underset{\beta_1}{H}}{\overset{CH_3}{C}}{-}\underset{H}{\overset{\overset{\beta_2}{CH_3}}{C}}{-}\wr\, O{-}\underset{H}{\overset{CH_3}{C}}{-}\underset{H}{\overset{CH_3}{C}}{-}OR'' + BuLi \longrightarrow BuH + Li{-}O{-}\overset{CH_3}{CH}{-}\overset{CH_3}{CH}{-}OR''}\ \xrightarrow{H^+}\ \text{(above)} \qquad (6)$$

$$+\ \mathrm{R'O{-}\overset{CH_3}{C}{=}\overset{CH_3}{CH}} \qquad (\beta_1)$$

$$+\ \mathrm{R'O{-}\overset{CH_3}{CH}{-}CH{=}CH_2} \qquad (\beta_2)$$

such as benzene at room temperature or at elevated temperature. In this reaction, a β-elimination occurs by attack of the butyl anion of butyllithium on a hydrogen beta to the ether atom [β_1 and β_2, eq. (6)] to yield a lithium alkoxide chain end and a double bond chain end. The lithium alkoxide chain end is, of course, readily converted with acid to the hydroxyl group. Further random reaction will ultimately yield some fraction of the product with hydroxyl groups on each end of the cleaved fragment. With this cleavage reaction, any size glycol fragment, as monomer, dimer, trimer, and even much higher, can be obtained in which the carbon atoms have retained the stereochemistry of the starting polyether.

Price and Spector[60] have developed an ozone method of cleaving polyethers which yields glycols only after the ketone-, aldehyde-, and ester-ended fragments are reduced with lithium aluminum hydride. This method would not be useful in our stereochemistry studies since only one carbon atom in a monomer unit retains its stereochemical identity.

Monomer Diol Studies and Their Implications. Our studies on the monomer diol cleavage fragments from the 2,3-epoxybutane polymers are summarized in Table III. In this work we used amylsodium in about a two- to fourfold excess over that which would be theoretically required to cleave the polymer to monomer units. The cleavage was performed in heptane solvent at 90°C. Amylsodium is preferred, since it gives higher yields of monomer fragments than does butyllithium. The amount of monomer diol was determined by gas chromatography and is expressed as per cent conversion, that is, the percentage of starting polymer converted to monomer diol. The monomer diols, i.e., the *meso*- and *dl*-2,3-butanediols, are quite stable to these cleavage conditions with excess amyl sodium; the *dl*-diol being completely unaffected and the *meso*-diol showing a 33% loss. The nature of the polymer cleavage results shows that there is no interconversion of one diol isomer into the other.

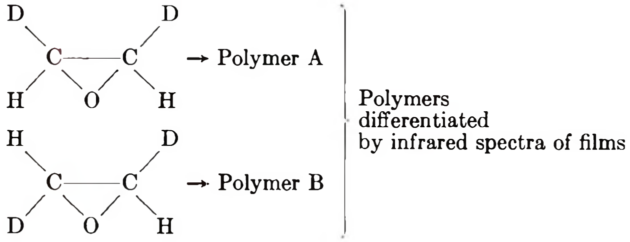
The amount of diol found is close to that expected from a random cleavage attack on the polymer; that is, 25% conversion. Also the monomer diol always corresponds to that expected from inversion of configuration of the ring-opening carbon atom. Thus, the polymer from the *trans*-oxide, which is always crystalline, gives only *meso*-diol with a wide variety of catalysts and reaction temperatures (−78 to 100°C). The catalysts studied are all presumably functioning by a cationic mechanism and include some which are clearly ordinary cationic catalysts, i.e., BF_3 etherate and Et_2AlCl, and others which are less obviously cationic in behavior, i.e., i-Bu_3Al–0.5 H_2O, Et_2Zn–1.0 H_2O, $Al(Oi\text{-}Pr)_3$ and the iron catalyst.

Both the crystalline and amorphous polymers obtainable from the *cis*-oxide with a wide variety of catalysts and reaction temperatures (−78 to 80°C) give only *dl*-diol, indicative again of inversion of configuration of the ring-opening carbon atom. The crystalline polymer was obtained with two coordination catalysts, the alkylaluminum–water–acetylacetone catalysts, and the iron catalyst. The amorphous polymer was obtained with a number of catalysts including i-Bu_3Al–0.5 H_2O, Et_2Zn–1.0 H_2O, BF_3 etherate, and the iron catalyst.

In this work, the *meso*- and *dl*-diols were further identified by isolating them from a typical cleavage reaction, preparing dinitrobenzoate derivatives, and establishing that these derivatives had the same x-ray pattern as the known derivatives. The minor diol, indicative of retention of configuration, is generally not detected. In the three cases examined most carefully, there was 0.5% or less of the minor diol. When there was 0.5%, the *cis*-monomer contained about 0.2% of the *trans*-oxide. Thus, at most, only a few tenths of a per cent of monomer, and perhaps none, polymerizes with retention of configuration.

Quite clearly, therefore, with either cationic or coordination catalysts, the *cis*- and *trans*-2,3-epoxybutanes polymerize with inversion of configuration of the ring-opening carbon atom. As a result of this finding, the author proposed that this conclusion would apply also to monosubstituted epoxides, contrary to early concepts.[9]

The correctness of our proposal has been recently established by Price and Spector[60] [eq. (7)]. In this work, *cis*- and *trans*-dideuteroethylene oxides were polymerized with a variety of catalysts, including an ordinary base catalyst, such as potassium hydroxide or potassium *tert*-butoxide; the triethyl-aluminum–water cationic catalyst; the diethylzinc–water catalyst; and the iron coordination catalyst. The polymer from each monomer was the same, regardless of the catalyst used; that is, polymer A from the *cis*-oxide and polymer B from the *trans*-oxide. The polymers were differentiated by means of the infrared spectrum of the polymer film. Since the base catalyst is known to give inversion of configuration, this work shows that inversion of configuration occurs at the ring-opening primary carbon atom with all types of epoxide catalysts, i.e., anionic, cationic, and coordination.

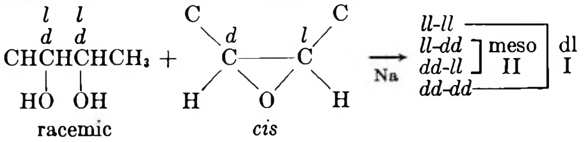


(7)

Dimer and Trimer Diol Studies. To obtain other structural details of polyethers that relate to mechanism and stereoregularity of polymerizations, dimer and even trimer fractions of the polymer must be characterized. Dimer fractions will broadly show whether the polymerization occurs in the usual head-to-tail way and if any abnormal head-head type polymerization occurs. Specifically, for the stereoregular 2,3-epoxybutane polymers, dimer data will show whether these products are diisotactic or disyndiotactic. Trimer fractions provide confirmatory data and information on the purity of the stereoregular polymers.

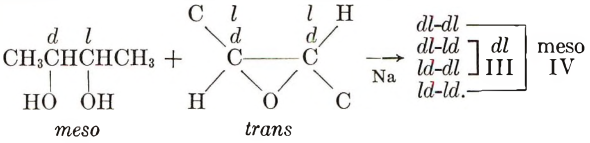
Synthesis and Identification of Reference Compounds. The four possible dibutylene glycols from the 2,3-epoxybutane homopolymers were synthesized by the method shown in eqs. (8) and (9). The dibutylene

Dibutylene glycols related to *cis*-oxide polymers:



(8)

Dibutylene glycols related to *trans*-oxide polymers:



(9)

glycols related to the *cis*-oxide polymers were prepared by reacting racemic 2,3-butanediol with the *cis*-oxide in the presence of sodium catalyst. This type of base-catalyzed reaction is known to proceed with inversion of configuration of the ring-opening carbon atom of the epoxide. There are four possible reactions, two with each stereoisomer of the racemic 2,3-butanediol, depending on whether the *cis*-oxide is attacked on one side or the other. Two disastereoisomers are formed, *dl*-dibutylene glycol I and *meso*-dibutylene glycol II. Similarly, the dibutylene glycols related to the *trans*-oxide are prepared by reacting meso-2,3-butanediol with the racemic *trans*-oxide. Again, four reactions are possible and give the *dl*-dibutylene glycol III and the *meso*-dibutylene glycol IV. In the same reactions, the tributylene glycols which would be expected to be found in either the *cis*-oxide polymers or the *trans*-oxide polymers are also formed.

All of these dibutylene glycols and three of the six tributylene glycols were isolated in pure form by an efficient fractional distillation. Within a given series of diols and triols, that is, those related to the *cis*-oxide polymers or those related to the *trans*-oxide polymers, these diols and the triols are all separable by gas chromatography, thus permitting the analysis of homopolymer cleavage products.

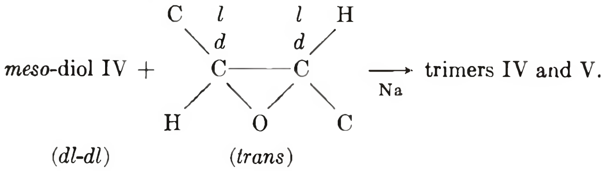
To identify the specific dibutylene glycols, we took advantage of the fact that in each series only one of the diols is a racemic mixture, the other being a *meso* compound. We established which was the *dl*-diol by the general resolution scheme previously described for 2-octanol.[14] The dibutylene glycols were converted to the acid phthalates and then to the brucine salts. Recrystallization of the brucine salts gave the optically active salts which were then decomposed to the free acid phthalates having high optical rotations. It is of interest that on purification dibutylene glycol I gave a monobrucine salt whereas dibutylene glycol II gave a dibrucine salt.

The tributylene glycols which are related to the *cis*-oxide and those which are related to the *trans*-oxide are shown in Table XI. There are three in each case. The stereochemistry of three trimers was determined from their appearance in the cleavage products from known polymer structures, for example, tributylene glycol III would be the preponderant tributylene glycol in the cleavage of crystalline poly-*cis*-2,3-epoxybutane and IV is the only trimer possible from the D(+) *trans*-oxide polymer. This is perhaps the first time the stereochemistry of low molecular weight compounds has been determined from the stereochemistry of a high polymer. In the one less certain case, trimer V, the synthetic method shown was used to establish the stereochemistry, i.e., the base-catalyzed reaction of *meso*-diol IV with racemic *trans*-oxide gives the known trimer IV plus the

TABLE XI
Tributylene Glycols

	Stereochemistry		Structure assignment method
Related to *cis*-oxide			
I	*dd-ll-dd* *ll-dd-ll*	*dl*	Predominates in amorphous polymer
II	*dd-dd-ll* *ll-ll-dd*	*dl*	
III	*dd-dd-dd* *ll-ll-ll*	*dl*	Predominates in crystalline polymer
Related to *trans*-oxide			
IV	*dl-dl-dl meso*		Only trimer from D(+) oxide
V	*dl-dl-ld* *ld-ld-dl*	*dl*	Synthesis[a]
VI	*dl-ld-dl meso*		

[a] Synthesis of V:



unknown V in about equal amounts. The two remaining trimers, II and VI, must have the assigned stereochemistry since these are the only other stereoisomeric trimers possible based on the two syntheses used.

Cleavage Results. In the di- and tri-butylene glycol studies (Tables XII and XIII) the polymer was cleaved in benzene solvent with a slight excess of butyllithium. The dibutylene glycols, except for III, were quite stable to these conditions. Even with a butyllithium concentration three times that initially present in the polymer cleavages, 76–100% of the dibutylene glycols were recovered. There was also little or no interconversion of isomers I, II, and IV. However, only 28% of dibutylene glycol III remained after exposure to this treatment with excess butyllithium. In addition, a small amount of dibutylene glycol IV was formed under these conditions (about 3% of the starting triglycol). Fortunately this result has no affect on the polymer cleavage data, since dibutylene glycol III is the minor component from the *trans*-oxide polymer cleavages (Table XIII). Also, dibutylene glycol III was 99% recovered when the excess butyllithium was eliminated from a control cleavage, i.e., when just enough butyllithium was used to form the lithium salt. Hence, the instability of dibutylene glycol III should have only a small effect on the polymer cleavage results.

The results on the crystalline *cis*-oxide polymer (Table XII) show quite

TABLE XII. Di- and Tributylene Glycols from Cleavage of *cis*-2,3-Epoxybutane Polymers[a]

Polymer (or glycol) cleaved			Dimer glycols			Trimer glycols			
			Conversion, %[c]		Minor dimer, % of total	Conversion, %			Minor trimers, % of total
Catalyst[b]	Polymerization temp, °C	Form	I	II		I	II	III	
Et_3Al–0.5 H_2O–0.5 acetylacetone–1.0 cyclohexanol	65	crystalline[d]	13.0	3.5	21	1.2	0.9	7.9	21
Et_3Al–0.5 H_2O–0.5 acetylacetone 1.0 cyclohexanol	65	crystallime[e]	18.2	1.3	6.9	0.7	<0.7	15.5	7
Et_3Al–0.5 H_2O–0.5 acetylacetone–1.0 cyclohexanol	65	Amorphous	4.8	13.8	26	5.8	1.4	2.9	43
i-Bu_3Al–0.5 H_2O	−78	Amorphous[f]	4.1	23	15	10.1	1.4	1.4	22
i-Bu_3Al–0.5 H_2O	−78	Amorphous[f,g]	2.7	16.7	14	6.4	1.4	0.7	25
i-Bu_3Al–0.5 H_2O	−120	Amorphous[f,g]	2.7	17.1	14	6.4	1.4	0.7	25
$Al(Oi\text{-}Pr)_3$	100	Amorphous[f]	3.5	17.4	17	5.8	2.2	1.4	38
Et_2Zn–1.0 H_2O	0	Amorphous[f]	4.3	17.2	20	5.1	2.2	1.5	42
BF_3 etherate	−78	Amorphous[f]	4.7	18.1	21	5.6	1.4	1.4	33
$FeCl_3$-PO	80	Amorphous fraction	6.1	17.6	26	5.6	1.4	1.4	33
Control cleavages									
Dibutylene glycol I[h]			91	<0.9	<1				
Dibutylene glycol II[h]			0.6	76	0.8				

[a] Conditions: 2.2 mmole C_4H_8O; 24 ml benzene; 2.7 mmole BuLi; 18 hr at 25°C plus 4 hr at 90°C.

[b] See Table I for specific catalyst preparation details.

[c] Control cleavage results given as % of initial glycol.

[d] Initial crystalline fraction.

[e] Recrystallized crystalline fraction.

[f] Prepared in ethyl chloride diluent.

[g] Total product.

[h] 8.2 mmoles BuLi in excess of active hydrogen content.

TABLE XIII. Di- and tributylene Glycols from Cleavage of *trans*-2,3-Epoxybutane Polymers[a]

				Dimer glycols					
				Conversion, %[c]		Minor glycol, % of total	Conversion of Trimer glycols, %		
Polymer (or diol) cleaved[b]	Catalyst	Polymerization temp, °C	Diluent	III	IV		IV	V	VI
From racemic oxide	i-Bu_3Al–0.5 H_2O	−78	*n*-Heptane	2.8	26	10.0	8.0	7.9	2.3
		−30	CH_2Cl_2	3.0	29x	9.5	8.7	7.0	2.3
		−30	CH_2Cl_2[d]	2.0	13.5	12.9	7.7	5.6	0.6
		−30	CH_2Cl_2[e]	2.4	19.5	14	5.0	2.5	0.5
		−30	CH_2Cl_2[f]	2.7	31	8	6.9	5.6	0.8
From D+ Oxide	i-Bu_3Al–0.5 H_2O	−78	*n*-Heptane	0.13[g]	24	0.5[g]	12.5	0.3[g]	0.3[g]
Control cleavages with dibutylene glycol									
III[h]				99	Not detected	—			
III[i]				36	3.1	8			
IV[i]				0.8[g]	77	1[g]			
III[j]				28	2.4	8			
IV[j]				0.8	100	0.8[g]			

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[a] Conditions same as Table XII.

[b] All polymers are crystalline.

[c] Control cleavage results given as % of initial glycol.

[d] 1.35 mmole BuLi.

[e] Heptane-insoluble (15%) obtained on recrystallizing total product from *n*-heptane (1%, dissolved at 120°C) for 3 days at 28.9°C (did not recrystallize at 30°C); mp 100°C.

[f] Heptane-soluble (4%) after removing 96% of polymer by recrystallization from 0.1% solution in *n*-heptane for 3 days at 20–25°C.

[g] Limits of detection. This component was not detected.

[h] BuLi equivalent to active hydrogen.

[i] 1.7 mmole BuLi in excess of active hydrogen.

[j] 8.2 mmole BuLi in excess of active hydrogen.

clearly that it is the racemic diisotactic polymer. The initial crystalline fraction from one of our best catalysts for preparing the *cis*-oxide crystalline polymer, i.e., the cyclohexanol-modified chelate catalyst, yielded dibutylene glycol I as the major dimer and dibutylene glycol III as the major trimer. Even so, this crystalline polymer yields surprisingly large amounts (21%) of the minor dimers and trimer diols. Recrystallizing this polymer substantially reduces these minor diols to 7%. Whether the presence of these minor dimers and trimers arises from entrainment of the amorphous fraction or is due to the existence of stereoblock structures in the crystalline fraction is not known. It is probable that both explanations apply. Indeed, as previously described, the mechanical properties of the crystalline *cis*-oxide polymer vary in a manner which indicates stereoblock character (Table II).

Surprisingly the amorphous fraction obtained from the *cis*-oxide with two coordination catalysts, the cyclohexanol-modified chelate catalyst or the iron catalyst, is largely a disyndiotactic polymer (*meso*$_2$, Table X). With the catalysts which behave in an ordinary cationic manner, i.e., i-Bu_3Al–0.5 H_2O, Et_2Zn–1.0 H_2O, BF_3 etherate, and Al(Oi-Pr)$_3$, the amorphous *cis*-oxide polymer is in general even more disyndiotactic. In these cases, dibutylene glycol II and tributylene glycol I, required for the disyndiotactic structure, are as high as 86 and 78%, respectively, of the total dimers and trimers. Thus, the amorphous *cis*-oxide polymer, particularly with the i-Bu_3Al–0.5 H_2O catalyst, is about as pure a disyndiotactic polymer as our crystalline *cis*- and *trans*-oxide polymers are pure *dl*- and *meso*-diisotactic. Lowering the polymerization temperature of the *cis*-oxide polymerization to −120°C in ethyl chloride diluent with the i-Bu_3Al–0.5 H_2O catalyst did not increase the stereoregularity of the product. Raising the polymerization temperature to 100°C by using the Al(Oi-Pr)$_3$ catalyst also did not significantly alter the nature of the product. We have attempted to obtain this disyndiotactic polymer in crystalline form by low temperature crystallization but without success. Whether the disyndiotactic stereosequences are not long enough or the disyndiotactic polymer is inherently amorphous is not known. In any event, this amorphous *cis*-oxide polymer is the first example of a disyndiotactic polymer in the polyepoxide series.

The disyndiotactic *cis*-oxide polymer apparently is forming in an ordinary cationic process involving the S_N2 type, oxonium ion mechanism proposed for the *trans*-oxide [eq. (5)]. In this case we must conclude that the stereoregularity is due to polymer chain-end control, i.e., the stereochemistry of the last monomer unit (or units) added to the chain determines the configuration of the next unit added. To form the disyndiotactic polymer in this way requires that steric effects due to the last chain unit (or units) cause the epoxide in the oxonium ion to be preferentially attacked at the carbon atom with the same configuration as the carbon atoms in the last chain unit. The resultant polymerization is of the head-to-head, tail-to-tail type. The observation that coordination catalysts such as the modified chelate catalyst and the iron catalyst also give some of this disyndiotactic polymer affords another example where a coordination catalyst can function in a dual manner, i.e., in a coordination mechanism to give diisotactic polymer and in a cationic manner to give disyndiotactic polymer.

The predominance of dibutylene glycol IV in the dimer cleavage fraction from the *trans*-oxide polymer (Table XIII) clearly confirms that this polymer is the *meso*-diisotactic polymer, as indicated by our earlier work on optically active monomer. The data on the polymer from racemic *trans*-oxide indicate that it is a surprisingly impure stereoregular polymer. The dibutylene glycol III results are of necessity on the low side because of the instability of this dimer under the cleavage conditions. However, the results obtained with one-half the usual butyllithium level, i.e., 12.9% III, are probably close to the correct value, and thus the *trans*-oxide polymer gives about 15% of the minor diol.

The trimer diol results further confirm that the racemic *trans*-oxide polymer is a rather impure stereoregular polymer. Thus, trimer V was found at only a slightly lower level than the major and expected trimer IV. This result indicates that the polymer is a stereoblock type having rather short blocks, i.e., growth switches from one enantiomorph to the other frequently during chain propagation. The presence of appreciable amounts of trimer VI is also in accord with this conclusion. Trimer VI represents the extreme case where the block length is only one monomer unit. There does not appear to be any reason to doubt these data. Similar results were obtained with a carefully recrystallized, less soluble fraction (15% of total) as well as a more soluble fraction (4%) from this polymer. The less soluble fraction had proportionately somewhat less of trimer V and thus probably longer block lengths. Unfortunately we did not have pure trimer diols V and VI to check their stability to cleavage. Actually any relative instability of trimers V and VI would add support to our conclusions. It also appears unlikely from our control cleavage studies that there would be sufficient interconversion of these isomers to influence our conclusions greatly.

The results on the cleavage of the polymer from the optically active *trans*-oxide (Table XIII) certainly indicate the general reliability of our cleavage data. Thus, as one would expect, we obtained only one dimer diol (IV) and only one trimer diol (IV); the other dimer and none of the other trimers were detected. This results shows that dibutylene glycol IV and tributylene glycol IV are reasonably stable to cleavage and do not yield any interfering products.

In view of the evident stereoblock nature of the crystalline *trans*-oxide polymer, it is surprising that this polymer has such good physical properties (about like low-density polyethylene) and that it crystallizes quite readily from the melt (Table II).

TABLE XIV
Dipropylene Glycols from the Cleavage of Poly(propylene Oxides)[a]

Polymer (or glycol) cleaved			Conversion of dipropylene glycol %[b]				
					Diprimary		
Catalyst	Polymerization temp, °C	Fraction	Mixed	Disec.	I	II	Disec. + diprimary, % of total
Et_3Al–0.5 H_2O–0.5 acetylacetone[c]		Total	8.2	0.8	0.6	09	22
Et_3Al–0.5 H_2O–0.5 acetyl acetone[c]		Crystalline	8.2	0.2	0.2	0.2[d]	7
$FeCl_3$–PO[e] crystalline	80	Crystalline	10.4	0.1	0.05	0.05[d]	2
$FeCl_3$–PO[e] amorphous	80	Amorphous	10.8	1.7	1.7	1.7	32
Et_2Zn–0.9 H_2O[f]	30	Total	8.9	0.1	0.1	0.1[d]	3
Dipropylene glycol control cleavages							
50:50 mixed:disec.[g]			24.4	60.5	Trace	—	
50:50 mixed:diprimary I[g]			17.1	2.2	44	—	
50:50 mixed:diprimary[g]			41	0	4.0	29	
50:50 mixed:disec.[h]			74	94	1.4	1.4	
50:50 mixed:diprimary[h]			76	1.4	60	1.4	
50:50 mixed:diprimary[h]			86	1.4	1.4	100	

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[a] Conditions: 2.7 mmole C_3H_6O; 8 ml benzene; 1.5 mmole BuLi; 18 hr at 25°C plus 4 hr at 90°C.

[b] Control cleavage results given as per cent of initial concentration of mixed glycol.

[c] Propylene oxide (10 g) polymerized in 96 ml n-heptane for 19 hr at 50°C with 2 mmole catalyst (Et_3Al basis). Total polymer [100% conversion, η_{inh} (0.1% benzene, 25°C) 8.8] isolated and recrystallized from acetone. Much of the −20°C crystalline fraction dissolved in acetone at 25°C. The 25°C acetone-insoluble was 1.5%. The 25°C acetone-soluble crystalline fraction, used for cleavage, was recovered and purified by two additional recrystallizations from acetone at −20°C to give 9.4% of a snappy strong rubber, η_{inh} 5.8, mp 57°C.

[d] Assumed value since not measured.

[e] Catalyst prepared as described by Price and Osgan,[9] used as a $1.2M$ ($FeCl_3$ basis) dispersion in diethyl ether. Propylene oxide (10 g) polymerized in bulk with 1.2 mmole $FeCl_3$ for 115 hr at 80°C. Total polymer, [73% conversion, η_{inh} (0.1% benzene, 25°C) 0.6] isolated as described in Experimental for *cis*-oxide with chelate catalyst, was separated by recrystallization from a 1% solution in acetone at −20°C. The crystalline fraction was washed with room temperature acetone and dried. The acetone-soluble, amorphous fraction was recovered by evaporation of the acetone and drying.

[f] Catalyst prepared by diluting $1.5M$ Et_2Zn in *n*-heptane to $0.5M$ with ether, adding water with agitation at 0°C, and then agitating for 20 hr at 30°C. Propylene oxide (10 g) polymerized in 42 ml *n*-heptane with 4 mmole catalyst (Et_2Zn basis) for 19 hr at 30°C. The total polymer [100% conversion, η_{inh} 10.7] isolated as described in footnote e contained 4% crystalline fraction.

[g] 1.5 mmole BuLi in excess of active hydrogen.

[h] BuLi equivalent to active hydrogen.

Mechanism Studies Based on Poly(propylene oxide)

General. Having learned a great deal from our dimer studies on the 2,3-epoxybutane polymers, we applied this same cleavage technique to poly(propylene oxide). This polymer is, of course, quite different from the 2,3-epoxybutane polymers, since it offers the possibility of structural variations rather than only stereochemical variations. Head-to-tail and head-to-head polymerizations yield structural variations which cannot exist in the 2,3-epoxybutane series. Table VII shows the structures of the three possible dipropylene glycols: the mixed primary-secondary glycol from head-to-tail polymerization, and disecondary glycol from head-to-head polymerization, and the diprimary glycol from tail-to-tail polymerization. Each of these structural variations exists in two diastereoisomeric forms. These structural isomers were obtained by carefully fractionating a commercial sample of dipropylene glycol. The two diastereoisomeric forms of the diprimary isomer were also obtained in this work.

Cleavage Results. Our cleavage studies (Table XIV) were carried out in benzene with about a stoichiometric amount of butyllithium for dimer formation. Competitive cleavages of the known mixed dipropylene glycol in combination with each of the other glycols, that is, with the disecondary and with both of the diprimarys, were run to be certain of our conclusions. With excess BuLi equivalent to that used at the start of the polymer cleavages, the disecondary and diprimary I glycols are about 2-fold more stable, and the diprimary II glycol is 30% less stable than the mixed glycol. However, when the excess BuLi was eliminated, the stability of the lithium salts of these glycols were very similar, being within 12 to 27% of one another. The actual situation during the polymer cleavages would be intermediate between these conditions. Thus, there may be some tendency for the disecondary and diprimary isomers to be increased in amount, probably not in excess of 50%, relative to the mixed glycol, over the actual amount of the abnormal precursor head-head and tail-tail units in the orginal polymer. This effect is probably even smaller, since the glycol concentrations during polymer cleavage are 6-to-10-fold lower than those used in our control experiments. In support of this conclusion, is the fact that the total amount of dipropylene glycols found in the polymer cleavages, 9–16%, is not far from the theoretical maximum of 13.9% based on a random cleavage reaction. Also, no deleterious conversion of one dipropylene glycol into another was observed. Thus, our cleavage results should be reliable on a comparative basis and probably close on an absolute basis.

The results show that crystalline poly(propylene oxide) from either our triethylaluminum–water–acetylacetone catalyst or the iron catalyst is largely the expected head-to-tail polymer. The iron catalyst product is the purer, as expected, since this catalyst generally gives the highest melting crystalline poly(propylene oxide). Also the crystalline polymer examined from the chelate catalyst was a less crystalline fraction which was soluble in acetone at room temperature and which had rubbery properties typical of a stereoblock polymer. Surprisingly, the total largely amorphous product from our chelate catalyst gives a substantial amount of head-to-head, tail-to-tail polymerization, i.e., ca. 22%. The amorphous fraction from the iron catalyst gives the largest amount of head-to-head, tail-to-tail polymerization, 32%. On the other hand, the total polymer from the diethylzinc–water catalyst, which is largely amorphous, showed only 3% head-to-head, tail-to-tail polymerization. The large amounts of head-to-head type polymerization observed could conceivably be due to a minor fraction of low molecular weight polymer formed by an ordinary cationic mechanism.* This possibility cannot be completely excluded with the iron catalyst, except to note that this catalyst appears to be only a weak cationic catalyst with the 2,3-epoxybutanes and propylene oxide does not polymerize as well cationically as do the 2,3-epoxybutanes. On the other hand, with the chelate catalyst, this possibility does not appear at all likely since the poly(propylene oxide) formed from this catalyst is all of very high molecular weight and thus typical of a coordination catalyst.

Our results are in general accord with Price's recently published data obtained by the ozone cleavage method followed by reduction to obtain the dipropylene glycol fragments.[60] One significant difference, however, is that Price's polymer prepared with the diethylzinc–water catalyst shows a large amount of head-to-head polymerization. This difference, of course, could be due to different methods of preparing this catalyst. Since the catalyst is heterogeneous, the method of preparing it should be quite important in obtaining the proper species.

CONCLUSIONS

Our studies on epoxide polymerization have yielded technically important catalysts and polymers. In addition, we have found a new method of cleaving polyethers with Group IA organometallics to monomer, dimer, trimer, and higher glycol fragments which have the same stereochemistry and structure as the original polyether. This work has enabled us to establish unequivocally the stereochemistry of the 2,3-epoxybutane polymers as well as to show that the amorphous fraction from propylene oxide polymerization with a coordination catalyst contains substantial head-to-head and tail-to-tail polymerization along with the expected head-to-tail polymerization.

As a direct result of our work, we now have a much better understanding of the mechanism of epoxide polymerization. It is now evident that epox-

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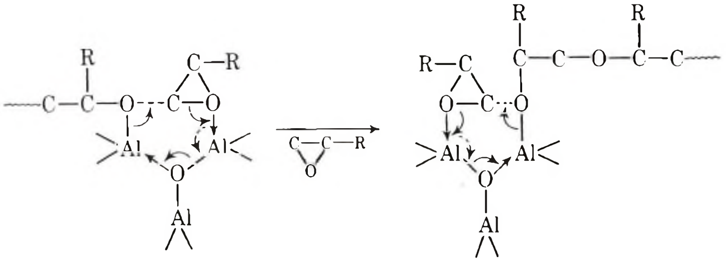
* This possibility was suggested by Dr. R. O. Colclough, University of Manchester, in private discussion.

ides polymerize with inversion of configuration of the ring-opening carbon atom. This conclusion is true for both monosubstituted and symmetrically substituted diepoxides and applies to all presently known mechanisms of polymerization, i.e., cationic, anionic and coordination. This finding has important mechanistic implications for coordination type polymerization.

It is now clear that coordination polymerization cannot propagate through a four-membered-ring intermediate containing a single metal atom, as previously postulated,[9] since such an intermediate cannot accommodate the essentially linear, three-centered transition state necessary for inversion at carbon. In any event, the catalysis mechanism must be formulated to provide for inversion of configuration of the ring-opening carbon atom through a rearward attack on the epoxide. If propagation involves making and breaking metal–oxygen bonds, as commonly postulated for coordination, the catalytic species must contain at least two and probably more than two metal atoms. A simple mechanism that fits these requirements, based on two metal atoms, is shown in [eq. (10)]. This is essentially the mechanism the author presented in 1960 for the coordination polymerization of monosubstituted epoxides,[3] except that we have now up-dated it to include the necessity of a rearward attack on the epoxide. In this mechanism the coordination bonds in the catalyst structure are needed to move the growing polymer chain from one metal to an adjacent one without altering the valence of the metal. Although two four-coordinate aluminum atoms are shown in eq. (10), more than two aluminum atoms and/or five or six coordinate aluminum may be required to fit all of the experimental facts. Thus, more than two aluminum atoms may be needed to facilitate sterically a rearward attack on the epoxide. The fifth or sixth coordinate positions of aluminum may be needed, at least under some conditions, since effective catalysts are obtained when all of the fourth coordinate positions of aluminum are occupied by a chelating agent such as acetylacetone. The mechanism of eq. (10) can readily be written to incorporate these possible requirements. Also this mechanism is shown for aluminum, but could apply to any of the coordination metal catalysts. Recently, Price[60] has also presented a similar but less detailed mechanism.



(10)

One important feature of the coordination polymerization mechanism of eq. (10), as it relates to propylene oxide and monosubstituted epoxides in general, is that propagation must occur largely by rearward displacement at the primary carbon atom of the epoxide rather than by the front-side displacement on its asymmetric carbon atom as previously suggested.[9] This conclusion is required to explain the retention of configuration of the asymmetric carbon of *l*-propylene oxide observed by Price and Osgan[9] in the coordination polymerization of this monomer to crystalline polymer. Such attack on the primary carbon of an epoxide is in accord with the anionic aspects of coordination polymerization, i.e., attack of the negative chain end on the epoxide.

On the other hand, the amorphous, atactic fraction from a coordination polymerization of propylene oxide shows that a substantial amount of head-to-head, tail-to-tail polymerization occurs along with the normal head-to-tail type. Tail-to-tail polymerization occurs when the preferred primary carbon attack on propylene oxide is followed immediately by secondary carbon attack on the propylene oxide, or vice versa for head-to-head polymerization. This result now explains the important anomaly which Price observed earlier in his work with the iron catalyst on optically active propylene oxide, that is, the formation of largely racemized amorphous polymer. It is now clear that propagation can occur with coordination catalysts by attack at the asymmetric secondary carbon atom of propylene oxide as well as at the primary carbon atom. Such attack at the secondary carbon gives inversion of configuration of this asymmetric carbon atom and thus the reacemization observed. Ring opening at the secondary carbon of an epoxide is readily accomplished with coordination catalysts as shown by our polymerization studies of *cis*-2,3-epoxybutane where ring opening must occur by attack on a secondary carbon atom. Apparently, it takes a very sterically hindered site in a coordination catalyst to yield solely head-to-tail polymerization of propylene oxide or, in other words, propagation solely by attack on primary carbon. Indeed, a solid surface may be the best way of providing the required steric hindrance for head-to-tail polymerization, as our work with the $Et_2Zn–H_2O$ catalyst suggests.

The occurrence of both primary and secondary carbon attack with a coordination catalyst is also in accord with the general mechanism for a coordination polymerization. Thus, the process which activates the epoxide for insertion in the polymer chain, that is, coordination of the epoxide with a Lewis acid center, is essentially cationic in nature. It is well known that the ordinary cationic ring opening of propylene oxide occurs at primary carbon and secondary carbon with about equal ease.[61]

Because of the dual cationic and anionic features of the coordination propagation mechanism, it appears best not to label it specifically as cationic or anionic, but rather just as a coordination mechanism.

Polymerization studies on the *cis*- and *trans*-2,3-epoxybutanes have been very useful in revealing mechanism aspects of epoxide polymerizations. The *cis*- and *trans*-2,3-epoxybutanes are very readily polymerized and favorably copolymerized by ordinary cationic catalysts. On the other hand, a coordination catalyst such as our chelate type polymerizes the *cis*-oxide to crystalline polymer but does not readily polymerize the *trans*-oxide and greatly favors the *cis*-oxide in a copolymerization of the *cis*- and *trans*-oxides. These differences in behavior between cationic and coordination catalysts with the 2,3-epoxybutanes have enabled us to show that coordination catalysts can often polymerize by two different mechanisms, i.e., coordination and cationic. The prevailing mechanism in any particular case depends, in part, on the relative ease with which the epoxide used polymerizes in a cationic manner as compared to a coordination manner. The *trans*-2,3-epoxybutane is an unusual case, since it has a strong tendency to polymerize in a cationic manner and only a slight tendency, due to steric factors, to polymerize in a coordination manner. Thus, *trans*-2,3-epoxybutane polymerizations provide a measure of whether a coordination or other catalyst can also behave as a cationic catalyst.

With coordination catalysts, it appears quite certain that chain propagation occurs on metal sites and that stereoregularity and copolymerization behavior are controlled by steric hindrance inherent in those metal sites, i.e., so called catalyst site control. Since stereoblock polymer formation appears to occur with coordination catalysts for both *cis*-oxide and propylene oxide polymerizations, we propose that the growing site in coordination polymerization can readily change in steric hindrance during chain propagation to give either more or less stereoregularity. The polymerization mechanism proposed [eq. (10)] in which the growing chain alternates between two metal sites joined to one another by a coordinating oxygen atom provides a simple way in which this can be accomplished. Thus, such a metal coordination complex can be very easily altered or rearranged during chain propagation. For example, the metal site which is coordinated to the metal atom with the polymer chain attached could be displaced by an epoxide molecule to stop chain growth. Subsequently, a different but favorable metal-oxygen grouping could recoordinate at this site and enable the polymerization to continue by the mechanism proposed but now at an overall site with different steric hindrance.

Studies on the *cis*- and *trans*-2,3-epoxybutanes with cationic catalysts where the mechanism involves a propagating oxonium ion [eq. (5)] indicate that methods other than steric hindrance at a catalyst site can control the stereoregularity of epoxide polymerizations. Thus, the racemic *trans*-oxide gives stereoregular polymerization to diisotactic polymer. The stereoregularity of this polymerization appears to be due solely to a difference in steric hindrance between the two enantiomorphs, i.e., it is more favorable sterically to add the same enantiomorph than the opposite one and it does not require a favorable steric site in the catalyst. The latter conclusion is supported by the finding that stereoregularity is independent of the catalyst used and that the stereoregular product is obtained in quantitative yield.

With the *meso cis*-oxide, cationic catalysts give disyndiotactic polymer. Here too, the stereoregularity is independent of the cationic catalysts used. In this situation, we propose that steric factors inherent in the last unit of the growing polymer chain cause the next unit added to have an opposite steric configuration. This proposal is a case of polymer chain-end control. Recently Price[62] proposed polymer chain-end control in the base-catalyzed polymerization of phenyl glycidyl ether to isotactic polymer and of *tert*-butylethylene oxide to syndiotactic polymer.

Our polymerization work with phenyl glycidyl ether with alkyl-aluminum–water catalysis is of interest since we obtained nearly quantitative yields of isotactic polymer. We presume that this is a case of catalyst site control and is an example in which the alkylaluminum–water catalyst is operating largely by a coordination mechanism rather than by a cationic mechanism, particularly since these favorable results were obtained in ether diluent. Saegusa[63] has also recently presented evidence that alkylaluminum–water catalysts polymerize epichlorohydrin by both cationic and coordination mechanisms. Such high yields of isotactic polymer in the coordination polymerization of a monosubstituted epoxide as a phenyl glycidyl ether are unusual, since propylene oxide, with the same catalyst or the more hindered chelate catalyst, gives relatively small amounts (10–20%) of isotactic polymer. This greater stereoregularity with phenyl glycidyl ether may be due to the greater steric hindrance caused by the bulkier side chain and/or due to the coordination of the ether side chain with the catalyst to provide a more hindered site as recently suggested by Price [62] for the base-catalyzed polymerization of this monomer.

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Polymerization and Copolymerization of Some Epoxides by Potassium *tert*-Butoxide in DMSO*

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Synopsis

Copolymerization of tritiated PGE with analogs and with propylene oxide by potassium *tert*-butoxide in DMSO shows that this anionic polymerization is favored by electron-withdrawing groups. The homopolymerization of PGE and its *p*-chloro and *p*-methoxy analogs gives polymer with molecular weight limited by chain transfer. For PGE, where this limit is about 7000, some of the polymer is insoluble, crystalline isotactic material.

INTRODUCTION

Since early systems for base-catalyzed polymerization of epoxides were at least partially heterogeneous,[1,2] studies of copolymerization would be complicated by this fact. Since the system potassium *tert*-butoxide in dimethyl sulfoxide (DMSO) is homogeneous and an active system for epoxide polymerization,[3] we now wish to report some studies of copolymerization in this medium. Since the monomers include phenyl glycidyl ethers (PGE), we have also reported on their homopolymerization in this medium.

EXPERIMENTAL

The monomers, including tritiated PGE, were prepared as before.[4] Sublimed potassium *tert*-butoxide (Alfa Inorganic Chemicals, Inc.) was dissolved in purified DMSO ($0.2M$) and stored in small sealed test tubes. Resublimation of the material did not change its properties as a catalyst.

The DMSO (Matheson, Coleman and Bell) was refluxed over calcium oxide powder[5] for about 8 hr under vacuum (8–9 mm Hg) at 65–70°C and then distilled through a 0.5 × 20 in column packed with glass helices. The middle 70% of the distillate was used for the copolymerization experiments.

Copolymerization Procedure

The test tubes were cleaned with dichromate–sulfuric acid cleaning solu-

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tion and water, dried overnight at 110–120°C, thoroughly flushed with nitrogen and stoppered with a serum stopper. After cooling, 3.6 ml of purified DMSO was introduced into the tubes through the serum stopper by means of a hypodermic syringe and the test tubes were weighed. A predetermined amount of the comonomer (M_2) was then injected into the test tubes, and the test tubes were weighed to give the exact amount of the comonomer. In the same way, tritiated phenyl glycidyl ether (M_1) was injected and weighed. The total amount of the two monomers was about 10 mmole. The test tube was shaken well to homogenize the ingredients. The catalyst solution (0.4 ml, 0.20*M*) was injected last, and the test tubes were placed on a test tube rack supported in a thermostatted bath to immerse the lower two-thirds of the tubes. The bath temperature was kept at 30 ± 0.1°C.

After polymerization for 10–20 min (5–10% conversion) the reaction mixture was poured into a 250-ml beaker containing about 200 ml of methanol. The beakers were covered with aluminum foil and kept 3–4 days until all the polymer precipitated. The methanol was decanted and the resulting polymer was dispersed again in 200 ml of methanol. After two days, the methanol was decanted and the polymer was dried under vacuum (5–10 mm Hg) at room temperature for at least 5 days. The amount of PGE in each sample was then determined by combustion and scintillation counting as before.[4]

The weight fraction of phenyl glycidyl ether in a copolymer sample was determined as the ratio of the number of disintegrations per minute per milligram of the copolymer to the number of disintegrations per minute per milligram of phenyl glycidyl ether homopolymer.

Monomer reactivity ratios (Table I) were determined by the Mayo-Lewis method[6] and the Fineman-Ross method.[7]

TABLE I
Monomer Reactivity Ratios
M_1:PGE

M_2	r_1	r_2	r_1r_2
p-Cl-PGE	0.65 ± 0.05	1.45 ± 0.1	0.94
m-CH_3O-PGE	0.90 ± 0.05	1.05 ± 0.15	0.94
p-CH_3-PGE	1.08 ± 0.05	0.92 ± 0.1	0.99
p-CH_3O-PGE	1.19 ± 0.02	0.85 ± 0.05	1.01
PO	7 ± 1	0.2 ± 0.2	—

The products r_1 r_2 are, as in many other ionic copolymerizations, close to unity.

Homopolymerization of Phenyl Glycidyl Ether

The method of polymerization was essentially the same as for the copolymerizations. At the end of the reaction time, the tubes were opened and the contents were poured into a beaker containing 600 ml of methanol and a small amount of hydrogen chloride sufficient to destroy the catalyst. After 2–3 days, when all the methanol-insoluble polymer had precipitated, the methanol was decanted and fresh methanol was added. After three more days, the polymer was collected on a glass filter (fine), washed with methanol, and finally dried under vacuum at room temperature for 7 days.

Fractionation of Polymers

About 500 mg of the polymer was dispersed in 40 ml of acetone at room temperature (24–28°C) for 1 day (20–24 hr) with occasional shaking, and then the acetone-insoluble polymer was collected on a glass filter (fine) and dried under vacuum at room temperature.

Determination of Intrinsic Viscosity

An Ubbelohde-type dilution viscometer was used. An initial polymer solution (about 1.6 g/100 ml) was prepared in a 25-ml volumetric flask at 30°C. Benzene was used as solvent. A 10-ml portion of this solution was used for the first viscosity measurement. Then 5 ml of solvent (at 30°C) was added into the viscometer to get a slightly diluted solution for which the second viscosity measurement was done. In the same way, four η_{sp}/c values were obtained at decreasing concentrations on each polymer. The intrinsic viscosity was determined by extrapolating the straight line of the η_{sp}/c versus c plot to $c = 0$.

TABLE II
Effect of Catalyst Concentration on Molecular Weight
in Polymerization of 5*M* PGE in DMSO at Room Temperature for 4 Days

Catalyst, %	Polymer, % Soluble	Polymer, % Insoluble[a]	$[\eta]$[b]	Molecular weight[c]
5	79	9	0.031	1600
5	88	—	—	2050 (1200)
2.5	95	—	—	3320 (1500)
1	85	11	0.054	6900[d]
1	98	—	—	4600 (1800)
0.9	88	3	0.072	7500
0.8	90	3	0.078	7650
0.75	98	—	—	6500 (2200)
0.7	93	1	0.067	7350
0.6	91	1	0.062	7350
0.5	None	None	—	—

[a] These polymers had mp. 120°C and x-ray patterns essentially identical to isotactic poly-PGE.[8]

[b] Of benzene-soluble fraction.

[c] By Mechrolab vapor osmometer. The values in parentheses are those calculated from mercuric acetate titration for unsaturation, assuming one double bond per molecule.

[d] ANAL. Calcd. for $C_9H_{10}O_2$: C, 71.98%; H, 6.71%. Found: C, 71.56%; H, 6.51%.

Melting Points

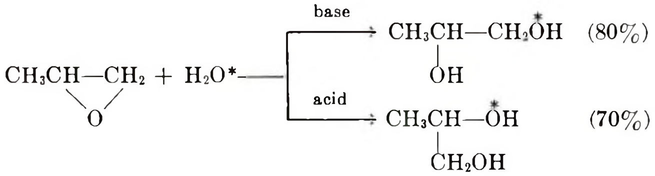
Polymer melting points were determined in a Hoover capillary melting point apparatus.

Other homopolymerization data relating molecular weight to polymerization conditions are summarized in Table II.

RESULTS AND DISCUSSION

The copolymerization data for phenyl glycidyl ether (PGE) with analogs and with propylene oxide (PO), as summarized in Table I, fit well with expectations for an anionic polymerization since electron withdrawal favors polymerization. Thus the inductive effect of the phenoxy group in PGE makes it seven times more reactive than PO. The electron-withdrawing *p*-Cl ($\sigma = 0.23$) and *m*-MeO ($\sigma = 0.12$) groups enhance the reactivity of PGE, whereas the electron-donor groups, *p*-MeO ($\sigma = -0.27$) and *p*-methyl ($\sigma = -0.17$) retard reactivity. These results are just the reverse of those observed for the Lewis acid catalyst, triethylaluminum–water.[4]

The possibility of cationic propagation from the coordination-type catalysts is strongly supported also by the observation of substantial amounts of head-to-head, tail-to-tail units in the amorphous polymer produced from PO by such systems.[9] Long[10] has earlier reported data on the reversal of the mode of addition of water to PO and isobutylene oxide on changing from basic to acidic catalysis.



(1)

TABLE III
Polymerizations of Substituted PGE[a]

Substituent	Catalyst, %	Yield, %	Molecular weight[b]
p-Cl	10	99	1940
	5	99	2150[c]
	2.5	15	1800
	1.25	None	—
p-MeO	5	92	2230
	2.5	98	2390[d]
	1.0	93	2450
	0.75	15	1700
	0.5	5	1800

[a] $0.02M$ monomer, 4 ml of DMSO, 5 days at room temperature.

[b] By Mechrolab vapor osmometer.

[c] ANAL. Calcd for $C_9H_9O_2Cl$: C, 58.55%; H, 4.91%; Cl, 19.20%. Found: C, 58.54%; H, 5.07%; Cl, 19.16%.

[d] ANAL. Calcd for $C_{10}H_{12}O_3$: C, 66.65%; H, 6.71%. Found: C, 66.20%; H, 6.58%.

TABLE IV

Effect of Potassium *tert*-Butoxide Concentration on Polymerization of PGE[a]

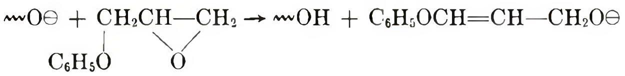
Monomer, mmole	Catalyst, mmole	Polymer, %	Solubility			$[\eta]^{30°C}_{benzene}$	Mp of acetone-insoluble polymer, °C
			Acetone-soluble, %	Benzene-soluble, %	Benzene-insoluble, %		
51.46	2.50	86.5	87.7	3.7	8.6	—	—
50.25	1.00	—	90.6	4.4	5.1	—	—
50.60	0.50	95.2	93.7	6.3	~0	0.050	120–125
50.91	0.25	96.1	95.5	4.5	0	0.054	—
51.14	0.13	40.6	98.9	1.1	0	0.052	120–123
52.14	0.50[b]	96.0	94.8	5.2	0	0.051	121–124
50.42	0.25[b]	94.1	96.0	4.0	0	0.056	—

[a] 20.0 ml solvent (DMSO), 6 days at polymerization temperature, 30°C.

[b] Unpurified catalyst was used; in other experiments the potassium *tert*-butoxide had been resublimed.

The activating effect of methyl and deactivating effect of chloromethyl on acid-catalyzed polymerization[4] is also parallel to the effect of these groups on acid-catalyzed hydrolysis.[10]

The molecular weight data for homopolymers (Tables II and III) support the view that for PGE and its analogs, as for PO,[3] the molecular weight is limited by a chain-transfer process. Titration data for unsaturation (see Table II) support the view that, as for PO, this leads to incorporation of a double bond. The process analogous to that for PO would be as shown in eq. (2).



$$\sim\!\sim O^{\ominus} + \underset{\substack{|\\ C_6H_5O}}{CH_2}\underbrace{CH-CH_2}_{O} \rightarrow \sim\!\sim OH + C_6H_5OCH{=}CH-CH_2O^{\ominus} \qquad (2)$$

The formation of isotactic polymer in the base-catalyzed polymerizations is favored by conditions which would favor ion pair association, as contrasted to "free" alkoxide ions. Thus the increase in the total potassium alkoxide concentration or the decrease in the polar DMSO solvent increases the crystalline, insoluble fraction of polymer obtained (Tables II, IV, and V). These observations are concordant with the mechanism for stereoselectivity in base polymerization of epoxides recently proposed.[11] There are also other recent reports of isotactic poly-PGE from polymerizations using *tert*-amines as catalysts.[12]

TABLE V
Effect of Monomer-Solvent Ratio on PGE Polymerization[a]

Monomer, mmole	DMSO, ml	Polymer, %	Acetone-soluble, %	Benzene-soluble, %
51.3	1.25	95.6	75.8	24.2
51.8	5	98.6	85.4	14.6
50.8	20	95.9	94.2	5.8
26.2	20	92.1	90.3	—

[a] 0.50 mmole *tert*-BuOK, 6 days at polymerization temperature, 30°C.

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Copolymerization of Some Epoxides by Coordination-Type Catalysts

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Synopsis

Copolymerizations of tritiated phenyl glycidyl ether with *p*- and *m*-methoxy, *p*-methyl, and *p*-chloro analogs, as well as with propylene oxide and epichlorohydrin are reported. The relative reactivities indicate greater Lewis acid character for triethylaluminum–water than for diethyl-zinc–water or ferric chloride–propylene oxide catalyst systems. The copolymerization of the PGE analogs is promoted by electron-donor groups and retarded by electron-withdrawing groups.

INTRODUCTION

In order to add to information on relative reactivities of epoxide monomers to polymerization under the influence of various catalyst systems, we wish to report copolymerization of phenyl glycidyl ether catalyzed by iron, zinc, and aluminum catalyst systems. Another paper will report on similar polymerization systems catalyzed by base in DMSO solution.[1]

EXPERIMENTAL

Preparation of Tritiated Phenyl Glycidyl Ether

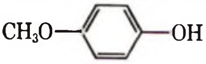
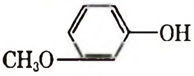
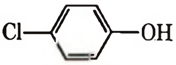
In a 500-ml round-bottomed flask equipped with a reflux condenser and magnetic stirrer was placed 1 g of ^3H_2O (obtained from New England Nuclear Corporation; specific activity, 100 mCi/g) and 99 ml of H_2O. Phenol (70.5 g, 0.75 mole) was added together with 14 g of sodium hydroxide and the mixture refluxed, with stirring, for 31 hr. Heating was then discontinued, and an additional 16 g of sodium hydroxide added to bring the total amount of sodium hydroxide to 0.75 mole. The flask was allowed to cool to room temperature and 78.6 g (0.1 molar excess) of epichlorohydrin was added all at once. Stirring at room temperature was continued overnight, and the reaction mixture then extracted with ether. The ether solution was washed with cold 1% sodium hydroxide until it gave a negative test for phenol with phosphomolybdic acid and ammonium hydroxide (a positive test for phenol consisted of the formation of a heavy, dark-blue precipitate upon addition of ammonium hydroxide to a mixture of two drops of the ether solution and one drop of a saturated solution of phosphomolybdic acid). The phenol-free ether solution was washed well with water and dried over anhydrous magnesium sulfate. Distillation under reduced pressure afforded 48.3 g of colorless, radioactive phenyl glycidyl ether, bp 117°C/10 mm Hg.

The radioactivity of the phenyl glycidyl ether was found to be sufficiently high (5915 disintegrations per minute per 2×10^{-5} ml of monomer) so that, for the purposes of this research, a dilution of 1:100 was made with pure, unlabeled phenyl glycidyl ether (Matheson, Coleman and Bell, redistilled). The resulting "diluted" monomer was used in the copolymerization study.

Preparation of Substituted Phenyl Glycidyl Ethers

The glycidyl ethers were readily prepared by dissolving 0.5 mole of the appropriate phenol in 250 ml of 2*N* sodium hydroxide solution and adding 0.6 mole of epichlorohydrin. The work-up procedure was the same as has already been described for the labeled, unsubstituted phenyl glycidyl ether.[2] Results are summarized in Table I.

TABLE I

Phenol	Yield, %	Boiling point, °C/mm Hg
	66	110/1.3 (mp 46–47°)
	53	163/17
	58	155/13
	61	95/2.5

Propylene oxide and epichlorohydrin (Matheson, Coleman and Bell) were redistilled from calcium hydride prior to use.

Ferric chloride–propylene oxide complex catalyst was prepared as reported by Pruitt and Baggett.[5]

Polymerization Procedure

Triethylaluminum was obtained as a 1.45*M* solution in *n*-heptane from the Hercules, Inc., Wilmington, Delaware. It was found experimentally that 5 μl of water as a cocatalyst with 1 ml of the heptane solution afforded the optimum polymerization conditions (5/1 ratio of Al to H_2O). The diethylzinc was obtained from K & K Laboratories, Jamaica, New York, in the form of a 1.35*M* solution in *n*-heptane. With 5 μl of water, 300 μl of the diethylzinc solution was found to provide the most rapid polymerization (1.4/1 ratio of Zn to H_2O).

Constrictions were drawn in 15 × 125 mm Pyrex test tubes. In the cases of polymerization by the triethylaluminum–water and the diethylzinc–water catalysts, the following procedure was employed: The constricted test tubes were weighed and the tritiated phenyl glycidyl ether added. If the comonomer was nonvolatile, it also was weighed into the tubes to bring the total monomer content to 5 mmoles. The tubes were then flushed with nitrogen and covered with a rubber serum stopper. Next, 5 μl of water was injected into the tubes together with the metal alkyl solution and 1 ml of toluene (distilled from calcium hydride) as a diluent. The tubes were cooled in a Dry Ice–acetone bath and sealed in the oxygen flame. In the cases where the comonomer was volatile, the polymerization tubes were flushed with nitrogen and covered after the phenyl glycidyl ether was weighed in. The 5 μl of water was added and the tubes reweighed. The volatile monomer was injected into the tubes, which were then weighed and immediately placed in the Dry Ice–acetone bath. The toluene and the metal alkyl solution was then added and the tubes sealed.

For polymerization by the ferric chloride–propylene oxide complex catalyst, two drops (about 25 mg) of the catalyst was added to the polymerization tubes containing the phenyl glycidyl ether plus nonvolatile comonomer and the tubes were flushed with nitrogen and covered. Then 1 ml of toluene was added, and the tubes were cooled and sealed. For volatile comonomers, the comonomer was injected after the tubes containing the phenyl glycidyl ether and the catalyst were flushed with nitrogen, covered and weighed. All of the tubes were placed in a constant temperature bath at 85 ± 3°C.

The tubes were opened, and their contents were washed into a beaker containing 150 ml of methanol and 0.5 ml of concentrated hydrochloric acid (necessary to destroy the catalyst). The polymers were filtered and added to fresh methanol. This step was repeated and the polymers were finally filtered, dried under vacuum at room temperature, and weighed to determine the per cent conversion.

Method of Tritium Analysis

The tritium in the copolymers was converted to ^3H_2O by utilization of the Schöniger microcombustion procedure.[6] The polymer sample was weighed onto a piece of low ash filter paper (Whatman No. 44, double-washed, thin). The paper was folded to form a packet, with a paper wick, containing the polymer sample. The packet, with the wick extended, was placed in a nichrome wire clip which was sealed into a ground glass stopper. A 500-ml Erlenmeyer flask containing 5 ml of water, delivered by a pipet, was flushed with oxygen. The tip of the filter paper wick was ignited, and the stopper immediately inserted into the Erlenmeyer flask which was then inverted to form a water seal (care was taken not to wet the filter paper). When the combustion was complete, the flask was cooled in ice water and shaken to absorb all the ^3H_2O in the H_2O. A 1-ml aliquot of the water was pipetted

TABLE II
Copolymerization Data

	System			$M_1:M_2$ ratio,	con- version,	Soften- ing	
	M_2	Catalyst	Time	mmoles	%	range, °C[a]	η[b]
A	*p*-CH_3O–PGE	$AlEt_3$–H_2O	3 hr	4:1	7.0	158–190	
			"	3:2	7.6		1.16
			"	2.5:2.5	7.4	160–200	
			"	2:3	8.0		
			"	1:4	8.1	187–220	1.19
B	*p*-CH_3O–PGE	$ZnEt_2$–H_2O	44 min	4:1	8.1	147–175	1.13
			41 "	3:2	9.0		
			23 "	2.5:2.5	6.1	134–156	
			15 "	2:3	5.6		
			29 "	1:4	6.1	150–185	1.04
C	*p*-CH_3O–PGE	$FeCl_3$–PO	92 hr	4:1	3.5	154–165	
			"	3:2	5.3		1.03
			"	2:5:2.5	6.2	149–166	
			"	2:3	7.2		
			"	1:4	8.3	176–188	1.03
D	*p*-CH_3–PGE	$AlEt_3$–H_2O	3 hr	4:1	5.2	169–202	1.22
			"	3:2	4.4		
			"	2.5:2.5	4.2	173–185	
			"	2:3	5.0		
			"	1:4	3.9	192–196	1.14
E	*p*-CH_3–PGE	$ZnEt_2$–H_2O	15 min	4:1	12.3	165–185	1.23
			"	3:2	10.1		
			"	2.5:2.5	9.7	162–180	
			"	2:3	8.7		
			"	1:4	3.4	184–193	1.16
F	*p*-CH_3–PGE	$FeCl_3$–x PO	134 hr	4:1	3.2	167–172	1.02
			"	3:2	3.5		
			"	2.5:2.4	4.5	171–179	
			"	2:3	4.7		
			"	1:4	4.6	187–195	1.05
G	*m*-CH_3O–PGE	$AlEt_3$–H_2O	5 hr	4:1	7.1	160–204	1.23
			6 hr	3:2	7.1		
			"	2.5:2.5	7.1	118–145	
			"	2:3	7.1		
			"	1:4	5.2	109–149	1.25
H	*m*-CH_3O–PGE	$ZnEt_2$–H_2O	40 min	4:1	3.7	120–158	1.13
			20 min	3:2	1.8		
			"	2.5:2.5	3.2	112–141	
			"	2:3	0.8		
			40 min	1:4	5.5	120–160	1.17
I	*m*-CH_3O–PGE	$FeCl_3$–PO	12 days	4:1	10.2	158–166	1.06
			"	3:2	10.8		
			"	2.5:2.5	9.8	117–124	
			"	2:3	6.5		
			"	1:4	8.8	100–104	1.06

(continued)

TABLE II (*continued*)

	System			M_1:M_2 ratio, mmoles	conversion, %	Softening range, °C[a]	η[b]
	M_2	Catalyst	Time				
J	*p*-Cl-PGE	$AlEt_3$–H_2O	3.3 hr	4:1	6.1	172–201	1.19
			"	3:2	5.1		
			"	2.5:2.5	5.2	176–201	
			"	2:3	4.2		
			"	1:4	4.0	174–210	1.25
K	*p*-Cl-PGE	$ZnEt_2$–H_2O	17 min	4:1	6.2	162–175	1.14
			20 min	3:2	7.6		
			"	2.5:2.5	5.9	160–175	
			265 min	2:3	4.1		
			"	1:4	4.5	153–165	1.04
L	*p*-Cl-PGE	$FeCl_3$–PO	112 hr	4:1	4.6	168–174	1.03
			"	3:2	4.7		
			"	2.5:2.5	3.5	165–176	
			"	2:3	2.2		
			"	1:4	3.4	163–172	1.03
M	*p*-CH_3O-PGE	$AlEt_3$–H_2O + 50 μl acetylacetone	117 hr	4:1	5.6	154–163	1.09
			"	3:2	5.8		
			"	2.5:2.5	6.3	154–163	
			"	2:3	6.2		
			"	1:4	7.7	176–185	1.04
N	PO	$AlEt_3$–H_2O	7 hr	4:1	4.9	170–180	1.21
			"	3:2	4.6		
			"	2.5:2.5	5.1		1.18
			8 hr	2:3	5.1		
			15 hr	1:4	5.2	165–185	
O	PO	$FeCl_3$–PO	8 days	4:1	5.0	145–172	1.05
			"	3:2	6.0		
			—	2.5:2.5	—		
			8 days	2:3	6.2	146–168	1.04
			"	1:4	4.1		
P	ECH	$AlEt_3$–H_2O	6 hr	4:1	1.2	160–183	
			"	3:2	2.2		
			"	2.5:2.5	2.6		1.14
			"	2:3	4.7	155–210	
			"	1:4	2.4		
Q	ECH	$FeCl_3$–PO	21 days	4:1	9.0	117–161	1.05
			"	3:2	9.7		
			"	2.5:2.5	13.0		
			"	2:3	14.7		
			"	1:4	16.0	98–130	1.04

[a] PGE homopolymer, mp 196–201°C (lit.[2] mp 210°C). Determined by the capillary method.

[b] Relative viscosity (0.1% solution in *o*-dichlorobenzene at 100°C.) η of PGE homopolymer = 1.39 (lit.[2] 1.8, 0.1% solution in α-chloronaphthalene at 135°).

into a glass counting vial, and 10 ml of the scintillation counting medium was added.

The tritium counting was done on a Packard Tricarb liquid-scintillation counter, in 20 ml glass vials with polyethylene-lined screw caps as supplied by the Wheaton Glass Company, Millville, New Jersey. The scintillation counting medium was prepared in a 1-liter volumetric flask from 7 g of the primary scintillator, PPO (2,5-diphenyloxazole, scintillation grade) and 150 ml of the secondary scintillator, dimethyl POPOP [1,4-bis-2-(4-methyl-5-phenyloxazolyl)benzene, scintillation grade], obtained from the Packard Instrument Company, Inc., LaGrange, Illinois. To this was added 126 g of naphthalene (Baker reagent) and 100 ml of absolute ethanol (synthetic, not distilled from grain). The flask was filled to the mark with spectral grade dioxane (Matheson, Coleman and Bell) and was inverted to dissolve the solid materials.

The counting efficiency was determined for each set of samples run by the addition of a known volume of a standard solution of ^3H_2O and was found, in every case to be 27% ± 0.5%. Two or more samples of pure, tritiated phenyl glycidyl ether homopolymer, prepared by triethylaluminum–water catalysis, were burned with each set of samples. The per cent of phenyl glycidyl ether in each sample was calculated as a direct ratio of the number of disintegrations per minute per milligram of polymer sample compared to the number of disintegrations per minute per milligram of phenyl glycidyl ether homopolymer. Five or more 10-min counting cycles were run on each sample, and an average number of counts per minute (CPM) was calculated. By correcting for the efficiency of the counting process, the CPM were converted into disintegrations per minute (DPM). Subtracting the DPM of the blank (1 ml of distilled H_2O plus the counting medium) from the DPM of each sample and then dividing by the number of milligrams of sample combusted gave the DPM per mg of polymer.

Determination of Relative Viscosity (η)

Measurements of the relative viscosities of the copolymers were obtained by the use of an Ostwald viscometer. The solutions (0.1% in *o*-dichlorobenzene) were prepared by dissolving the polymers in boiling solvent and cooling to 100°C, the temperature at which the readings were taken.

RESULTS AND DISCUSSION

The experimental data in Table II have been converted into r_1 and r_2 values both by the Mayo[7] and the Fineman and Ross[8] methods and the values are summarized in Table III.

The greater Lewis acid character of the triethylaluminum–water catalyst[9] is supported by the copolymerization data for phenyl glycidyl ether (PGE) with propylene oxide (PO) and epichlorohydrin (ECH). The relative rate for PO is greater than PGE, while for ECH it is less than PGE. These results would be in accord with cationic character for the polymerization

TABLE III
Monomer Reactivity Ratios[a]

	AlEt$_3$–H$_2$O		ZnEt$_2$–H$_2$O		FeCl$_3$–PO	
M$_2$[b]	r_1	r_2	r_1	r_2	r_1	r_2
p-CH$_3$O–PGE	0.71 ± 0.1	1.37 ± 0.2	0.91 ± 0.1	1.75 ± 0.2	0.70 ± 0.1	1.49 ± 0.2
	0.88 ± 0.1	2.38 ± 0.2[c]				
p-CH$_3$–PGE	0.90 ± 0.1	0.90 ± 0.1	1.11 ± 0.1	0.92 ± 0.1	1.06 ± 0.1	0.98 ± 0.1
m-CH$_3$O–PGE	1.00 ± 0.2	0.98 ± 0.1	1.24 ± 0.2	0.88 ± 0.1	0.90 ± 0.2	0.60 ± 0.2
p-Cl–PGE	0.89 ± 0.1	0.60 ± 0.1	1.20 ± 0.1	0.73 ± 0.1	1.09 ± 0.1	0.68 ± 0.1
	0.87 ± 0.2	0.50 ± 0.2[d]				
PO	0.65 ± 0.1	1.52 ± 0.2	—	—	1.32 ± 0.2	0.52 ± 0.1
ECH	1.40 ± 0.1	0.66 ± 0.1[d]	—	—	1.05 ± 0.2	1.07 ± 0.1[d]

[a] M_1 = PGE.

[b] Comonomers: PGE = phenyl glycidyl ether; PO = propylene oxide; ECH = epichlorohydrin.

[c] AlEt$_3$–H$_2$O–acetylacetone.

[d] From elemental analysis.

and with the expected electron-donor character of $CH_3 > C_6H_5OCH_2 > ClCH_2$.

The results with the Pruitt-Baggett catalyst indicate it is less acidic in character and more clearly a coordination-rearrangement type[10] with some degree of anionic (S_N2) character as indicated by the reversal in order of reactivity of PO, PGE and ECH. For the substituted PGE analogs with Pruitt-Baggett and Furukawa catalysts examination of r_2 data indicate that the electron-donor groups (p-CH_3O, $\sigma = -0.27$; p-Me, $\sigma = -0.17$) favor the polymerizability, while the electron-withdrawing groups (m-OCH_3, $\sigma = 0.12$; p-Cl, $\sigma = 0.23$) retard the reactivity. This is not the order expected from simple predictions based on an anionic process and may indicate that competition among PGE analogs is dictated by the coordination process which would be cationic rather than the rearrangement step which would be anionic.

The copolymers appear to retain a high degree of isotacticity since all are relatively high melting (see Table II), although not quite as high melting as isotactic poly-PGE.[2,7-11]

With the three catalyst systems we employed, PGE failed to copolymerize with isobutylene oxide, bis(chloromethyl)oxetane and tetrahydrofuran. Only the homopolymer of PGE was isolated with the use of either triethylaluminum–water or the Pruitt-Baggett catalyst.

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Electron-Transfer Polymers. XXXVIII. Further Investigation of "Polymer Effects" with Self-Protected Polymer

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Synopsis

3-Methacrylyloxymethyl-5,7,8-trimethylchroman-6-01 (MMC) was prepared, polymerized, and copolymerized. Poly-MMC, a reduced redox polymer, is stable to air and is oxidized readily. The redox behaviors of poly-MMC and copolymers with vinyl acetate were compared with that of 3-propionyloxymethyl-5,7,8-trimethylchroman-6-ol (PMC), the model monomer. The titration curves of the polymers were flat as is usual with redox polymers, and showed higher midpoint potentials than the model monomer. One factor in this "polymer effect" was found to be adsorption of oxidized polymer on the electrode. But there seem still to be present other factors yet to be clarified.

Earlier studies with tetrasubstituted hydroquinone polymers showed them to be unstable in the presence of oxygen: they are readily oxidized to the benzoquinone forms.[1] The tetrasubstituted hydroquinone, α-tocopherol hydroquinone, has been reported similarly unstable,[2] but α-tocopherol itself is very stable because of the presence of a six-membered ether ring which engages one of the hydroquinonyl oxygens. We conceived, then, of a polymer so designed that a hydroxyl group is placed in the γ-position to the hydroquinone function.[3] This makes it possible to form a six-membered ether ring with one hydroquinone hydroxyl (Scheme I). Such a ring stabilizes the reduced form of the function. The problem solved in this way arose because, in the attempt to make the hydroquinone ring stable (except for its redox function), the available hydrogens were replaced with methyls. But this lowers the oxidation potential. The reduced form of such substituted hydroquinones becomes susceptible of attack by atmospheric oxygen, as noted.[1,4] The first model chosen was a copolymer of 3-acetoxy-6-methoxy-2,4,5-trimethyl-styrene[1] with vinyl acetate (Scheme I). After hydrolysis and oxidation, the copolymer was

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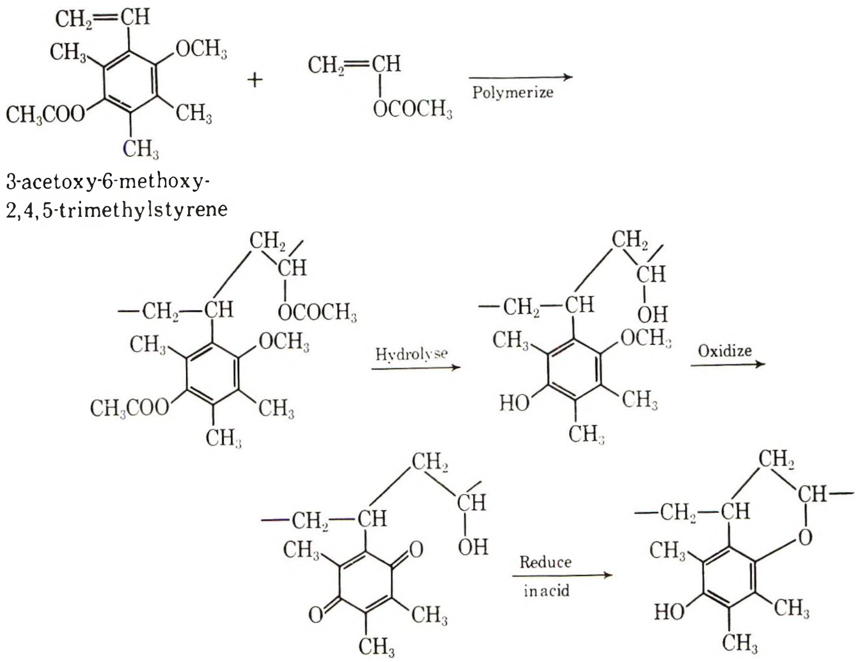
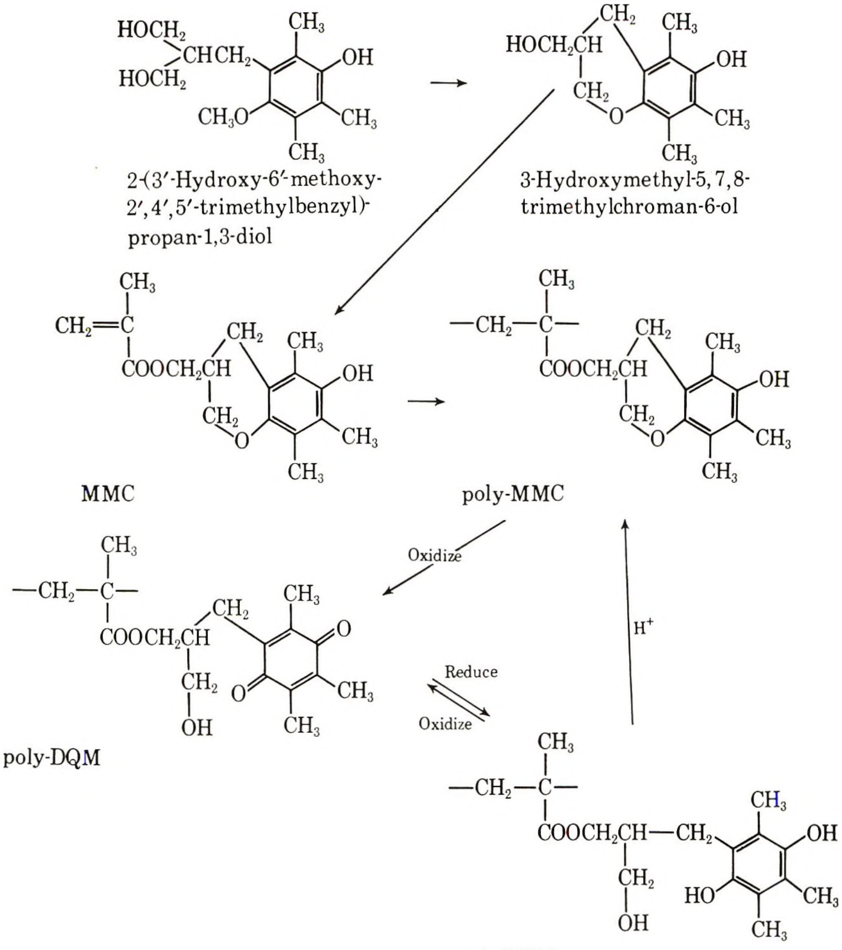


Scheme I.

reduced under acid conditions conducive to ether ring formation, but the product was found to oxidize slowly in air.

We then changed to polymer prepared from the monomer 3-methacrylyloxymethyl-5,7,8-trimethylchroman-6-ol (MMC) (Scheme II). This was prepared by an ester-exchange reaction between methyl methacrylate and 3-hydroxymethyl-5,7,8-trimethylchroman-6-ol[3] in the presence of sulfuric acid. From this so-to-speak "self-protected" hydroquinone monomer could be prepared polymers and copolymers stable to air but readily oxidized in solution. For comparison purposes, as a reference monomer, 3-propionyloxymethyl-5,7,8-trimethylchroman-6-ol (PMC) was prepared in the same way as MMC.

When a small molecule representing the repeating, metameric section of a polymer chain containing a hydroquinone group is oxidatively titrated, it yields a curve for two-electron transfer (Nernst equation). The free energy change of such a model monomer, relative to a standard reference compound, and reflected in the potential at the midpoint of the titration, can be correlated to inductive effects of substituents upon the position of the quinone–hydroquinone equilibrium.[5] Such effects disappear when the substituent is separated by five or more carbon atoms from the ring. The titration curves of polymers that consist of a linear array of such metameres are not ideal.[6] The differences between reference monomer and polymer titration curves are ascribed to polymer effects. These have been thought to be related to changes in polymer shape, e.g., coiling or uncoiling, concomitant with the change in ratio of reduced (hydrophilic, hydrogen-bonding)



Scheme II.

to oxidized (hydrophobic) groups along the chain during titration.[5,7] We report here on another factor which must be considered with respect to departures from ideality.

EXPERIMENTAL

Preparation of MMC

A mixture of 5.0 g (0.0225 mole) of 3-hydroxymethyl-5,7,8-trimethylchroman-6-ol[3] and 25.3 g (0.255 mole) of methyl methacrylate was refluxed for 2 hr in the presence of one drop of concentrated sulfuric acid and a small amount of hydroquinone. Methanol and excess methyl methacrylate were distilled out azeotropically. The remaining methyl methacrylate was evaporated *in vacuo*. The residue was dissolved in benzene, the solution washed with water, and dried over magnesium sulfate. The dried solution was concentrated by distillation of some of the benzene, and a very small amount of *n*-hexane was added. After a short while nearly all the colored impurities present had settled out. The nearly colorless supernatant was then decanted and more *n*-hexane was added. A white powder precipitated. This was recrystallized from aqueous acetonitrile. The yield was 4.55 g (69.8%) of powdery material melting at 100–101°C.

ANAL Calcd for $C_{17}H_{22}O_4$: C, 70.32%; H, 7.64%. Found: C, 70.23%; H, 7.68%.

The NMR spectrum, taken in $CDCl_3$, showed peaks at 3.37 (1), 4.43 (1) (vinyl); 5.78 (4) (two methylenes next to oxygen); 7.51 (2) (4-methylene); and 7.90 and 8.06 τ (13) (four methyls and 3-methyne). The numbers in parentheses are relative weights (intensities) of the signals.

Poly-MMC

MMC (1 g, 0.0033 mole) and 0.001 g of AIBN were sealed in an ampoule under nitrogen. Polymerization was carried out for 24 hr at 115 ± 1°C. The resulting glassy mass was dissolved in THF and poured into *n*-hexane. Upon reprecipitation, carried out twice from THF–*n*-hexane, the polymer was obtained as a white powder. Viscosity, measured at 25°C in THF, 0.49 g/100 ml, was η_{sp}/c 0.06.

ANAL. Calcd for $(C_{17}H_{22}O_4)_n$: C, 70.32%; H, 7.64%. Found: C, 70.13%; H, 7.63%.

3-Propionyloxymethyl-5,7,8-trimethylchroman-6-ol (PMC)

A mixture of 5.0 g (0.0225 mole) of 3-hydroxymethyl-5,7,8-trimethylchroman-6-ol,[3] 22.0 g of methyl propionate, and 10 ml of dry THF was refluxed in the presence of a drop of concentrated sulfuric acid for 2 hr. Methanol, THF, and methyl propionate were distilled off at normal pressure over a period of 2.5 hr. The residue was evacuated to remove all volatiles, and the resulting PMC was recrystallized from benzene–*n*-hexane. The yield was 4.4 g (70%) of white powdery material, mp 93°–4°C.

ANAL. Calcd for $C_{16}H_{22}O_4$: C,69.04%; H, 7.97%; equivalent weight, 139. Found: C, 68.97%; H, 7.95%; equivalent weight 132.

The NMR confirmed the structure in detail, the oxymethylene and 2-methylene, 5.78 (4); α-methylene of the propionyl group and 4-methylene of the chroman ring, 7.53 (4); 3-methine, and 5, 7, and 8 methyls of the chroman ring, 7.85, 7.90 (10); and the β-methyl of the propionyl group, 8.84 (3) τ in $CDCl_3$.

Poly(2-duroquinonyl-3-hydroxypropyl methacrylate) Poly-DQM

A solution of 0.114 g of poly-MMC in 100 ml of 95% aqueous THF was prepared. In this was dissolved 0.45 g of ceric ammonium nitrate, and the mixture was stirred for 2 hr at room temperature. The yellow polymer solution was poured into water and the yellow powder was collected. The yield was 0.083 g; η_{sp}/c 0.05 (at 25°C in THF, 0.50 g/100 ml.).

ANAL. Calcd for $(C_{17}H_{22}O_5)_n$: C, 66.64%; H, 7.24%. Found: C, 66.47%; H, 7.35%.

2-Duroquinonyl-3-hydroxypropyl Propionate (DQP)

To a stirred solution of 0.50 g (1.8 mmole) of PMC in 20 ml of water and 20 ml of THF was added either 0.5 g of lead tetraacetate or 1.07 g (1.95 mmole) of ceric ammonium nitrate; the reaction was carried out for 1 hr at room temperature. The mixture was extracted by ether, and the ethereal solution dried over magnesium sulfate. A quantitative amount of red oil was obtained after evaporation of the ether. It was purified on an aluminum oxide column (*n*-hexane–benzene) to give yellow oil.

ANAL. Calcd for $C_{16}H_{22}O_5$: C, 65.29%; H, 7.53%. Found: C, 65.06%; H, 7.60%.

Preparation of Vinyl Acetate and MMC Copolymer (V-12)

A mixture of 21.0 g of freshly distilled vinyl acetate and 0.60 g of MMC was stirred and refluxed under nitrogen with 0.02 g of AIBN for 18 hr. The viscous solution was poured into *n*-hexane: the copolymer precipitated as white flakes. It was dissolved in THF, reprecipitated with *n*-hexane, and dried *in vacuo*. The yield was 3.65 g, $[\eta] = 0.18$, 25°C, 100 ml of 90% acetic acid/g. Analytical data are listed in Table I.

DISCUSSION

Reduction

The infrared and ultraviolet spectra of poly-MMC are very similar to those of PMC, as shown in Table II and Figure 1. When poly-DQM was reduced in the presence of acid to poly-MMC (the ultraviolet spectrum showed no quinone), the product was found to be less stable to air than the very stable, original poly-MMC from which it has been produced by oxidation. The re-formed poly-MMC was oxidized by air very slowly, with the appearance of quinone absorption. This observation can be explained if, in the acid reduction process, a small percentage of hydroquinone groups fails to be protected by ring ether formation because of the steric requirements on ring formation present in the polymer but not exigent in the monomer. When the reduction was carried out with palladium–carbon catalyst or sodium borohydride in the absence of acid, so that the protective ring was not formed to any extent (poly-DHM), air oxidation set in as soon as the polymer solution was exposed, as was found in other cases.[1,4] The accompanying viscosity change from poly-DHM reduced with palladium–charcoal to poly-DQM during the oxidation is shown in Figure 2. The spectral change is referred to in Table II.

TABLE I
Composition of MMC Copolymers

Sample	MMC units by titration, %	Absorption coefficient, l./g cm at $\lambda_{\max}$, mμ	Elementary analysis			
			MMC units in polymer, %[a]	C, %	H, %	MMC units in polymer, %[b]
Poly-MMC	—	10.0 (293)	100	70.13	7.63	100
IV-88	40	4.5 (293)	45	63.18	7.92	51
V-12	9.3	1.2 (293)	12	57.08	7.00	8.8
Poly-DQM	—	33.7 (264)	100	65.06	7.60	100
Oxidized-V-12[c]	—	4.7 (263)	14	57.84	7.01	17

[a] Calculated from the spectrum on the basis of pure polymer = 100%.

[b] Calculated from C and H analysis.

[c] According to the viscosity ($[\eta] = 0.22$ in 90% acetic acid at 25°C, 100 ml/g) it appears that the high value of % MMC calculated from C and H of oxidized V-12 compared to that found for the original V-12 is due to the loss of low molecular weight vinyl acetate-rich moities during reprecipitation and preparation of the analytical sample.

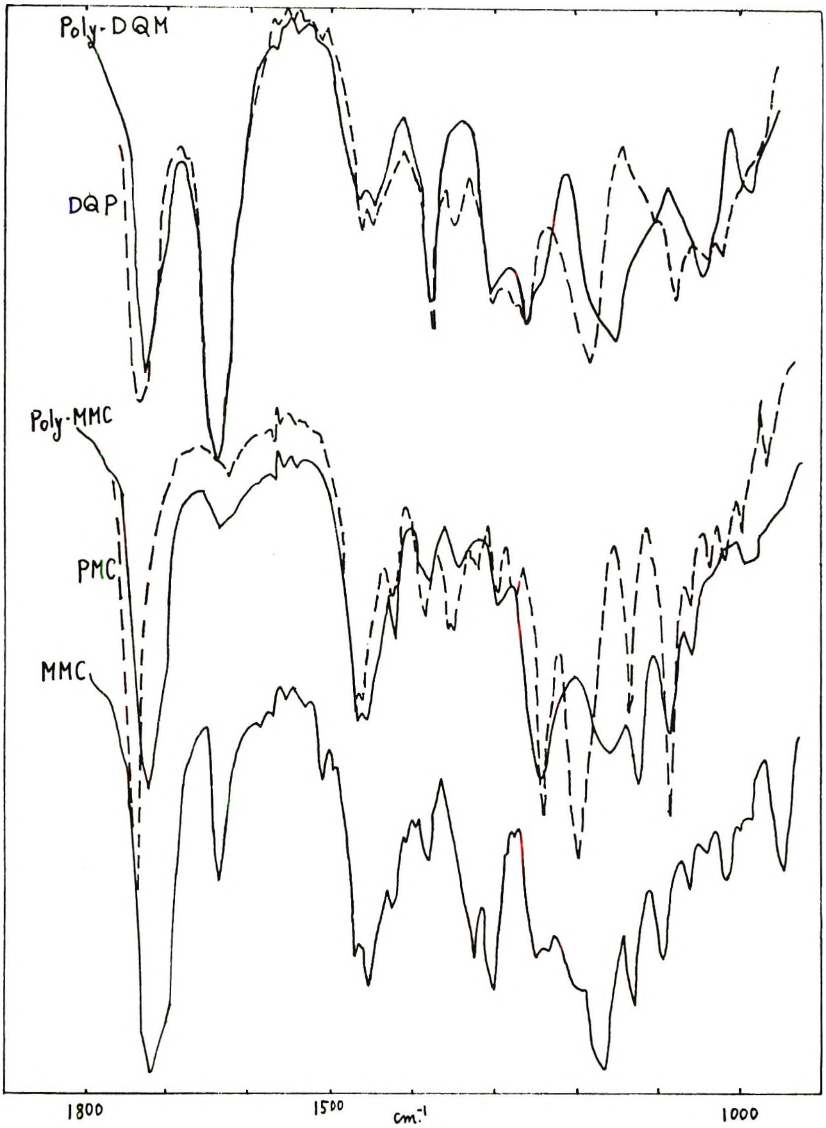


Fig. 1. Infrared spectra of MMC in KBr, PMC in KBr, poly-MMC film, DQP (liquid), and poly-DQM film.

Oxidative Titrations

Poly-MMC from polymerization of MMC is stable to air and oxidizable, but it is not soluble in 90% aqueous acetic acid. Copolymers of MMC with vinyl acetate are soluble and upon titration remain in solution (no precipitate) to the endpoint. Their composition could be determined by elementary analysis, titration, and photometric comparison in 95% THF with poly-MMC at 293 mμ, or poly-DQM at 264 mμ (as the case may be).

TABLE II
Ultraviolet Spectra of Discussed Compounds Measured in 95% Aqueous THF

Compound	λ_{max} mμ	ϵ[a]
MMC	294	3.35×10^3
PMC	294	3.60×10^3
Poly-MMC	294	2.90×10^3
	(295)	(3.00×10^3)[b]
Poly-DHM	290	1.8×10^3
Poly-DQM	264	1.03×10^4
DQP	264	1.58×10^4

[a] In cases of polymer, based on repeating units.

[b] Reduced from poly-DQM by Pd-C in the presence of hydrochloric acid.

Rather good agreement among these methods is obtained (Tables I and III).

Upon oxidative titration of these copolymers, the usual flattened curves are obtained. Figure 3 allows comparison between monomer PMC, which gives a curve of normal slope, as has also been observed in detail with other tocopherol-type compounds, and the flattened slope of copolymer V-12. That the oxidation of PMC gives a curve of normal shape even though one oxygen of the hydroquinone is engaged in an ether link, suggests that the energy required to break the C–O bond in the ring is of the same order of

TABLE III
Titration Data

Sample	Sample wt, mg[a]	Temp, °C	Content of MMC, wt-%[b]	Observed E_m, mV	Index potentials, mV: $E_m - E_{25}$	Index potentials, mV: $E_{75} - E_m$
PMC	28.58	25		650	15	15
PMC	9.88	30		646	13	12
HMC		25		657	12	12
PMC	6.95	25		657	2	15
V-12	62.33					
V-12	100.2	20	9.1	697	−4	−1
V-12	97.7	22.5	9.2	685	−3	6
V-12	99.2	25	9.4	671	−1	11
V-12	98.3	30	9.4	658	6	15
V-12	155	25	9.4	670	6	12
V-12	208	25	9.5	667	7	13
V-12	312	25	11.0	697	7	4
IV-88	42.2	25	39.8	709	5	16
V-12	99.0[c]	20	9.2	668	11	14
V-12	101.0[d]	25	9.2	660	14	15

[a] Wt (mg) of sample/100 ml 90% acetic acid, to show effect of concentration.

[b] Content of MMC in the polymer by titration.

[c] In the presence of 0.20 g poly(ethylene glycol).

[d] In the presence of 0.15 g poly(ethylene glycol).

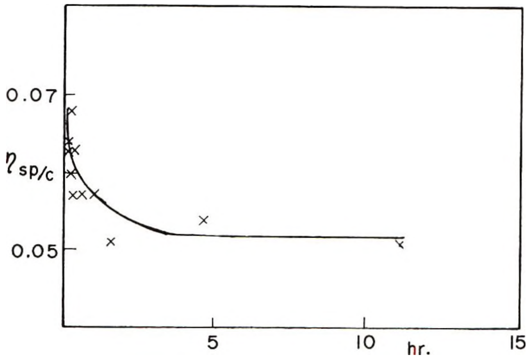


Fig. 2. Change of viscosity with time as poly-DHM is oxidized by air to poly-DQM.

magnitude as that required to break the H–O bond of hydroquinone during oxidation under these acid conditions. Oxidation (with ceric ammonium nitrate in 90% acetic acid) occurs almost instantly and with exact stoichiometry, according to spectroscopic data (Fig. 4).[5] A stable potential is established slowly ($^1/_2$–1 hr). In these copolymers the functional groups are sufficiently far apart not to influence each other,[5] yet there is found a considerable and reproducible difference between the titration curves of PMC monomer and MMC copolymers (Fig. 3, *a* and *d*). The curves differ in shape and in potential (e.g., at the midpoint). Studies of the effects of temperature (Fig. 5) and of concentration (Fig. 6) did not help in interpreting these differences as due to configurational changes. Nor were the small viscosity changes ($\eta_{sp}/c = 0.01$) helpful. Instead, the question arose

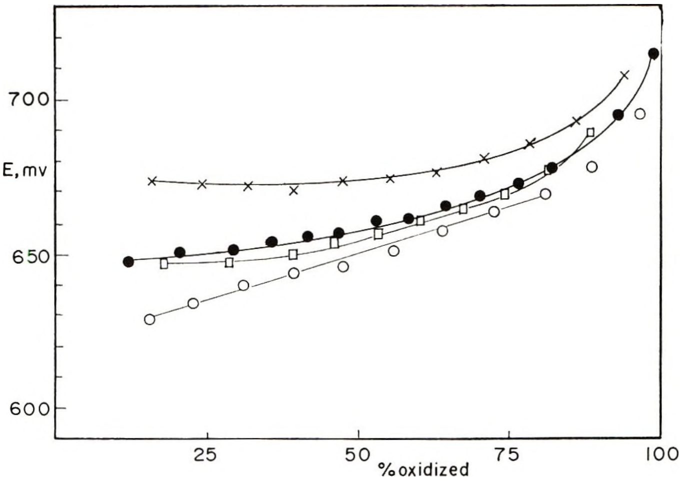


Fig. 3. Oxidative titration curves for pure monomer (PMC) and pure polymer (V-12), and mixtures: (*a*) (○) PMC (reduced); (*b*) (□) oxidized V-12, 20%, plus reduced PMC, 80%; (*c*) (●) reduced V-12 plus reduced PMC, 1:1; (*d*) (×) reduced V-12. All titrations carried out in 90% acetic acid at 25°C.

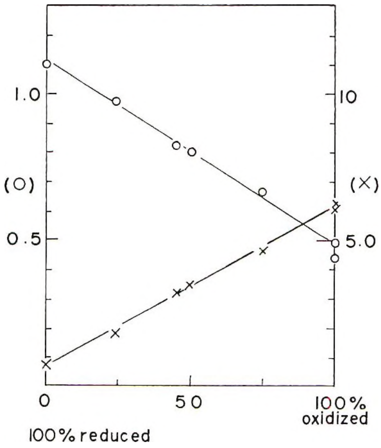


Fig. 4. Relation between ultraviolet absorption and degree of oxidation of V-12 in 90% acetic acid: (O) absorption coefficient, l./g-cm at 293 mμ; (X) absorption coefficient, l./g-cm at 271 mμ.

whether some phenomenon related to the electrode surface might be operative.

The DQM part of the oxidized copolymer seems to have a strong effect in changing the observed potential. Thus when monomer PMC is mixed with oxidized V-12, the quinoid groups of which are calculated to be equimolar to the PMC hydroquinoid groups, so that essentially an averaged mid-point potential should be approximated, the actual potential is found to be high i.e., 1.09 V. Upon addition of a small amount of oxidant the potential rises in the usual way[6] then falls over a period of 8 hr or more to a value of about 1 V. This is much higher than is found when a mixture of the reduced forms is titrated (Fig. 3c). The interpretation of this behavior is that oxi-

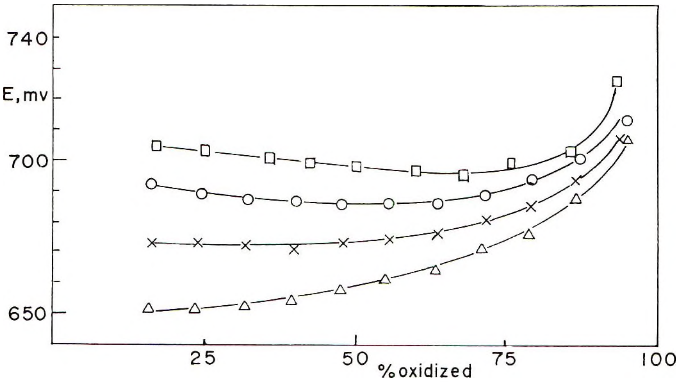


Fig. 5. Oxidative titration curves of copolymer V-12 at several temperatures. (*a*) (□) at 20°C; (*b*) (O), at 22.5°C; (*c*), (X) at 25°C; (*d*), (Δ) at 30°C. 100 mg of V-12 in 100 ml of 90% aqueous acetic acid, titrated with ceric ammonium nitrate in 90% acetic acid.

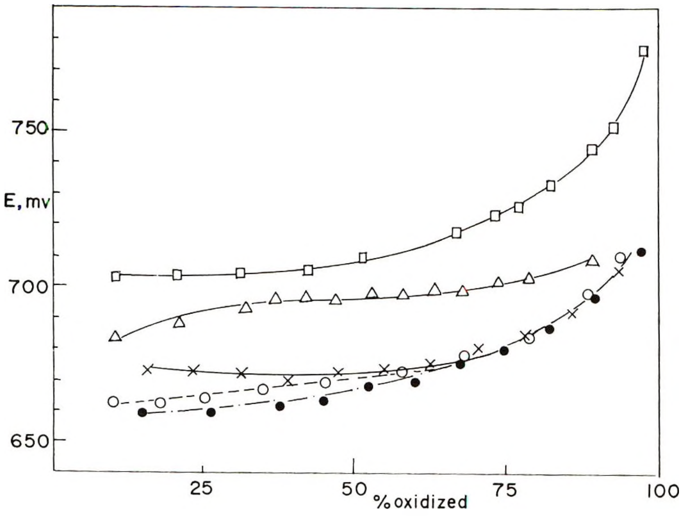


Fig. 6. Effect of concentration (mg polymer/100 ml 90% acetic acid) on potential and shape of titration curve: (△) 312 mg V-12; (●) 207 mg V-12; (○); 155 mg V-12; (×) 100 mg V-12; (□) (for comparison), IV-88.

dized polymer (V-12) is quickly adsorbed to the electrode, which then gives essentially an endpoint reading. The stability of this surface layer would be expected to increase with increase in the number of quinoid groups along a chain. Thus, fully oxidized polymer chains would be expected to adhere and to coat the surface more effectively than reduced polymer or polymer, the functional groups along the chains of which are not all oxidized. This would explain why copolymer with a higher ratio of MMC units (IV-88) yields titration curves at higher potential than reference monomer (Table III). When oxidized PMC is mixed with reduced V-12, the mixture titrates normally for polymer, at a slightly higher potential. When the titration mixture is made of 20% of oxidized V-12 plus 80% of PMC, the curve is close to that of a mixture of reduced monomer plus copolymer (Fig. 3, *b* and *c*). Looking back at earlier work it is noted that also in the case of polycarbonate based on hydroquinonyl glycol[8] the higher molecular weight polycarbonates which had larger numbers of functional groups per chain gave progressively higher potentials as oxidation proceeded (greater slope to the curve) than the lower molecular weight polycarbonates. In all the polymer titrations reported here the shapes of the titration curves between about 50 and 75% oxidation seemed to be normal. The first parts of the curves, up to about 50% oxidation are flat, or even slightly concave. This may be laid to configurational changes with associated breaking of hydrogen bonds, as previously suggested.[5,6] At the same time, also, redistribution of oxidized and reduced groups along the chains after each oxidation step may decrease the tenacity of adherence to the electrode, and so account for the fact that the potential does not go to ∽1 V until the endpoint.

The suspicion that adsorption of oxidized polymer to the electrode is responsible for increased potentials during titration was strengthened by the observation that when detergent, poly(ethylene glycol) of molecular weight 380–420, was added to the titration medium, the shape of the curve changed and approached the ideal. Compare, for example, Figure 5*c*, without detergent, at 25°C with Figure 7*a* with detergent; and 5*a* without detergent, at 20°C, with 7*b* with detergent, at 20°C. The presence of detergent is associated with decreased potential and a change in the shape of the curve towards ideal. At 20°C, however, the detergent appears not to be completely effective in displacing the oxidized polymer from the electrode (by this hypothesis). This would appear to be the reason why lower temperature is associated with higher potential in the absence of detergent (Fig. 5).

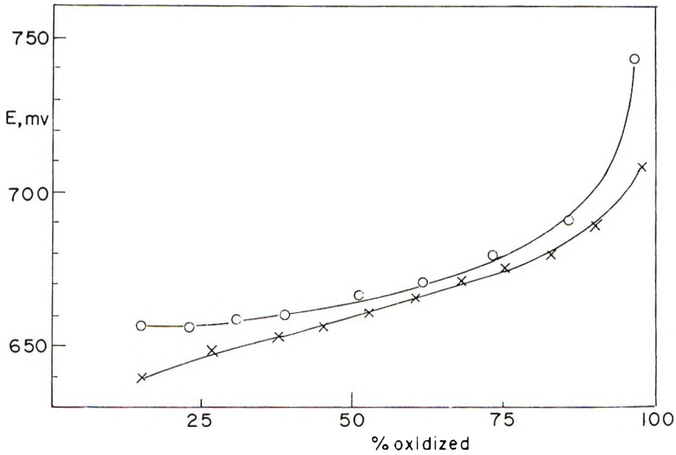


Fig. 7. Titration of copolymer V-12 carried out in solution containing polyethylene glycol (see Table III): (*a*) (×) 25°C; (*b*) (○) 20°C.

In sum, then, so far it is clear that the oxidative titration behavior of model monomer, which resembles the polymer metamere in chemical structure, cannot explain the entire behavior of the polymer when it is oxidatively titrated. The differences between the two, reflected in flattening or steepening of the potential versus concentration curves (in whole or in part of the curve), and in the relative position of the midpoint, all of which we must continue to refer to as "polymer effect," may be laid to configurational changes in the solution, adsorption of the oxidized form to the platinum electrode, and possibly other phenomena which are associated with free energy changes.

We wish to thank the Research Grants Branch, National Institute of General Medical Sciences, Public Health Service, for support of this work through Research Grant GM 10864 and Mrs. Irmlind Stronkowski for technical assistance.

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4. N. Nakabayashi, G. Wegner, and H. G. Cassidy, to be published.
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Polyimides Having Pendant Hydroxy and Acetoxy Groups. I. Synthesis of Polyimides from Pyromellitimide and Bisepoxides

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Synopsis

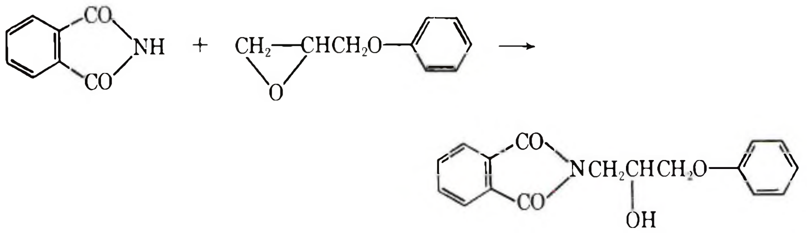
Polyimides having pendant hydroxy groups were prepared by addition of pyromellitimide with bisepoxides. Tertiary amines and quaternary ammonium halides were effective as a catalyst. The polyimides were soluble in dichloroacetic acid and had inherent viscosities in the range 0.16–0.19 dl/g. Thermogravimetric analysis showed that a rapid weight loss of the polymers occurred at about 400°C. The pendant hydroxy groups were easily acetylated by treating the polymers with a mixture of acetic anhydride and pyridine. The acetylated polyimides were soluble in dimethylformamide, dimethylacetamide, and dioxane and melted at 120–150°C.

INTRODUCTION

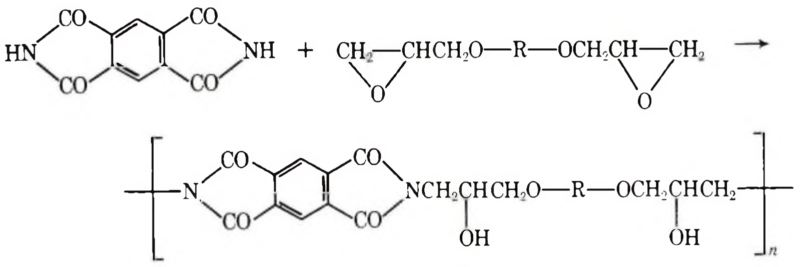
Aromatic polyimides have been extensively investigated because of their outstanding thermal stabilities, and they have gained wide acceptance in technological applications. However, aromatic polyimides are completely insoluble in the usual organic solvents, so that a special technique was necessary for fabrication. The synthesis of the aromatic polyimide usually involves an initial condensation of the dianhydride with the diamine in a polar solvent to give a solution of the polyamic acid, which can be employed for the formation of films, coatings, and fibers, the intermediate polyamic acid being subsequently converted to the insoluble polyimide.[1,2]

The synthesis of polyimide having pendant hydroxy groups (hydroxypolyimide) is of considerable interest, because the pendant hydroxy groups can be employed for various reactions such as acylation or gelation in order to alter the properties of the polymers.

In our previous papers on addition reactions of urethanes, ureas, and anilides with phenyl glycidyl ether, 2-oxazolidones were reported to be formed.[3–5] Polyoxazolidones were prepared by the reactions of bisurethanes with bisepoxides.[6] These results lead us to a study of the reaction of imides with phenyl glycidyl ether. Brief mention was made of this reaction by Petrow and Stephenson,[7] and by Roth.[8] We reinvestigated this reaction and found that phthalimide, as well as urethane, urea, and anilide, added to phenyl glycidyl ether in the presence of tertiary amine catalyst give 1-phenoxy-3-phthalimido-2-propanol in good yield [eq. (1)].


(1)

Polyimides containing pendant hydroxy groups were prepared from pyromellitimide and bisepoxides as an extension of reaction (1) [eq. (2)].

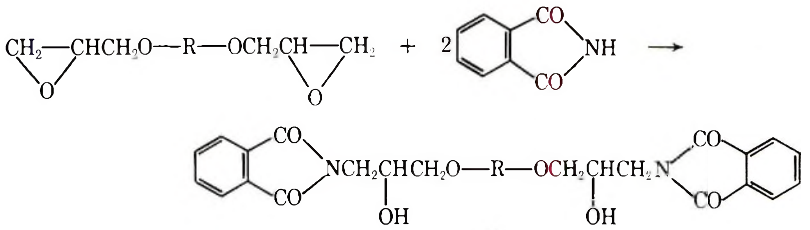

(2)

I

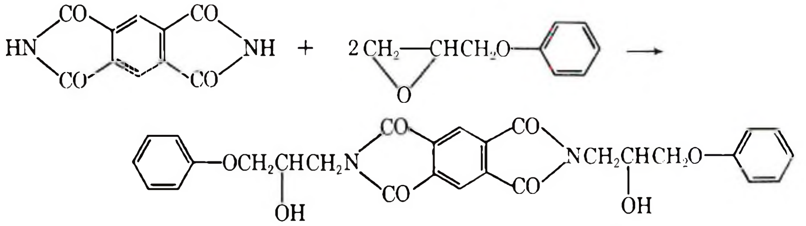
RESULTS AND DISCUSSION

Model Compounds

Model compounds II and III were prepared according to eqs. (3) and (4). Triethylenediamine was used as a catalyst.


(3)

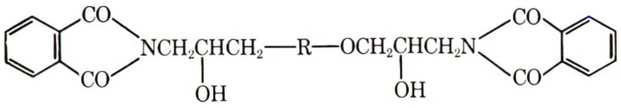
II

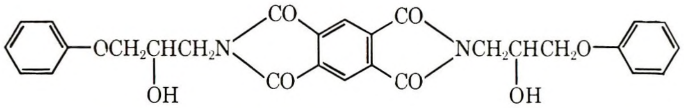

(4)

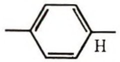
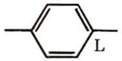
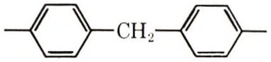
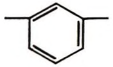
III

The results are summarized in Table I. Elemental analysis and infra-

TABLE I
Bisimides II and III


(II)


(III)

	R^a	Yield, %	Mp, °C	Elemental analysis					
				C, %		H, %		N, %	
				Calcd	Found	Calcd	Found	Calcd	Found
IIa		60	214–216	65.11	64.86	4.68	4.92	5.42	5.39
IIb		71	182–184	65.11	64.78	4.68	4.72	5.42	5.34
IIc		86	144–146	69.30	69.06	4.99	5.10	4.62	4.99
IId				Not crystallized					
III		72	279–282	65.11	65.28	4.68	4.77	5.42	5.66

[a] 1,4-Bis(2,3-epoxypropoxy)benzene was separated as two isomers by fractional recrystallization from acetone and methanol. We use subscripts (or suffixes) H and L for the higher-melting bisepoxide and its derivatives and the lower-melting one and its derivatives, respectively.

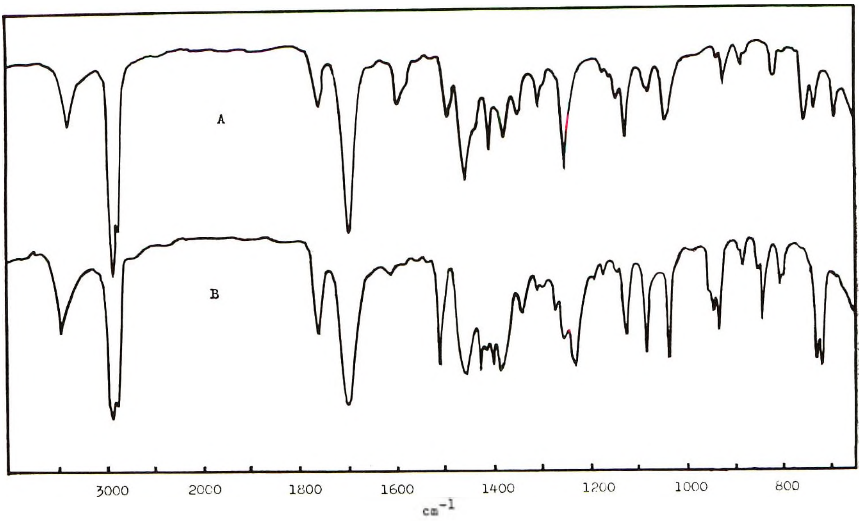


Fig. 1. Infrared spectra in Nujol of model compounds: (*A*) III; (B) II [see eqs. (3) and (4)].

red spectra indicated the formation of expected bisimide containing pendant hydroxy groups. In the infrared spectra of bisimides shown in Figure 1, absorption bands at 1775 and 1710 cm^{-1} which were characteristic of imide carbonyl, and at 3500 cm^{-1} (OH stretching) were observed.

Polyimides

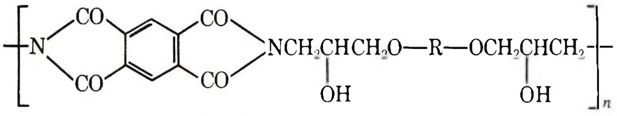
Polyimides were prepared by addition reactions of pyromellitimide with bisepoxides. The polyaddition was carried out in dimethylacetamide (DMAc) or hexamethylphosphoramide (HMPA) at 150°C for 1 hr in the presence of triethylenediamine (TED) or triethylbenzylammonium chloride (TEBAC) as a catalyst. Polymers precipitated during the polyaddition except for the polymer derived from 1,3-bis(2,3-epoxypropoxy)-benzene. The results are summarized in Tables II and III.

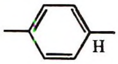
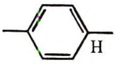
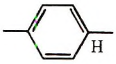
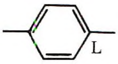
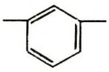
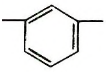
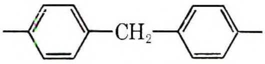
Inherent viscosities of the hydroxypolyimides were in the range 0.15–0.19 dl/g. Triethylenediamine was more effective as a catalyst than triethylbenzylammonium chloride.

In these polyadditions it is to be expected that high molecular weights are attainable by a very close approach to equivalence in the reactant ratio. Results in Table IV suggest that disturbance of the reactant ratio did not affect the inherent viscosity. Moreover, prolonged reaction time did not improve the inherent viscosity even in the preparation of soluble *m*-phenylene derivatives which did not precipitate during the polyaddition. These results seem to indicate that low molecular weight of the polyimides is to be attributed to some side reactions.

The infrared spectra of polymers shown in Figure 2 were similar to those of bisimides. Absorption bands at 1775, 1710 (C=O stretching), and 3500

TABLE II
Hydroxypolyimides



	R	Solvent	Catalyst	Time, hr	Yield, %	η_{inh}, dl/g[a]
Ia-1		DMAc	TED	1	82	0.19
Ia-2		"	TEBAC	1	49	0.16
Ia-3		HMPA	TED	2	79	0.15
Ib		DMAc	"	1	87	0.17
Ic-1		"	"	1	83	0.16
Ic-2		"	"	7	70	0.14
Id		"	"	2	76	0.18

[a] Determined at a concentration of 0.5 g/100 ml in dichloroacetic acid at 30°C.

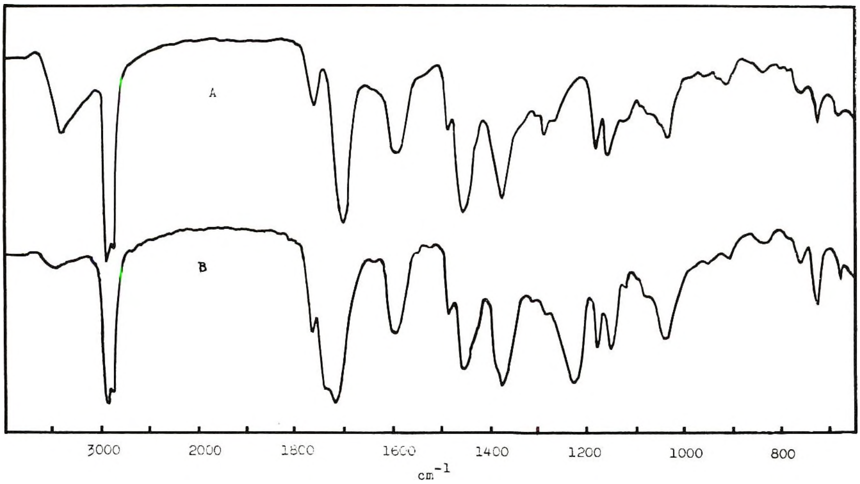
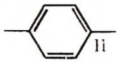
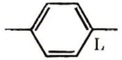
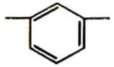
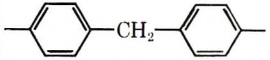


Fig. 2. Infrared spectra in Nujol of polyimides: (*A*) hydroxypolyimide, R = *p*-C_6H_4; (*B*) acetoxypolyimide, R = *p*-C_6H_4.

TABLE III
Properties of Hydroxypolyimides

R	PMT, °C[a]	DT, °C[b]	Elemental analysis					
			C, %		H, %		N, %	
			Calcd	Found	Calcd	Found	Calcd	Found
	310 (dec)	400	60.27	59.82	4.14	5.53	6.39	6.15
	310 (dec)	370	60.27	59.59	4.14	5.24	6.39	6.02
	200	390	60.27	59.19	4.14	5.47	6.39	6.00
	305	400	65.90	65.34	4.58	5.58	5.30	5.13

[a] Polymer melt temperature determined on iron hot stage.
[b] Temperature at which rapid weight loss was observed in thermogravimetric analysis (5°C/min, in N_2).

TABLE IV
Effect of Reactant Ratio on Inherent Viscosity

Imide/epoxide, mole	Yield, %	η_{inh}, dl/g[a]
0.05/0.055	76	0.16
0.05/0.05	83	0.16
0.0525/0.05	78	0.15

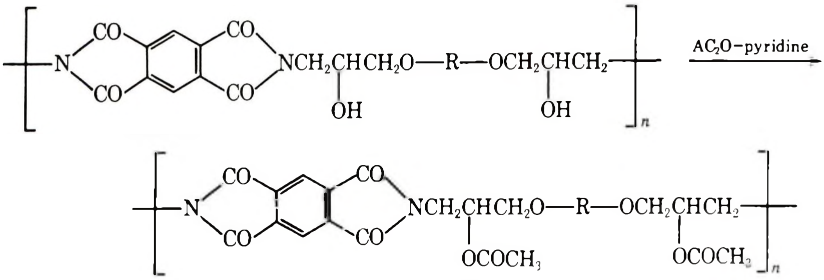
[a] Determined at a concentration of 0.5 g/100 ml in dichloroacetic acid at 30°C.

cm^{-1} (OH stretching) support the structure of polyimides containing pendant hydroxy groups.

Although aromatic polyimides were insoluble in organic solvents and infusible, the hydroxypolyimides were soluble in dichloroacetic acid. Moreover, polyimides derived from 1,3-bis(2,3-epoxypropoxy)benzene and 4,4′-bis(2,3-epoxypropoxy)diphenylmethane (Ic and Id) have melting points of 200 and 305 °C, respectively, which were determined on a preheated iron hot stage. When the melting point was measured in the usual way Ic, melted at 240°C and Id did not melt, presumably because partial crosslinking between hydroxy groups occurred prior to melting. The others derived from 1,4-bis(2,3-epoxypropoxy)benzene (H and L) were infusible and decomposed at above 310°C.

Acetylation of Hydroxypolyimides

The pendant hydroxy groups were easily acetylated by treating the hydroxypolyimides with a mixture of acetic anhydride and pyridine [eq. (5)].

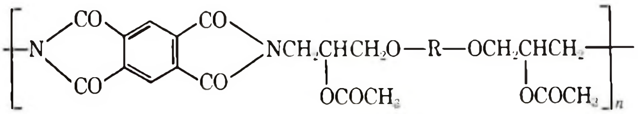


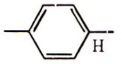
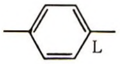
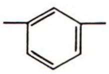
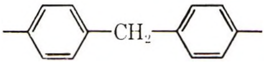
(5)

IV

The reaction time was varied from 1 to 7 hr, depending on the solubility of hydroxypolyimides. The acetylated polyimides (acetoxypolyimides) were very different from hydroxypolyimides in solubility and melting point; the acetoxypolyimides were soluble in dimethylformamide, dimethylacetamide, dichloroacetic acid, and dioxane, whereas the hydroxypolyimides were soluble only in dichloroacetic acid; melting points of the acetoxypolyimides were much lower than those of the hydroxypolyimides, as shown in Table V.

TABLE V
Acetoxypolyimides



	R	Time, hr[a]	Yield, %	η_{inh}, dl/g[b]		PMT, °C
				Acetoxy	Hydroxy[c]	
IVa		5	80	0.14	(0.16)	149
IVb		5	80	0.16	(0.17)	148
IVc		1	76	0.16	(0.15)	120
IVd		7	74	0.18	(0.18)	117

[a] Time of reaction between hydroxypolyimides and acetic anhydride.

[b] Determined at a concentration of 0.5 g/100 ml in dichloroacetic acid at 30°C.

[c] Inherent viscosities of starting hydroxy-polyimides.

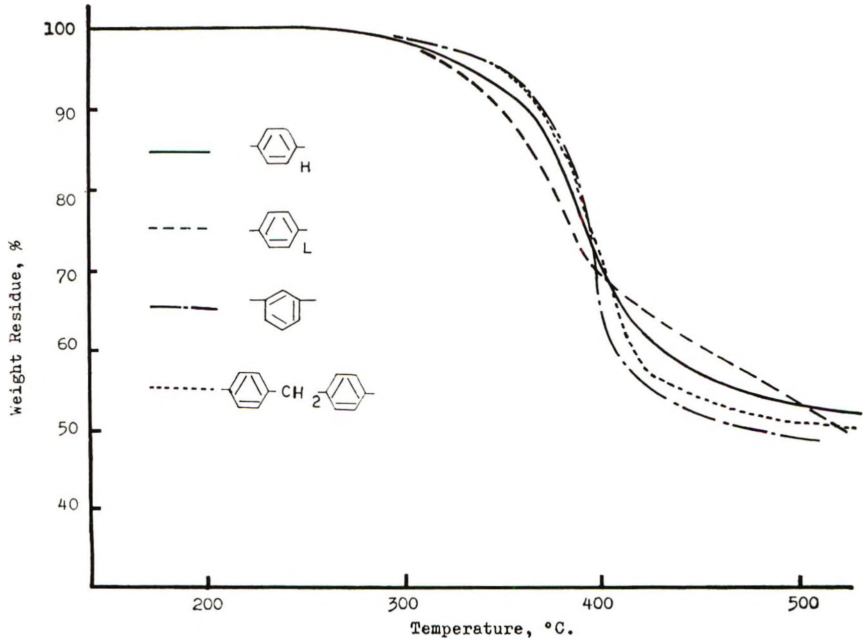


Fig. 3. Thermogravimetric analysis curves (5°C /min, in N₂) for hydroxypolyimides.

Thermal Stability

The thermal stability of the hydroxypolyimides in nitrogen atmosphere was determined by the thermogravimetric analysis. The rapid weight loss occurred at about 400°C independently of the R groups, as shown in Figure 3. The weight residue at 500°C was about 50%.

Crystallinity

The x-ray diffraction diagrams of hydroxypolyimides shown in Figure 4 were obtained by the powder method with the use of nickel-filtered CuK$_\alpha$ radiation. The diagram indicated that the hydroxypolyimides derived from 1,4-bis(2,3-epoxypropoxy)benzene (H and L) and 4,4′-bis(2,3-epoxypropoxy)diphenylmethane are highly crystalline, but the polyimide derived from 1,3-bis(2,3-epoxypropoxy)benzene is amorphous. The former three polyimides were insoluble in dimethylacetamide, so that the polymers precipitated at polyaddition temperature. On the contrary, the polyimide derived from 1,3-bis(2,3-epoxypropoxy)benzene did not precipitate during the polyaddition, and the polymer was precipitated by pouring polymer solution into acetone. This difference of forming precipitates is perhaps due to the crystallinities of the polymers.

EXPERIMENTAL

Model Compounds

1,4-Bis(2-hydroxy-3-phthalimidopropoxy)benzene (L). A solution of 1.111 g (5 mmole) of 1,4-bis(2,3-epoxypropoxy)benzene (L), 1.471 g (10 mmole) of phthalimide, and 0.1 g (0.9 mmole) of triethylenediamine in 5 ml of dimethylacetamide was heated at 120°C for 2 hr with stirring. Dimethylacetamide was removed under reduced pressure. Residual solid was washed with 30 ml of hot methanol to remove unreacted phthalimide to give 1.83 g (71%) of 1,4-bis(2-hydroxy-3-phthalimidopropoxy)benzene (L). It was purified by repeated recrystallization from Methylcellosolve, mp 182–184°C.

***N,N′*-Bis(2-hydroxy-3-phenoxypropyl)pyromellitimide.** The mixture of 4.5 g (0.03 mole) of phenyl glycidyl ether and 0.112 g (0.001 mole) of triethylenediamine was heated at 100°C, and then 1.081 g (0.005 mole) of pyromellitimide was added to the mixture. Pyromellitimide was not completely dissolved before the reaction product began to precipitate. After heating for 1 hr, the precipitated product was filtered and washed with 30 ml of acetone to give 1.865 g (72%) of *N,N′*-bis(2-hydroxy-3-phenoxypropyl)pyromellitimide. It was purified by recrystallization from dimethylacetamide, mp 279–282°C.

Polyimides

Hydroxypolyimides (Ia-1). In a 50-ml three-necked flask equipped with a mechanical stirrer and reflux condenser, 1.081 g (0.005 mole) of pyromel-

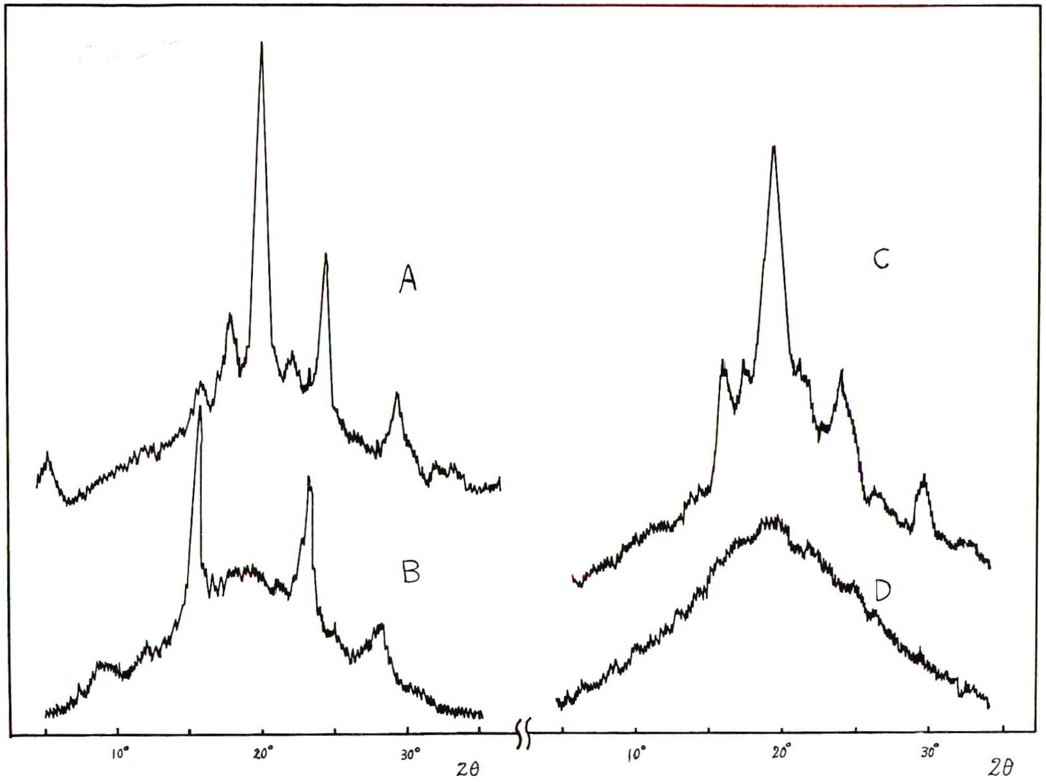


Fig. 4. X-ray diffraction diagrams for hydroxypolyimides: (*A*) R = *p*-C_6H_{4H}; (*B*) R = *p*-C_6H_{4L}; (*C*) R = *p*-C_6H_4-CH_2-C_6H_4; (*D*) R = *m*-C_6H_4.

litimide, 1.112 g (0.005 mole) of 1,4-bis(2,3-epoxypropoxy)benzene (H), and 0.1 g (0.0009 mole) of triethylenediamine were dissolved in 10 ml of dimethylacetamide at 150°C. The mixture became a clear solution, and then a pale yellow solid precipitated in a few minutes. After heating the mixture for an additional hour, it was poured into acetone. The precipitated polymer was then collected by filtration. The isolated polymer was washed with acetone in a Soxhlet extractor for 6 hr and dried to give 1.796 g (82%) of hydroxypolyimide (Ia-1). The inherent viscosity was 0.19 dl/g (determined at a concentration of 0.5 g/100 ml in dichloroacetic acid at 30°C).

Acetoxypolyimide (IVc). Into a mixture of 5 ml of acetic anhydride and 5 ml of pyridine was added 1.000 g of hydroxypolyimide derived from 1,3-bis(2,3-epoxypropoxy)benzene. The mixture was heated at 80°C for 1 hr. The polymer dissolved gradually as the acetylation proceeded. Excess acetic anhydride and pyridine were removed under reduced pressure, and the residual viscous liquid was poured into methanol. Precipitated polymer was collected by filtration and dried to give 0.907 g (76%) of acetylated polyimide (IVc). The melting point of the acetoxypolyimide measured in a capillary glass tube was 120°C. Inherent viscosities of acetoxypolyimide and starting hydroxypolyimide were 0.16 and 0.15 dl/g, respectively.

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Polyimides Having Pendant Hydroxy and Acetoxy Groups. II. Polyimides Derived from Bisaminoalcohols

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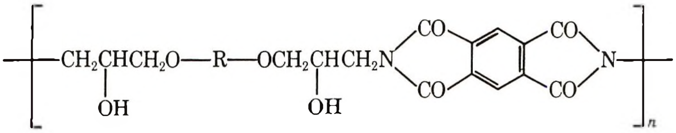
Synopsis

Polyamic acids were prepared from bisaminoalcohols and pyromellitic dianhydride. They were converted to polyimides having pendant hydroxy groups by heating them in toluene or xylene (η_{inh} = 0.22–0.34 dl/g). Treatment of these polyamic acids with a mixture of pyridine and acetic anhydride gave polyimides having pendant acetoxy groups (η_{inh} = 0.22–1.04 dl/g). These acetoxypolyimides were converted to hydroxypolyimides (η_{inh} = 0.20–0.81 dl/g) by an ester-exchange reaction. Furthermore, the hydroxypolyimides were easily acetylated to give acetoxypolyimides.

INTRODUCTION

In the preceding paper,[1] the polyimides having pendant hydroxy groups with structures such as I



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were synthesized by the addition reaction of bisepoxides with pyromellitimide. They were soluble in dichloroacetic acid and showed fairly good thermal stability. However, they could not be cast as films because of their relatively low molecular weights.

The present investigation was undertaken to prepare high molecular weight and soluble polyimides having pendant hydroxy groups (hydroxypolyimides) and those having pendant acetoxy groups (acetoxypolyimides) with the same structures reported in the preceding paper, and to establish the mutual convertibility between hydroxy- and acetoxypolyimides.

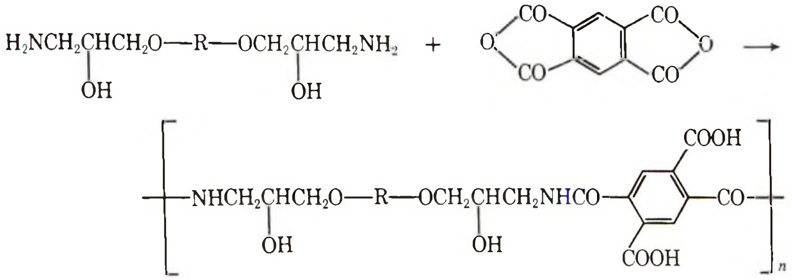
The preparation of the polymers was performed according to the usual two-step technique, starting from diamines with two hydroxy groups (bisaminoalcohols) and pyromellitic dianhydride to form polyamic acid precursors initially; these subsequently underwent cyclodehydration to yield polyimides.

RESULTS AND DISCUSSION

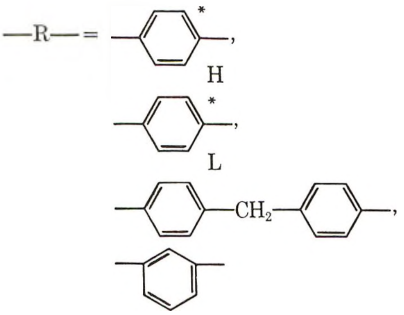
Preparation of Polyamic Acids

The bisaminoalcohols, reported before,[2] were subjected to polyaddition reaction with pyromellitic dianhydride to form polyamic acids having hydroxy groups (hydroxypolyamic acids).

where*



(1)



The preparation of polyamic acids was carried out by adding solid pyromellitic dianhydride to a solution of the bisaminoalcohols in dimethylacetamide. As the original slurry of the dianhydride dissolves in dimethylacetamide the reaction mixture became viscous. The hydroxypolyamic acids, isolated by pouring the reaction mixture into toluene, were white, fibrous materials, soluble in dichloroacetic acid, dimethylformamide, and *N*-methylpyrrolidone, and insoluble in benzene, acetone, and methanol. Tough, transparent films of the polyamic acids were cast from the above solution below 70°C.

Table I summarizes the yields, the inherent viscosities, and the melting points of the polyamic acids. Polyamic acids are well known to be very sensitive to hydrolysis by water,[3] and a reduction of molecular weight by hydrolytic cleavage of the polymer main chain is observed even during the measurement of viscosity.

Melting points of the polymers, except polyamic acid IV, could not be obtained, since dehydration with formation of polyimides occurs on heating.

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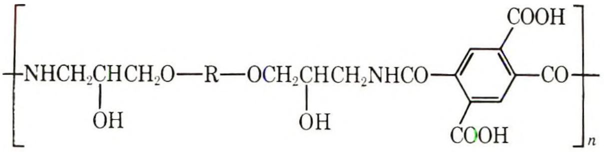
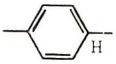
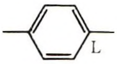
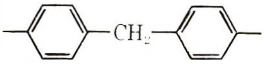
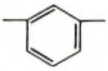
* We use subscripts H and L for the higher melting bisaminoalcohol and the lower melting one, respectively, as used in the preceding paper.[1]

TABLE I
Polyamic Acids



	—R—	Yield, %	η_{inh}, dl/g[a]	PMT, °C[b]
I		86	0.51[c]	—
II		83	0.43[d]	—
III		77	0.24[c]	—
IV		70	0.22[d]	80

[a] Measured about 1 hr after solvents were added to the polyamic acids, and at a concentration of 0.2 g/100 ml at 30°C.

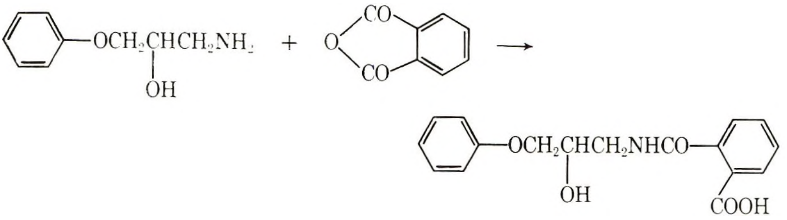
[b] Polymer melt temperature.

[c] In dimethylformamide.

[d] In dichloroacetic acid.

Model Compounds

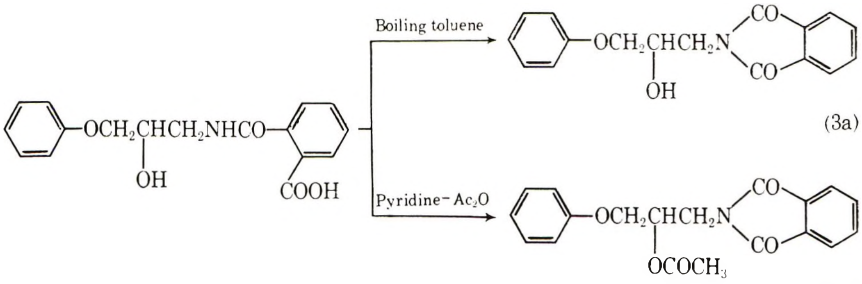
In order to make possible identification of the polymers and to investigate the imide formation from the polyamic acids, amic acid with an hydroxy group (hydroxyamic acid) was prepared from an aminoalcohol and phthalic anhydride [eq. (2)].



(2)

Infrared spectra of the amic acid and the polyamic acid obtained above were essentially the same, and the most characteristic absorption bands were found at 3300–3400 (NH and OH stretching), 1700–1710 (CO stretching in carboxyl group), 1650 (amide I), and 1550 cm^{-1} (amide II).

This hydroxyamic acid was cyclized by heating it in toluene or by treating it with a mixture of pyridine and acetic anhydride. When this amic acid was heated in dry toluene for several hours and the resulting water then removed by azeotropic distillation with toluene, imide with hydroxy group (hydroxyimide) was obtained quantitatively [eq. (3a)]. On the other hand, on treating the amic acid with pyridine and acetic anhydride, imide with acetoxy group(acetoxyimide) was also obtained quantitatively [eq. (3b)].



(3a)

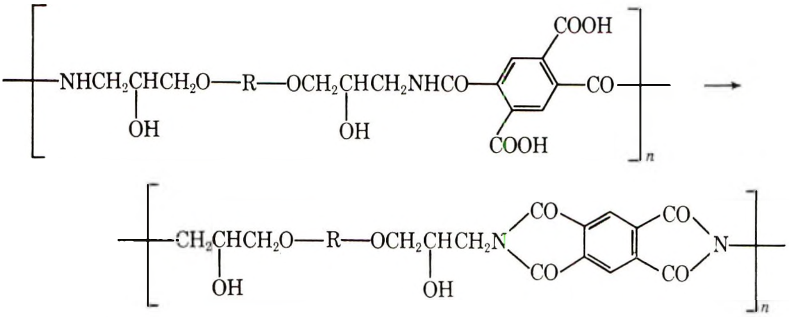
(3b)

The hydroxyimide obtained here was converted easily to the acetoxyimide in the usual manner by acetylation, and the acetoxyimide was converted to the hydroxyimide by an ester-exchange reaction in absolute methanol, sodium metal or *p*-toluenesulfonic acid being used as catalysts. When the ester exchange reaction was carried out in methanol which was not dried, selective deacetylation to prepare hydroxyimide was unsuccessful, since the imide linkage was hydrolyzed at the same time.

Thermogravimetric analysis of amic acid showed that the dehydration reaction occured at about 130°C. The hydroxy- and acetoxyimides were stable, and no weight loss was observed till 320°C.

Preparation of Polyimides

Conversion of Hydroxypolyamic Acids to Hydroxypolyimides. Cyclization of polyamic acid to polyimide by heating was shown by thermogravimetric analysis to occur at about 120°C. However, cyclodehydration by heating the polyamic acid in a solid state under reduced pressure yielded insoluble polyimide. Dehydration to obtain linear hydroxypolyimide was successfully carried out by heating the polyamic acid in boiling toluene or xylene and removing water by azeotropic distillation.



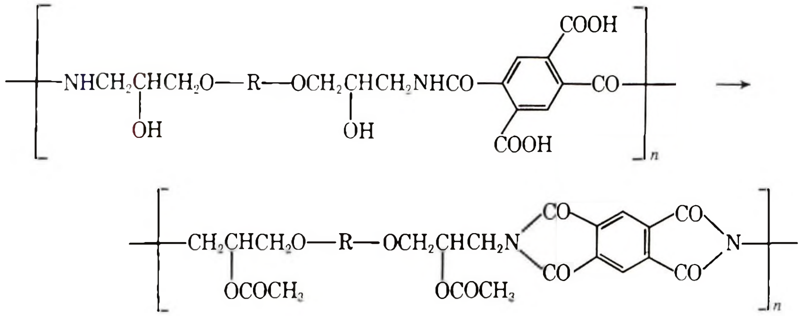
(4)

The imidization reaction proceeded heterogeneously. The powdered white polyamic acids became yellowish polyimides on heating in boiling toluene or xylene for a few hours, but to complete the reaction, additional heating for 20–50 hr was required.

Table II lists the physical properties of the hydroxypolyimides obtained here. Only hydroxypolyimide IV was gelled under this mild cyclization condition and became insoluble in dichloroacetic acid, but the others were soluble in dichloroacetic acid and insoluble in common organic solvents. Physical properties such as melting points and solubilities were virtually identical with those described in the preceding paper.[1]

The formation of hydroxypolyimides was confirmed by infrared spectra and elemental analysis. In the infrared spectra of both the hydroxyimide and hydroxypolyimide, the absorption bands characteristic of amide at 3300–3400, 1700–1710, 1650, and 1550 cm^{-1} disappeared, and new absorptions at 3500, 1775, and 1710 cm^{-1}, characteristic of hydroxyimides, were observed.

Conversion of Hydroxypolyamic Acids to Acetoxypolyimides. Treatment of the polyamic acids with a mixture of pyridine and acetic anhydride resulted in the formation of acetoxypolyimides.



(5)

The reaction was carried out by two procedures, by adding a mixture of pyridine and acetic anhydride to the polymerization solution without isolating the polyamic acids (method A), or to the dimethylformamide solution of polyamic acids which were once isolated (method B). As seen in Table III, the acetoxypolyimides obtained by method A gave higher inherent viscosities than those of the polymers obtained by method B. This indicates that the polyamic acids were very susceptible to hydrolysis during purification, which caused the cleavage of the main chain of the polymers.

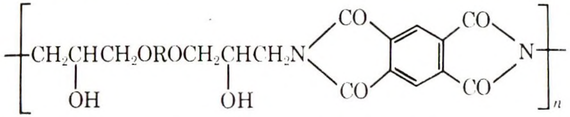
Infrared spectra of the acetoxypolyimides showed absorption bands at 1775, 1740, and 1725 cm^{-1}, indicating the presence of imide linkages having acetoxy groups and no hydroxy groups.

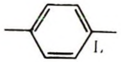
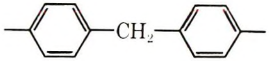
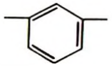
These acetoxypolyimides were soluble in dichloroacetic acid, dimethylformamide, *N*-methylpyrrolidone, *m*-cresol, and dioxane. Very tough, transparent films of acetoxypolyimides were cast from dioxane solution.

Ester-Exchange Reaction of Acetoxypolyimides to Hydroxypolyimides. The ester-exchange reaction of the polymer proceeded in a similar manner

TABLE II

Preparation of Hydroxypolyimides from Hydroxypolyamic Acids.

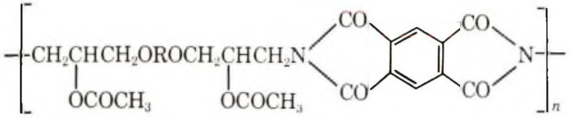


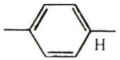
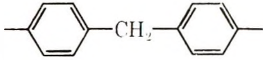
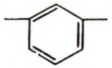
	—R—	Solvent	Reaction time, hr	η_{inh}, dl/g[a]	DT, °C[b]	Elemental analysis					
						C, %		H, %		N, %	
						Calcd	Found	Calcd	Found	Calcd	Found
I		Xylene	50	0.34	410 (380)	60.27	60.34	4.14	4.71	6.39	6.20
II		Xylene	35	0.33	410 (380)	60.27	60.04	4.14	4.86	6.39	6.22
III		Toluene	28	0.22	420 (375)	65.90	65.31	4.58	5.01	5.30	4.66
IV		Toluene	27	Gelation	380 (325)	60.27	61.76	4.14	4.87	6.39	6.38

[a] Determined at a concentration of 0.2 g/100 ml in dichloroacetic acid at 30°C.

[b] Temperature at which rapid weight loss was observed (at which weight loss began) in thermogravimetric analysis (5°C/min, in N_2).

TABLE III
Acetoxypolyimides



	—R—	Method	Yield, %	η_{inh}, dl/g[a]	PMT, °C[b]	DT, °C[c]	Elemental analysis C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found
I		A	79	1.04	146	395 (350)	59.77	58.89	4.24	4.36	5.36	5.40
		B	82	0.58								
II		A	73	0.91	148	400 (360)	59.77	58.83	4.24	4.39	5.36	4.50
		B	77	0.69								
III		A	81	0.37	128	405 (340)	64.70	63.97	4.61	4.78	4.57	4.81
		B	83	0.36								
IV		A	70	0.22	117	400 (355)	59.77	58.89	4.24	4.41	5.36	4.69
		B	55	0.21								

[a] Determined at a concentration of 0.2 g/100 ml in dichloroacetic acid at 30°C.

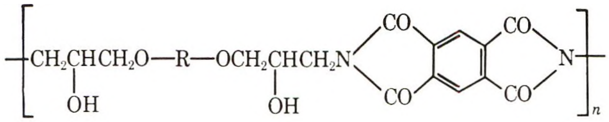
[b] Polymer melt temperature.

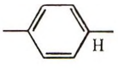
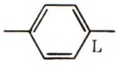
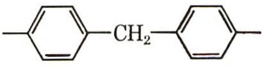
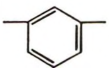
[c] Temperature at which rapid weight loss was observed (at which weight loss began) in thermogravimetric analysis (5°C/min, in N_2).

as with the model compound. Acetoxypolyimides were subjected to the ester-exchange reaction in a solution of dry dioxane and dry methanol. When sodium metal was used as a catalyst, the reaction proceeded very rapidly, and the hydroxypolyimides precipitated immediately at room temperature. However, the resulting hydroxypolyimides gave relatively low values of inherent viscosity, suggesting the probable attack of methoxide anion at the imide linkage.

On the other hand, *p*-toluenesulfonic acid, which was almost inactive to the imide linkage, proved to be very effective for ester exchange of these acetoxypolyimides. The reaction catalyzed with *p*-toluenesulfonic acid was slow, and precipitation of the resulting hydroxypolyimide from the solution was observed after several hours of heating the mixture on a water bath. By this method, very high molecular weight hydroxypolyimides were obtained as shown in Table IV. Hydroxypolyimide (IV′), which was apt to crosslink on heating, was thus obtained as a high molecular weight linear structure.

TABLE IV
Preparation of Hydroxypolyimides from Acetoxypolyimides



	—R—	Yield, %	η_{inh}, dl/g[a]	
			Hydroxy polymer	Original acetoxy polymer
I′		95	0.69	1.04
II′		97	0.81	0.91
III′		93	0.40	0.37
IV′		95	0.20	0.22

[a] Determined at a concentration of 0.2 g/100 ml in dichloroacetic acid at 30°C.

These hydroxypolyimides were soluble only in dichloroacetic acid and films were cast from the solution, but they were not tough compared with the acetoxypolyimides.

Acetylation of Hydroxypolyimide to Acetoxypolyimide. Treatment of the hydroxypolyimide II′ obtained above with pyridine and acetic anhydride resulted in acetoxypolyimide. The reaction was carried out at 80°C for 6 hr. Hydroxypolyimide II′ with an inherent viscosity of 0.81 dl/g, which was obtained from acetoxypolyimide II with an inherent viscosity of 0.91 dl/g by ester-exchange reaction, was acetylated to give an acetoxypolyimide with an inherent viscosity of 0.97. Therefore, in this deacetylation–acetylation cycle, there seemed to be no cleavage of polymer main chain, and the acetylation was confirmed to be reversible.

Thermal Analysis

The thermogravimetric analysis of the hydroxypolyimide in nitrogen showed initial weight loss at around 380°C and rapid weight loss above 410°C. The weight residue at 500°C was about 60%. Acetoxypolyimides gave relatively low melting points, in the range 120–150°C, but the thermogravimetric analysis showed that these polyimides have almost the same decomposition temperatures as hydroxypolyimides (Fig. 1).

Crystallinity

The x-ray diffraction diagrams which were obtained by the powder method with the use of nickel-filtered CuKα radiation, showed that all the hydroxypolyamic acids were amorphous. The acetoxypolyimides were also amorphous, while hydroxypolyimides prepared from hydroxypolyamic acids by heating or those prepared from aceoxypolyimides by ester-exchange

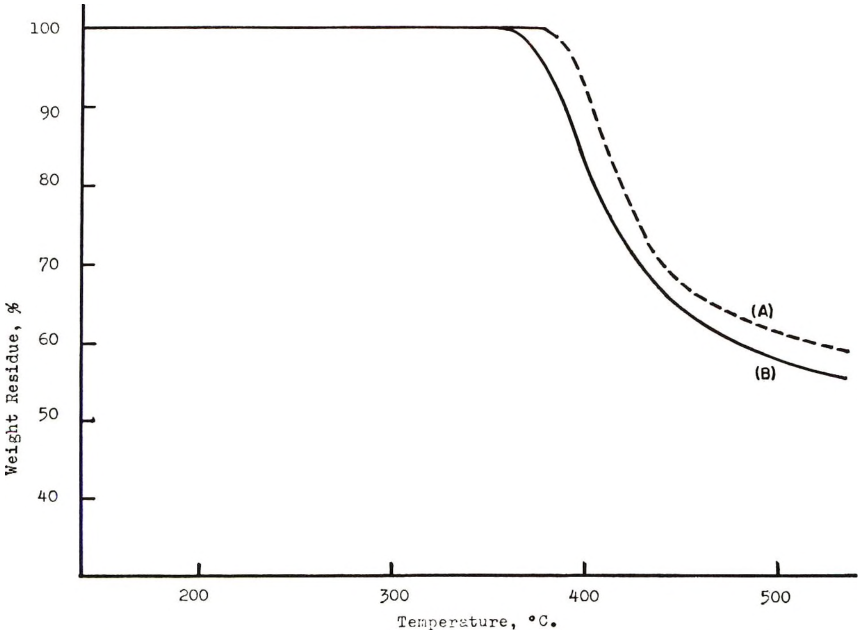


Fig. 1. Thermogravimetric analysis curves for polyimides (5°C/min, in N_2): (A) hydroxy-polyimide, R = p-C_6H_{4L}; (B) acetoxypolyimide, R = p-C_6H_{4L}.

catalyzed with *p*-toluenesulfonic acid were crystalline. However, hydroxypolyimides prepared from acetoxypolyimides by ester-exchange reaction catalyzed with sodium were amorphous. This phenomenon may be attributable to the instantaneous precipitation of the resulting hydroxypolyimides on adding catalyst.

EXPERIMENTAL

Polyamic Acids

Polymerization was carried out at −20 to 40°C for 1–2 hr in dimethylacetamide. A typical example was as follows.

To a solution of 0.500 g of 3,3′-*p*-phenylenedioxybis(1-amino-2-hydroxypropane) (H) in 10 ml of dimethylacetamide was added 0.426 g of pyromellitic dianhydride at 40°C. After stirring the mixture for 1 hr at room temperature, the product was precipitated by pouring the viscous solution into 500 ml of toluene. The yield of the polymer was 0.8 g (86%), and the inherent viscosity was 0.51 dl/g (determined at a concentration of 0.2 g/100 ml in dimethylformamide at 30°C).

Model Compounds

1-Phenoxy-3-[(*o*-carboxy)benzamido]-2-propanol. This compound was prepared from 1-phenoxy-3-amino-2-propanol and phthalic anhydride in tetrahydrofuran and was recrystallized from a mixture of tetrahydrofuran and petroleum ether (74%), mp 135–135.5°C.

ANAL. Calcd for $C_{17}H_{17}NO_5$: C, 64.75%; H, 5.43%; N, 4.44%. Found: C, 64.95%; H, 5.56%; N, 4.70%.

1-Phenoxy-3-phthalimido-2-propanol. To 40 ml of dry toluene was added 0.5 g of 1-phenoxy-3-[(*o*-carboxy)benzamido]-2-propanol. After refluxing the solution for 9 hr, the solvent was removed mostly at atmospheric pressure and finally under reduced pressure to avoid overheating. The residual oil soon solidified and recrystallization from methanol gave 0.38 g (81%) of white crystals, mp 112–113°C (lit.[4] 110°C).

1-Phenoxy-2-acetoxy-3-phthalimidopropane. To a mixture of pyridine (10 ml) and acetic anhydride (10 ml) was added 1.5 g of 1-phenoxy-3-[(*o*-carboxy)benzamido]-2-propanol. The mixture was allowed to stand at room temperature for 1 day, and the solvent was evaporated under reduced pressure. The residual oil soon solidified. The solid was recrystallized from ethanol to give 1.4 g (87%) of white crystals, mp 83–84.5°C.

ANAL. Calcd for $C_{19}H_{17}NO_5$: C, 67.25%; H, 5.05%; N, 4.13%. Found: C, 67.44%; H, 5.14%; N, 4.19%.

This compound was also prepared by acetylation of 1-phenoxy-3-phthalimido-2-propanol with a mixture of pyridine and acetic anhydride.

Ester-Exchange Reaction of Model Compound. A solution of 0.5 g of 1-phenoxy-2-acetoxy-3-phthalimidopropane in 10 ml of dry methanol was refluxed for 18 hr, *p*-toluenesulfonic acid being used as a catalyst. The solvent was removed under reduced pressure, and the white residual solid was washed well with water. The yield of 1-phenoxy-3-phthalimido-2-propanol was 0.43 g (98%).

When sodium metal was used as a catalyst, the ester-exchange reaction proceeded very rapidly, and 1.5 hr at room temperature was sufficient to complete the reaction. The yield was 89%.

Polyimides

Hydroxypolyimide I. To 40 ml of dry xylene was added 0.1 g of powdered polyamic acid I, and the mixture was refluxed. The imidization reaction proceeded heterogeneously, and the white polyamic acid turned to yellowish polyimide in about 2 hr. After heating for 50 hr, the solvent was removed mostly at atmospheric pressure and finally under reduced pressure to avoid the dehydration between hydroxy groups by overheating. The yield of hydroxypolyimide was quantitative. The inherent viscosity was 0.34 dl/g (determined at a concentration of 0.2 g/100 ml in dichloroacetic acid at 30°C).

Acetoxypolyimide II (Method A). To a polymerization solution of polyamic acid II, prepared from 0.500 g of 3,3′-*p*-phenylenedioxybis(1-amino-2-propanol) (L) and 0.426 g of pyromellitic dianhydride in 10 ml of dimethylacetamide, was added a mixture of 8 ml of pyridine and 8 ml of acetic anhydride. The reaction mixture has allowed to stand at room temperature for 1 day and was poured into 500 ml of methanol to give 0.74 g (73%) of yellow fibrous material. The inherent viscosity was 0.91 dl/g (determined at a concentration of 0.2 g/100 ml in dichloroacetic acid at 30°C).

Acetoxypolyimide II (Method B). A mixture of 2 ml of pyridine and 2 ml of acetic anhydride was added to a solution of 0.2 g of polyamic acid II in 1 ml of dimethylformamide. The acetoxypolyimide was isolated in the same way as described above. The yield was 0.17 g (77%), and the inherent viscosity was 0.67 dl/g (determined at a concentration of 0.2 g/100 ml in dichloroacetic acid at 30°C).

Ester-Exchange Reaction of Polyimide. To a solution of 0.13 g of acetoxypolyimide II in 7 ml of dry dioxane was added 2 ml of dry methanol and 0.13 g of *p*-toluenesulfonic acid. After heating on a water bath for 3 hr, powdery polymer began to precipitate. To complete the reaction, heating was continued for 38 hr. The mixture was poured into 200 ml of water and the powdery hydroxypolyimide II′ was filtered and washed well with water to remove the catalyst. The yield was 0.105 g (97%), and the inherent viscosity was 0.81 dl/g (determined at a concentration of 0.2 g/100 ml in dichloroacetic acid at 30°C).

Acetylation of Hydroxypolyimide II′. To 0.07 g of hydroxypolyimide II′ (η_{inh} = 0.81 dl/g) was added a mixture of 1 ml of pyridine and 1 ml of acetic anhydride. The mixture was heated at 80°C. The hydroxypolyimide went into solution gradually. After heating for 6 hr, the solution was poured into 100 ml of methanol and yellow fibrous acetoxypolyimide was obtained. The yield was 0.07 g (84%) and the inherent viscosity was 0.97 dl/g (determined at a concentration of 0.2 g/100 ml in dichloroacetic acid at 30°C).

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Preparation and Properties of Isomeric Polyphenylacetylenes

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Synopsis

Polyphenylacetylenes were prepared using ferric acetylacetonate and $(i\text{-Bu})_2AlH$, $RhCl[(C_6H_5)_3P]_3$ and thermal initiation. Color, infrared spectra, softening temperatures, ultraviolet fluorescence, solubility, and crystallinity are described. A method is presented for assigning to these three macromolecular species predominantly *cis*, *trans*, and *cis–trans* copolymer structures, respectively. The dominantly *cis* polymer is believed to form in a transoid conformation which can easily be transformed to a more helical arrangement which exhibits a degree of crystallinity. Pyridine promotes the isomerization of *cis* to *trans* structure. The rhodium phosphine is thought to effect chain growth by repeated additions of the acetylenic C—H of monomer across a terminal triple bond. Phenylacetylene thus behaves as a bifunctional molecule in this system. Color, polymer conformation, and crystallinity appear to be strongly interrelated.

A variety of initiators are known to polymerize substituted acetylenes.[1] In this study polyphenylacetylenes from several initiators are compared. These polymers prove not to be identical. Several isomeric polyphenylacetylenes exist. This communication attempts to discuss these syntheses, describe the polymer species and provide some insight as to the basic underlying structural differences. For discussion, these polyphenylacetylenes are grouped into Types I, II and III. Type I is further classed as I-A, I-B or I-C (see Table I).

RESULTS

Type I-A

This polyphenylacetylene is formed by certain combinations of transition metal compounds and reducing agents. Two combinations employed in this study are ferric acetylacetonate–diisobutylaluminum hydride and rhodium trichloride–lithium borohydride. I-A is bright yellow and is readily soluble in benzene or chloroform at 20–25°C. Unique to I-A is an intense band at 13.50 μ. A broad trough appears in the 11.0–11.5 μ region (Fig. 1). While stable as a solid at room temperature, I-A is readily transformed to another species, I-B, in solution or at temperatures above 100°C.

TABLE I
Properties of Phenylacetylene Polymers

Species	Initiator	Color	Softening temp, °C[a]	Ultraviolet fluorescence	$\bar{M}_n$[b]	Characteristics[c]
I-A	Transition metal–reducing agent	Bright yellow	Transforms	No	4900	Strong 13.5 μ; broad 11.0–11.5 μ cluster
I-B	"	Orange	203–208	No	4200(Fe) 5400(Rh)	11.25–11.36 μ doublet
I-C	"	Dark red	198–203	No	—	XRD periodicity
I-D	"	Yellow	216–219	Yellow	4900	Obtained by pyridine treatment
II	$RhCl[(C_6H_5)_3P]_3$	Tan	152–157	Yellow-orange	1100	Absence of 11.0–11.5 μ; 6.77–6.89 μ doublet
II-Py	"		213–217	Yellow-orange	"	Pyridine treatment of II
III	Thermal	Yellow	158–163	Yellow	700–900	Thermal initiation
III-Py	"	"	213–217	Yellow	"	Pyridine treatment of III

[a] Softening temperature determined by using Fisher-Johns apparatus.

[b] Vapor-phase osmometry in benzene.

[c] Numbers refer to infrabands; XRD = x-ray diffraction, for details see ref. 2.

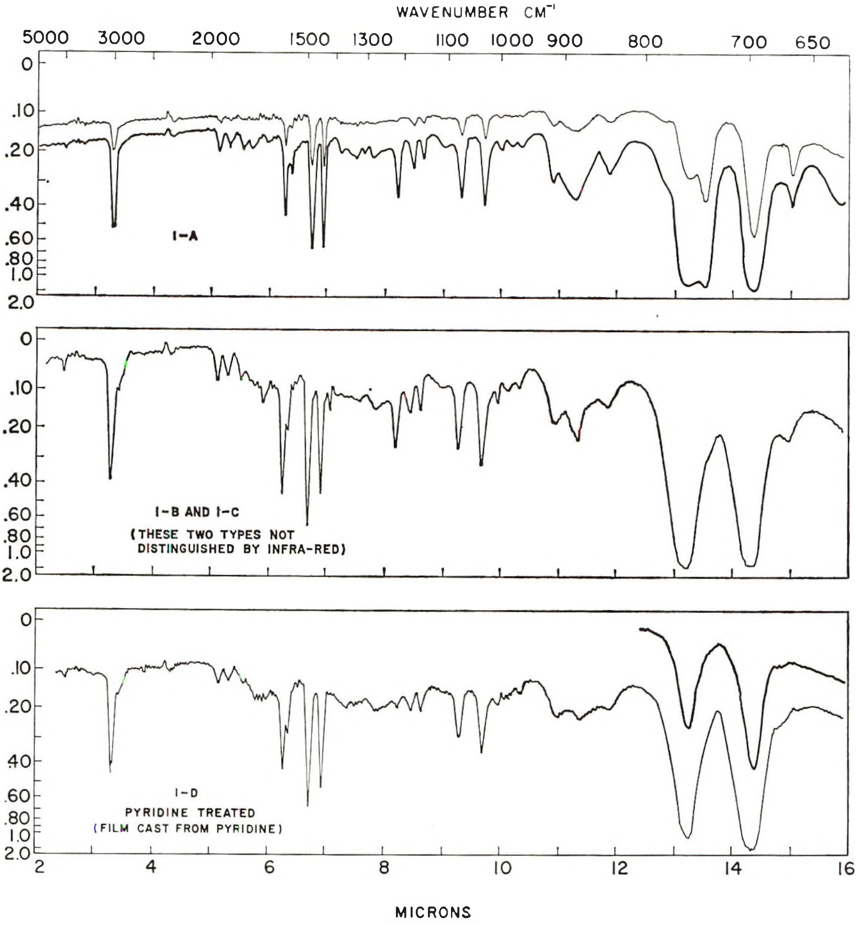


Figure 1.

Type I-B

This orange species swells to a gel in benzene at 20–25°C but solutions of at least 5% (w/v) can be obtained at 150°C. Once formed, solutions are stable. I-B has no band at 13.50 μ. The broad trough seen at 11.0–11.5 μ in I-A sharpens to a weak doublet at 11.25 and 11.37 μ. Distinct peaks in its x-ray diffraction spectrum reveal I-B to be partially crystalline.[2] Employing either of the two catalyst systems mentioned above, one observes appreciable transformation of I-A to I-B during polymerization. This has the effect of rendering the reaction mixture heterogeneous rather than a smooth solution. The amount of product transformed depends on the nature of polymerization media (see Experimental). I-A without attendant I-B can be formed by the bulk polymerization of monomer by using $RhCl_3$ alone.

Type I-C

The x-ray revealed crystallinity of I-B can be increased by immersion in certain liquids such as tetralin or toluene. The color shifts to a deep red. I-C has meaning in the solid state only. When dissolved in chloroform at 150°C its form is not distinguishable from I-B.

Type II

Tan-colored II arises from the use of RhCl $[(C_6H_5)_3P]_3$ with monomer at 40–80°C. II is soluble in all proportions at 20–25°C in acetone or benzene. It reveals no order in its x-ray diffraction spectrum. II fluoresces under ultraviolet radiation, whereas type I species do not. The infrared spectrum reveals nothing in the 11.0–11.5 μ region, nothing at 13.50 μ (Fig. 2). Melt-softening temperatures (second-order transition) for I and II differ by about 45°C (see Table I).

If the temperature of this synthesis is maintained at 0–20°C for several days, the mixture fills with crystals of *trans*-1,4-diphenylbutenyne, C_6H_5—CH═CH—C≡CC_6H_5. A 50% yield of this dimer can be obtained. Syntheses leading to I or III do not give rise to this dimer in more than trace amounts.

Type III

Thermal polymerization of phenylacetylene gives the pale yellow III.

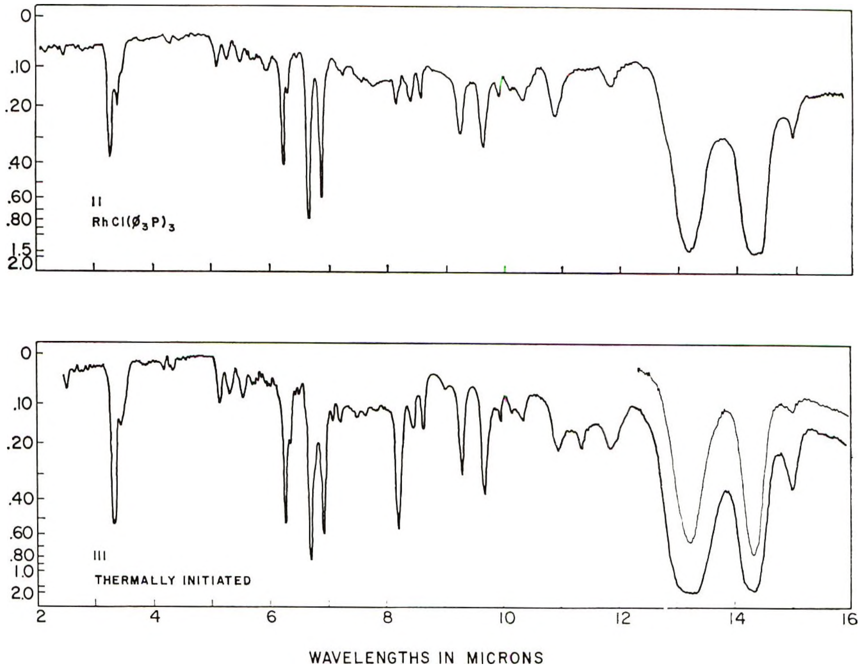


Figure 2.

It is readily soluble at 20–25°C and is noncrystallizable. It also differs clearly from II by the presence of weak bands in the 11.0–11.5 μ region (Fig. 2).

Effect of Pyridine

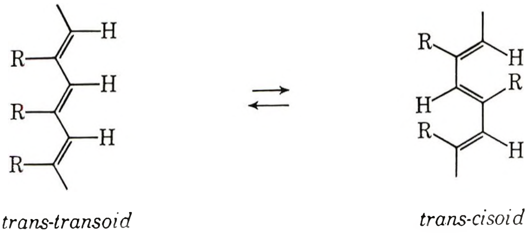
When I or III is dissolved in pyridine and then recovered, isomerization is seen to have occurred. Pyridine is not thereby incorporated in the polymer. Other polar organic solvents (like dimethylformamide) cause similar effects. The isomerized polymer is a yellow noncrystallizing solid which fluoresces yellow under ultraviolet radiation (nontreated I species do not). The envelope of infrared bands in the 11.0–11.5 μ region changes but does not disappear. The melt-softening temperature increases, especially in the case of III which rises about 50°C (see Table I). Pyridine-treated I could not be distinguished from pyridine-treated III in these studies.

When II is treated with pyridine, the only change observed was that the melt-softening temperature increased by about 50°C. Thus, when either I, II, or III is pyridine-treated the same unique species is obtained.

DISCUSSION

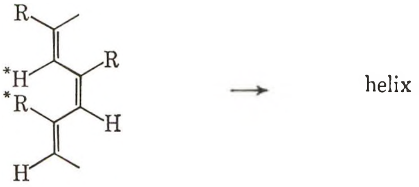
Structure Relations

Viewed as addition polymers, polyphenylacetylenes may be formulated $—(C_6H_5—C{=}CH)_n—$. An obvious factor involved in the different species described above involves the *cis* or *trans* nature of the double bond with respect to the chain. An important difference between all-*trans* and all-*cis* conjugated unsaturated chains becomes apparent from rotation about single bonds in the chains. A *trans-transoid* form converts to a *trans-cisoid* form (and vice versa) by an allowed 180° rotation about chain C—C single bonds.



(1)

A different situation exists for *cis* polymers. A sequence of three double bonds in *cis-cisoid* relation forms a six-membered ring. In a chain of alternating *cis* double bonds this limits rotation about C—C bonds. The consequence is helix formation. The closer these rotations in a *cis-transoid* form each approach 180°, the tighter the helix that forms.



cis-transoid (2)

Comparison of infrared spectra from polystyrene and the various polyphenylacetylenes suggests that bands in the 11.0–11.5 μ regions of I and III are involved with unsaturation. This was confirmed when hydrogenation caused disappearance of these bands. Analogous polymerizations of $C_6H_5C\equiv CD$ resulted in large shifts of these bands to longer wave lengths. Also, polymers of cyclohexylacetylene, *tert*-butylacetylene, 3-cyclohexylpropyne, and hexyne-1 (polymerized by using the ferric acetylacetonate–diisobutylaluminum hydride system) all exhibited patterns in the 11.0–11.5 μ region similar to I.

Chain double bonds in polyphenylacetylenes are analogous to trisubstituted ethylenes. (*Cis* and *trans* denote the relation of a particular double bond with respect to the chain.) The literature on infrared spectra does not readily allow choosing between *cis* or *trans* nature in this unsaturation.

Species I-A is considered to be a *cis-transoidal* polymer on the basis of transformations it undergoes. As stated above, I-A decreases solubility, develops crystallinity and changes color under conditions which facilitate the motion and rotation of chain segments. Preceding discussion has suggested also that rotation of chain segments in a *cis-transoidal* polymer leads to helix formation. Helices give rise to ordered structure, thence crystallinity and altered solubility characteristics (as observed in I-B). Optimization of the solvent environment leads to higher degrees of crystallinity characteristic of I-C. A related analogy exists in the crystallization of isotactic polystyrene.[3]

The characteristic strong 13.50 μ band of I-A disappears upon transformation to I-B. Models incorporating coplanar unsaturation in the *cis-transoidal* polymer reveal severe interaction between any given phenyl group and a proton two monomer units away. [Note asterisks in *cis-transoidal* structural formula, eq. (2)]. Coiling, that is, partial rotation about chain C—C bonds, alleviates this proton-ring interaction. The attendant disappearance of the 13.50 μ band may be related. Aromatic ring proton deformation vibrations are known to occur in the 13–15 μ region.[4]

No bands appear in the 11.0–11.5 μ region of spectra from polymer II. In this region the spectrum resembles polystyrene. Comparison of polystyrene and polymer II spectra reveal no bands assignable to chain unsaturation. However, hydrogenation of II gives rise to a product whose spectrum exhibits a strong new C—H stretching frequency at 3.40 μ and a CH_2 wag at 7.28 μ as does polystyrene. Thus, chain unsaturation must have been present in II. If the thesis concerning the presence of *cis* unsaturation in I is accepted, one must seriously consider unsaturation in II to be *trans* with respect to the chain.

Weak bands do appear in the 10.2–10.4 μ region in spectra of II (and III also) which are removed by hydrogenation. This region is characteristic of *trans* unsaturation.[3] However, it apparently arises from a terminal *trans* unit, not from chain unsaturation generally. The spectra of *trans*-1,4-diphenylbutenyne, two oligomers of molecular weights (by vapor-phase osmometry) 430 and 925 and II (molecular weight 1150) were compared in the 10.2–10.4 μ regions. Intensities of bands in this region decrease markedly as molecular weight increases. The dimer is believed to be a precursor of II, thus incorporating the unique disubstituted terminal double bond in the chain.

$$\textit{trans}\text{-}C_6H_5\text{—}CH\text{=}CH\text{—}C\equiv C\text{—}C_6H_5 \xrightarrow{n\text{-}C_6H_5\text{—}C\equiv CH} C_6H_5\text{—}CH\text{=}CH\text{—}(CH\text{=}CC_6H_5)_n\text{—}C\equiv CC_6H_5 \quad (3)$$

Rotation around chain single bonds permits interconversion of *trans-transoidal* and *trans-cisoidal* units. In contrast to Type I, no pathway exists to the development of ordered helical structures. Thus, II exhibits no crystallinity; no changes in solubility analogous to I.

III, thermal polymer, exhibits weak bands in the 11.0–11.5 μ region, weaker than are found in I. This indicates some *cis* bonds. On the other hand, it reveals no crystallinity or changes in solubility. It also fluoresces yellow under ultraviolet radiation. (II does so fluoresce; I does not.) These facts suggest a *cis–trans* copolymer. A copolymer of both *trans* and *cis* units is intuitively more reasonable in view of its thermal origin. No coordination centers exist to invoke geometric selectivity.

The pyridine effect is consistent with the idea that pyridine (and other polar solvents) causes isomerization of at least some *cis* unsaturation to *trans*. Thus, III and pyridine-treated III are both *cis-trans* copolymers, the latter being more *trans* than the former. The significance of the increases in meltsoftening (second order transition) temperatures for I, III and II is not understood.

The transformations described above provide an interesting example of a color-structure relation. Type I-A, the presumed *cis-transoid* species, can be transformed consecutively from yellow to orange to red to yellow without detectable molecular weight change. Color appears to be intimately related to chain conformation and/or crystallinity as well as *cis-trans* relations of the double bonds for a given degree of polymerization.

RhCl[$(C_6H_5)_3P$]$_3$-Catalyzed Propagation

By analogy to vinyl polymerization, the thermal and Zeigler coordination polymerizations are considered to proceed by additions of an active chain end across successive triple bonds. However, the rhodium phosphine-catalyzed polymerization appears unique. In particular, the dimer *trans*-1,4-diphenylbutenyne forms being the main product in reactions conducted below 20°C. Further, styrene, the vinyl analog, is polymerizable both thermally and by the coordination catalysts active here but is unaffected by $RhCl\ [(C_6H_5)_3P]_3$.

The dimer just mentioned results from the addition of C—H across another triple bond. Several years ago, Marvel and his students studied polymer formation resulting from the reaction of dithiols with dienes.[5]

$$H_2C{=}CH{\sim}HC{=}CH_2 + HS{\sim\sim}SH \rightarrow {\sim\sim}S{-}CH_2{-}CH_2{\sim\sim}CH_2CH_2{-}S{\sim\sim} \qquad (4)$$

The known chemistry of Rh and other transition metals of the second and third periods has demonstrated the facile formation of Rh—H and σ-bonded Rh—C. Several small molecules, such as H_2, HCl, and CH_3I, dissociatively add to the Rh^I coordination sphere.[6] All these facts make it tempting to consider phenylacetylene as a bifunctional molecule, the functional groups being C≡C and C—H.[7] C—H adds to the Rh coordination sphere forming Rh—H and σ-bonded $Rh{-}C{\equiv}C{-}C_6H_5$. These two species can be imagined then to react with still another π-bonded acetylenic group in the same coordination sphere. The scheme is shown in Figure 3.

EXPERIMENTAL

Phenylacetylene

Phenylacetylene was obtained from Chemical Samples Co., Columbus, Ohio 43221. It was distilled under nitrogen before use (46°/20 mm, n_D^{25} 1.5461, d^{20} 0.929).

RhCl$_3$–LiBH$_4$–Diluent Procedure

$RhCl_3$ hydrate (Engelhard 39.8% Rh) (0.40 g) was dissolved in 24 ml ethanol under nitrogen in a mechanically stirred 300ml reactor. To the red solution was added 24 ml phenylacetylene. The solution darkened. Tetralin (48 ml) was then added followed by 50 mg $LiBH_4$. Another 50 mg $LiBH_4$ was added after 5 hr, then 50 mg more after 24 hr. Agitation was stopped after 26 hr. After 70 hr, the hetereogeneous mixture was dispersed by stirring in 30 ml of 1:1 (v/v) benzene–acetone solution. The dispersion was centrifuged. The benzene–acetone dispersion wash was

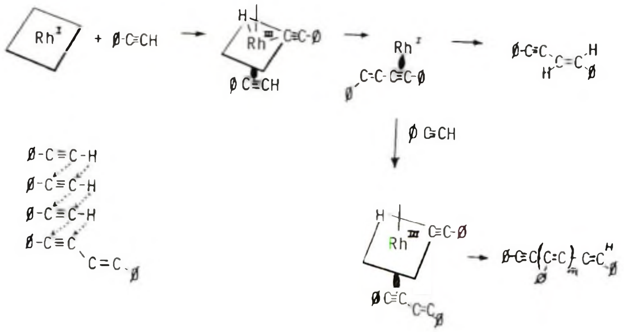


Fig. 3. Scheme for $RhCl[(C_6H_5)_3P]_3$-initiated polymerization.

repeated on the solids. Supernatant liquors were poured into eight volumes of acetone. Bright yellow solids precipitated and soon settled out. Upon recovery and drying, 2.0 g of bright yellow solids, type I-A, was obtained.

The centrifuged solids above were twice wash-dispersed in 30–40 ml benzene, then rinsed twice with acetone. Solids were whipped in a blender with acetone–water (3:1 v/v) containing a few drops of 12*M* hydrochloric acid. Solids were filtered, washed with water, then acetone and dried to obtain 4.2 g of orange or orange-red solids, type I-B.

The amount of I-A formed relative to I-B depends markedly on the reaction medium (Table II).

TABLE II

Environmental variable	Weight ratio I-A/I-B
No tetralin added	only I-A
Tetralin:ethanol (vol) = 6	1.4
Tetralin:ethanol (vol) = 2	0.45

The order of component addition above should be followed. Addition of $LiBH_4$ directly to the $RhCl_3$ ethanol solution results in a black inactive dispersion.

Phenylacetylene Polymerization by $RhCl_3$

$RhCl_3$ hydrate (50 mg) was dissolved in 4 ml of warm ethanol under nitrogen. Phenylacetylene (6 ml) was then injected whereon the wine-red solution assumed a brown tone. After one week at ambient temperature a brown gum deposited. It was isolated by decanting the supernatant liquors, dissolved in 15 ml CH_2Cl_2 and precipitated with 75 ml methanol. Yellow solids, I-A, 2 g, were obtained.

Ferric Acetylacetonate Procedure

A baked, nitrogen-purged stirred 1-liter reactor was used. $Fe(OAcAc)_3$ (1.5 g, 4.2 mmole) dissolved in 5 ml benzene was added, followed by 3.6 ml (20 mmole) $(i\text{-}Bu)_2AlH$. Exothermic reaction producing a black dispersion followed. After about 15 min agitation, 220 ml of dry benzene was added followed by a solution of 45 ml (0.4 mole) phenylacetylene in 120 ml dry benzene. Gelation occurred readily, rapid agitation being required to effect dispersal. The reaction mixture became a mushy semisolid in about 2 hr. More benzene (about 50 ml) was added to facilitate agitation. Stirring was stopped after 4 hr, and the mixture was allowed to stand in the stoppered reactor for 2 days.

The soft, firm solids were whipped in about 1 volume of a 1:1 benzene–acetone mixture. The resulting mush was centrifuged. Polymer I-A was recovered by precipitating supernatant liquors in acetone. Centrifuged solids were twice dispersed in benzene, recovered by centrifugation, then whipped in acetone, filtered and dried to give 36 g of orange type I-B polymer.

Type I-C

Orange I-B was covered with one of a group of alkylated aromatic liquids such as toluene, xylene, mesitylene, ethylbenzene, or tetralin. A deep red color developed in the solids. After a period of time (usually 1 day) liquors were centrifuged off. The dark red solids were slurried in benzene, recovered, and dried *in vacuo* at 60°C.

Thermal Polymerization

Phenylacetylene (36 g) was heated with magnetic stirring under nitrogen initially at reflux. As polymerization occurred, a red-brown color developed. The temperature was raised and controlled at 155–160°C. After 24 hr, a viscous but stirrable dope existed which set to a red-brown brittle glass at room temperature. The mass was dissolved in 50 ml CH_2Cl_2, then diluted with 125 ml acetone and the solution precipitated with stirring into 1 liter of methanol. The resulting yellow solids were filtered, washed with methanol, and dried; the yield was 25 g, 70% conversion.

ANAL. Calcd for C_8H_6: C, 94.1%; H, 5.9%. Found: C, 94.0%; H, 5.8%.

Filtrates from the above were stripped off at 70–90 mm. A dark, gummy resin remained which was swirled with 35 ml acetone, then centrifuged. Pale yellow solids (TPB) remained (see below). The liquors were precipitated in 40 ml methanol giving rise to 4 g canary-yellow solids upon drying (11% conversion).

The methanolic precipitation liquors were again stripped of solvent. The remaining tar was taken up in 10 ml acetone. Some whitish solids remained insoluble and were filtered out and combined with solids TPB above. The liquors, if now poured into methanol, gave rise only to a sticky tar (III), 1 g, no solids.

Combined solids TPB easily recrystallized from a hot acetone solution to form large pale-yellow crystals (0.3 g), mp 178–179°C. Infrared and NMR (A-60 proton) spectra compared to known material clearly showed this material to be 1,3,5-triphenylbenzene.

Polymerization Using $RhCl[(C_6H_5)_3P]_3$

This initiator was prepared by the method of Wilkinson.[8] When dissolved (0.3 g) in 20 ml of phenylacetylene, a clear wine-red solution formed. Heat evolved mildly at first. Cooling was briefly required to maintain the temperature below 70°C. A pronounced tendency exists for the reaction to run out of control to the monomer boiling point. After 16 hr at 60°C the reaction mixture was dissolved in 30 ml of a 1:1 (v/v) mixture of methylene chloride and acetone. This solution was precipitated in methanol to give 10.6 g of tan solids, type II.

Oligomerization of Phenylacetylene

RhCl $[(C_6H_5)_3P]_3$, 50 mg, was placed in a 50 ml flask under nitrogen. Phenylacetylene, 8 ml, was injected whereon a clear wine-red solution formed. Heat evolved but under these conditions the temperature did not rise above 30–35°C. On standing overnight, a mass of crystals formed in the syrupy reaction mixture. (An improved yield of crystals is obtained by keeping the initial wine-red solution at 0–10°C for 2 days.) These crystals were distilled-sublimed under vacuum into a goose-neck (3 g), then recrystallized from cyclohexane as pale yellow needles (IV), mp 99°C. The residue from this distillation was dissolved in about 10 ml acetone, and the solution precipitated in methanol to give 2.6 g of yellow solids. By extraction with diethyl ether, two fractions were obtained from these yellow solids which had weights (vapor·phase osmometry) of 430 and 925.

The yellow needles (IV) had a molecular weight of 204 as revealed by the mass of the parent molecular ion. The compound takes up 3 moles of hydrogen (71 g compound per gram H_2) giving rise to colorless white crystals, m.p. 54-5. These latter were shown by proton NMR and infrared spectra to be 1,4-diphenylbutane. The proton NMR spectrum of IV consisted of a narrow aromatic cluster centered at 2.66 τ and an AB quartet centered at 3.30 τ, $J = 17$ cps, chemical shift $\delta = 27$ cps. This proves IV to be 1,4-diphenylbutenyne. The *trans* isomer is a known compound, mp 99°C, the crystal structure having been determined by x-ray diffraction.[9] The *trans* nature is further indicated by a strong infrared band at 10.4 μ.

Deuterated Polymers

$C_6H_5C{\equiv}CD$ was prepared by base-catalyzed exchange of $C_6H_5C{\equiv}CH$ with D_2O by Dr. V. W. Weiss. Corresponding polymers of I-A, I-C, and III were prepared. The C-D stretching band appears at 4.45 μ. The band cluster seen in the 11.0–11.5 μ for the regular protonated polymers is missing. A new band appears at 13.65 μ.

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α-Trifluoromethyl Vinyl Acetate. II

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Synopsis

Low conversion, low molecular weight homopolymers of α-trifluoromethyl vinyl acetate have been obtained by pyridine initiation and also by employing very large amounts of benzoyl peroxide. Since allylic hydrogens are not present, it appears that the limiting factor in the polymerization of isopropenyl esters is a slow rate of chain growth rather than degradative chain transfer. Copolymerization of the fluoromonomer (M_2) with vinyl acetate (M_1) yields values of $r_1 = 0.25$ and $r_2 = 0.20$, and for the fluoromonomer values of 0.069 and 1.51, respectively, for Q and e. Whereas ultraviolet initiation of equimolar mixtures of α-trifluoromethyl vinyl acetate and vinyl acetate yields low molecular weight copolymers, diisopropyl percarbonate-initiated room temperature bulk copolymerizations and emulsion copolymerizations yield polymers of high $\overline{\mathrm{DP}}$. Differential thermal analysis of an equimolar copolymer of vinyl acetate and the fluoromonomer surprisingly yields a sharp endotherm reminiscent of crystalline polymers. The unhydrolyzed copolymers in acetone and the alcoholyzed copolymers in 0.1N alkali exhibit Huggins k' values of 0.3–0.4. Like ordinary poly(vinyl alcohol), the polyfluoroalcohols lose viscosity in dilute alkali due to retrograde aldol condensations. The solubilities of the polyfluoroalcohols, together with their thermal behavior, NMR spectrum, polarized infrared spectrum, refractive index, abilities to form visible polarizers, and other properties are also described.

Introduction

Several years ago[1] we synthesized α-trifluoromethyl vinyl acetate hoping that replacement of the allylic hydrogens of isopropenyl acetate might prevent degradative chain transfer during polymerization. We were unable to prepare the homopolymer, but the monomer readily copolymerized with a variety of vinyl monomers including styrene. At that time we also described the preparation and some of the properties of the polyfluoro-alcohols obtained by alcoholysis of vinyl acetate–α-trifluoromethyl vinyl acetate copolymers.

This paper will report on homopolymerization, in more detail on copolymerization with vinyl acetate, and on the properties of vinyl acetate copolymers and the derived polyols.

Homopolymerization

In our previous work,[1] using ultraviolet light, ionic, and relatively mild free-radical initiating conditions, we were unable to obtain poly(α-trifluoromethyl vinyl acetate). We have continued to work on the homopolymerization of this monomer. Sodium naphthalene and the conditions employed for the anionic polymerization of styrene[2] failed to yield polymer. Pyridine, which is used for the homopolymerization of maleic anhydride,[3] did produce some results. When 2.0 g of α-trifluoromethyl vinyl acetate was treated with 0.5% pyridine under nitrogen at 70°C for 6 days, a brown oily layer precipitated out of the bulk monomer. This phase was separated and purified by several reprecipitations from acetone into water (yield, 0.5 g). Casting this material from acetone on a AgCl disk for an infrared spectrum (Fig. 1) yielded a brown, solid, coherent film. When 2.0 g of the monomer was treated with 10% benzoyl peroxide and heated in a sealed, evacuated tube at 70°C for 8 days, the viscosity underwent a slight increase, and a low yield (30%) of a white, solid, low $\overline{DP}$ polymer was obtained upon precipitation into hexane. The infrared spectrum (also recorded in Fig. 1) showed carbonyl and C-F stretching absorptions similar to those of the pyridine polymer but there were numerous minor differences. Analysis (Clark Microanalytical Laboratory, Urbana, Illinois) of the benzoyl peroxide-initiated polymer gave a fluorine content of 31.66% which is below the theoretical value of 36.99%, but considering the very low molecular weight and high end-group content, the result is not too surprising.

The polymerization behavior of α-trifluoromethyl vinyl acetate is reminiscent of isopropenyl acetate,[4,5] which yields low molecular homopolymers under normal conditions of free-radical initiation when large amounts of initiator are used. Since high polymers of isopropenyl acetate are formed at higher pressures,[6] it would seem that degradative chain transfer is not the limiting factor. Walling and Pellon[7] have shown with allyl acetate that pressure has little effect on the competition between chain growth and chain transfer. With isopropenyl acetate, therefore, chain growth is probably slow and termination occurs before appreciable chain growth has occurred. The similarity in the polymerization behavior of α-tri-

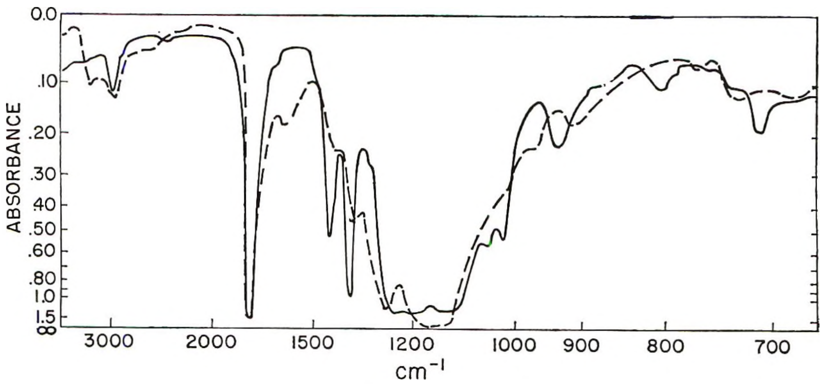


Fig. 1. Infrared spectrum of poly(α-trifluoromethyl vinyl acetate) (- - -) obtained from pyridine initiation; (——) obtained from benzoyl peroxide initiation.

fluoromethyl vinyl acetate, in which the allylic hydrogens have been replaced by fluorine which undergo essentially no transfer reactions, certainly supports the view that degradative chain transfer is not the chain length-determining factor for isopropenyl esters.

Copolymerization

The copolymerization of α-trifluoromethyl vinyl acetate and vinyl acetate has been studied quantitatively. Bulk copolymerizations were carried out in sealed evacuated tubes at 70°C. The copolymers were isolated by precipitation into hexane and purified by reprecipitation from acetone into hexane. Pertinent information is presented in Table I and the copolymerization curve in Figure 2. As the amount of the fluoromonomer in the feed increases, rates of copolymerization and the molecular weights of the copolymers, as indicated by viscosity, drop rapidly.

TABLE I

Copolymerization of α-Trifluoroethyl Vinyl Acetate (M_2) and Vinyl Acetate (M_1)

Monomer 2, g	Monomer 1, g	M_2[a]	AIBN, g	Time, min	Yield, g	F, %	m_2[b]
0.7787	3.8721	0.101	0.0093	35	0.23	13.93	0.253
2.3167	3.0028	0.301	0.0106	95	0.40	20.30	0.405
3.0791	1.7266	0.498	0.0096	170	0.24	23.74	0.501
3.5985	0.8630	0.700	0.0089	220	0.25	26.25	0.579
7.3020	0.4800	0.896	0.0130	720	0.30	28.80	0.659

[a] Mole fraction of monomer 2 in the feed.

[b] Mole fraction of monomer 2 in the initial copolymer.

Fitting the best theoretical curve to the data leads to values of r_1 = 0.25 and r_2 = 0.20. Following the Alfrey-Price[8,9] scheme for monomer reactivity factors and using values of $e_1 = -0.22$ and $Q_1 = 0.026$ for vinyl acetate,[10] we arrive at values for the resonance factor Q and for the electrical factor e of 0.069 and +1.51, respectively, for α-trifluoromethyl vinyl acetate. These results agree with our predicted behavior,[1] based on a series of qualitative copolymerization results, i.e., that this monomer should have a low reactivity and a fairly positive double bond from CF_3 induction effects.

Bulk copolymerization of vinyl acetate and α-trifluoromethyl vinyl acetate initiated by ultraviolet light at somewhat above room temperature lead to low molecular weight copolymers. Room temperature bulk copolymerizations employing diisopropyl percarbonate as catalyst and certain emulsion recipes lead to copolymers of reasonably high $\overline{DP}$. Typical conditions are described in Table II together with dilute solution viscosity data.

As noted previously,[1] copolymers of vinyl acetate and α-trifluoromethyl vinyl acetate, unlike poly(vinyl acetate), swell but do not dissolve in the

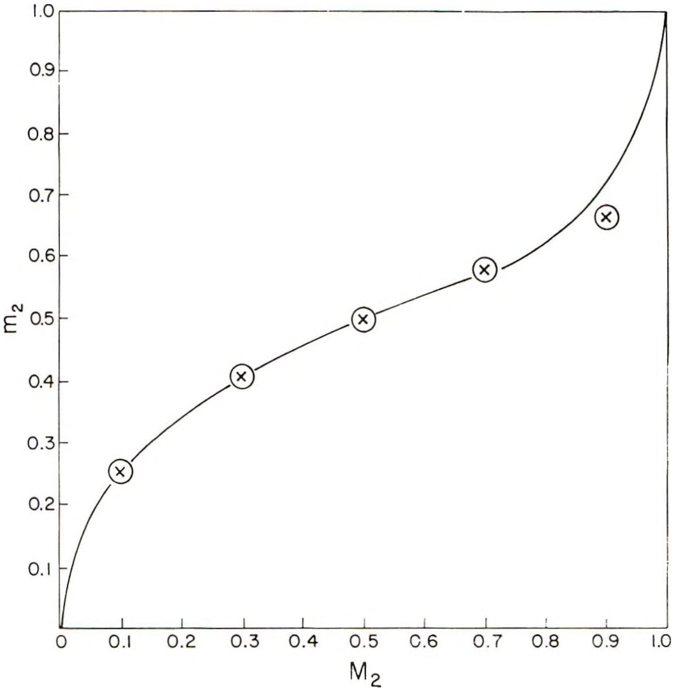
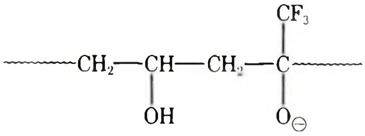


Fig. 2. Copolymerization plot of α-trifluoromethyl vinyl acetate (M_2) and vinyl acetate (M_1).

lower alcohols. In spite of this, alkoxide-catalyzed alcoholysis proceeds smoothly and to completion.

The Huggins[11] k' values for the unhydrolyzed copolymers in acetone and for the alcoholyzed copolymers in $0.1N$ NaOH fall in the range 0.3–0.4 and are in line with the values usually obtained for flexible copolymers in thermodynamically good solvents. Even though the hydrolyzed copolymer must dissolve and exist in $0.1N$ sodium hydroxide as the polyalkoxide,



$$\sim\sim CH_2-\underset{OH}{CH}-CH_2-\overset{CF_3}{\underset{O^{\ominus}}{C}}\sim\sim$$

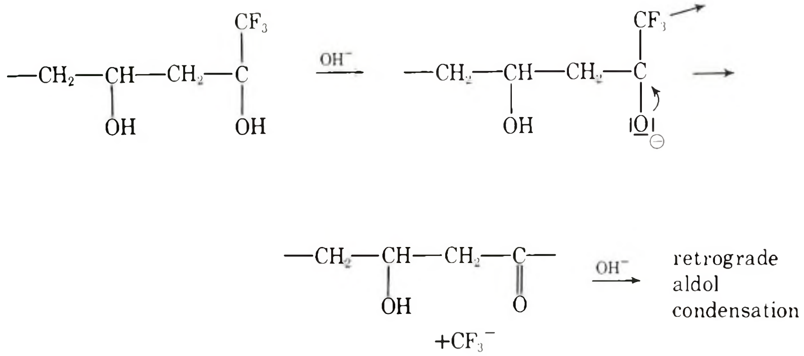
polyelectrolyte behavior is not observed, probably because of the high level of alkali which washes out the polyelectrolyte effect. Base titrations of the hydrolyzed equimolar copolymer under various conditions and attempts to interpret the results have met with failure.

Analysis of the alcoholyzed copolymer from an equimolar ultraviolet initiated copolymerization gave a value of 35.44% F compared to 36.5% predicted by copolymerization data. When the alcoholyzed copolymer [CF_3-substituted poly(vinyl alcohol)] is allowed to stand or is heated in

TABLE II
Copolymerization of Equimolar Mixtures of Vinyl Acetate and α-Trifluoromethyl Vinyl Acetate

No.	Polymerization Conditions	Purification	Alcoholysis	[η] (25°C)	Huggins k'
1	Vinyl acetate, 0.86 g, fluoro monomer, 1.54 g, sealed evacuated tube, 2 in. from a G.E. AH-4 lamp, 17 hr at ~50°C	Copolymer was reprecipitated from acetone into hexane	Methanol and sodium methoxide at reflux	0.15 in both 0.1N NaOH and methanol	—
2	Vinyl acetate, 3.44 g, fluoro monomer, 6.16 g, diisopropyl percarbonate, 0.1 g, room temperature, under N_2, 60 hr	Copolymer was reprecipitated from acetone into hexane	—	0.69 in acetone for the unhydrolyzed copolymer	0.36
3	Vinyl acetate, 3.44 g, fluoro monomer, 6.16 g, $(NH_4)_2S_2O_8$, 0.105 g, H_2O, 20.75 g, $NaHSO_3$, 0.042 g, Dupanol WAQE, 0.8 g, emulsion tumbled in soda pop bottle for 3 hr at 45°C under N_2	Latex was freeze dried and the copolymer reprecipitated from acetone into H_2O	Methanol and sodium methoxide at reflux	1.82 in 0.1N NaOH	0.33
				0.89 in acetone for the unhydrolyzed copolymer	0.30

dilute aqueous alkali solution, there is a significant loss in viscosity. This may result from the reaction scheme (1).



(1)

However, after isolation of the above alkali-treated copolymer by acidification, analysis shows a small increase in the fluorine content (38.12%) and the only difference in the infrared spectrum is a slight increase in the small carbonyl stretching band which was present initially.[1] Since the trifluoromethyl-substituted poly(vinyl alcohols) have the same ultraviolet absorption spectrum as normal poly(vinyl alcohols),[12] indicating the presence of carbonyl moieties, we conclude that degradation in alkali of the former is analogous to that of poly(vinyl alcohol) and results from normal retrograde aldol condensations and not from retrograde aldol condensations dependent on the initiating reaction outlined above.

Some years ago, we observed that poly(vinyl trifluoroacetate)[13] appeared fibrous in nature and that x-ray diffraction analysis of a highly oriented specimen yielded a fiber diagram with numerous meridial diffractions and clearly discernible layer lines. At the time we concluded that these properties resulted from substituion of CH_3 by CF_3 and were not the result of any regular spatial geometry. This conclusion was arrived at because all conversions of poly(vinyl trifluoroacetate) to poly(vinyl acetate) under conditions which could not stereochemically invert the carbon backbone, yielded the same familiar, amorphous, poly(vinyl acetate) with its diffuse x-ray diffraction pattern. At the same time, it was difficult to understand why substitution of CH_3 by CF_3 should produce such a profound change in both physical appearance and x-ray diffraction results since, if anything, CF_3 being larger should result in poorer packing and a lower cohesive energy density.

We have now observed that vinyl acetate–α-trifluoromethyl vinyl acetate copolymers prepared from equimolar monomer mixtures (emulsion) are fibrous in appearance after precipitation into hexane (see Table II) and on differential thermal analysis (with duPont Model 900 differential thermal analyzer) yield thermograms (Fig. 3) which are characteristic of crystalline polymers. Annealing the 1:1 copolymer, at 45°C for 1 hr results in a sharpening of the apparent first order phase endotherm at 49°C and a distinct difference in the heat capacities of the solid and molten

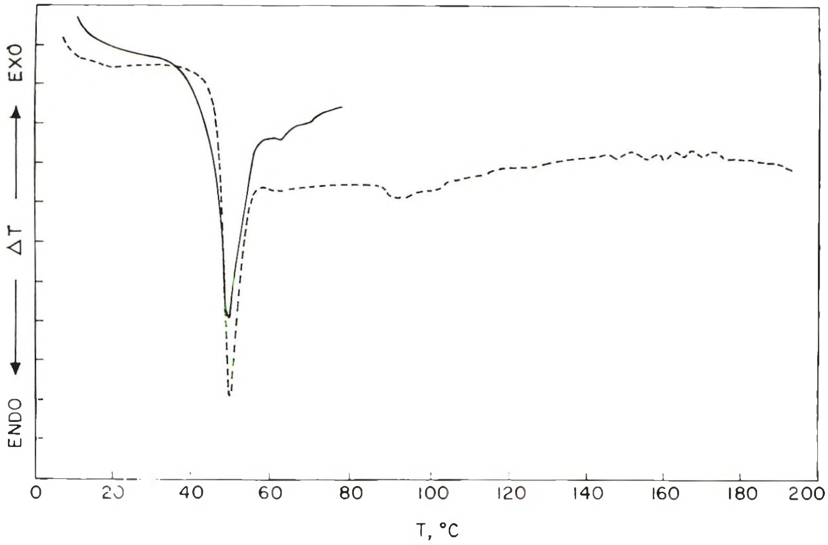


Fig. 3. Differential thermal analysis of equimolar vinyl acetate–α-trifluoromethyl vinyl acetate copolymer: (——) copolymer, no additional treatment; (- - -) after annealing at 45°C for 1 hr cooling slowly under N_2, and rerunning. Sample was fibrous and heating rate was 10°C/min.

phases. Preliminary x-ray analysis failed to support the apparent crystallinity observed by thermal analysis, but we intend to pursue this further. Stretching films of this copolymer results in marked fibrillation, completely unlike poly(vinyl acetate). At the same time, infrared dichroism measurements on oriented specimens, show little if any dichroism for the various infrared absorption bands. In short, the introduction of CF_3 groups into vinyl ester polymers appears to exert a remarkable effect on their physical properties. It now behooves us to see if copolymerization of α-trifluoromethyl vinyl acetate with other monomers, which under normal free-radical initiation, yield atactic, noncrystalline homopolymers might not result in some rather unusual results.

Trifluoromethyl Substituted Poly(vinyl Alcohols)

These polymers, obtained by alcoholysis of the corresponding vinyl acetate–α-trifluoromethyl vinyl acetate copolymers, have been described previously.[1] The polyol obtained from a low $\overline{DP}$ copolymer (see Table II and ref. 1) is alcohol-soluble. High molecular weight trifluoromethyl-substituted random copolymers, however, have the following solubility characteristics: soluble in dilute alkali, dimethyl sulfoxide, 3/2 pyridine–water, and hexafluoroisopropanol; swollen in methanol, pyridine, methanol–pyridine, and cyclohexanone; insoluble in water, chloroform, dimethylformamide, trimethylamine, and acetone.

Differential thermal and thermomechanical analyses place the glass transition for the equimolar polyol on repeated runs somewhere between

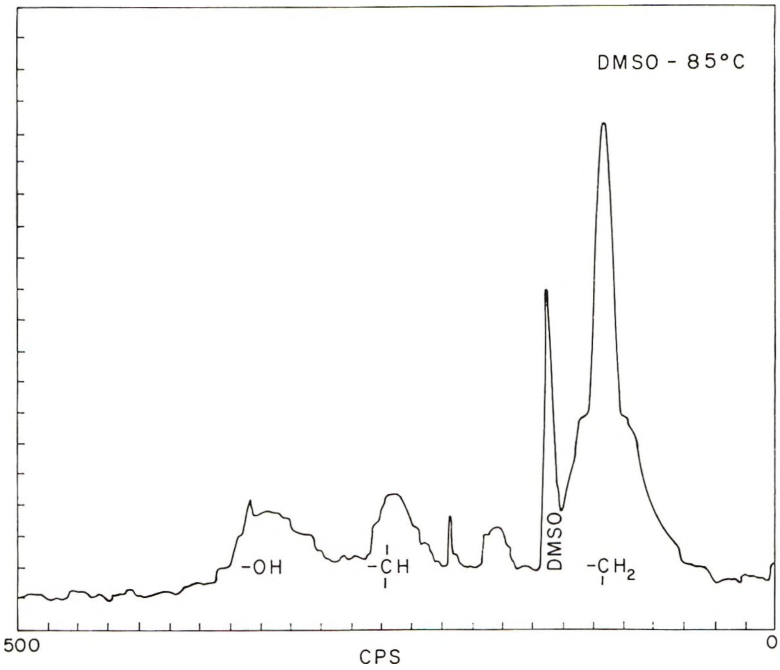


Fig. 4. Nuclear magnetic resonance spectrum at 85°C (10% in DMSO) of equimolar hydrolyzed copolymer from low $\overline{\mathrm{DP}}$, ultraviolet light-initiated copolymer.

46 and 49°C which is considerably below the T_g of 85°C for unmodified poly(vinyl alcohols). Depending on the particular sample and its past history, there seem to be metastable crystalline forms that result in first-order endothermic transitions in the range of 100–150°C. A fairly reproducible first-order endotherm is observed at 220°C.

The NMR spectrum of a low $\overline{\mathrm{DP}}$ equimolar polyol copolymer in deuterodimethyl sulfoxide was measured by using a Model A-60 Varian spectrophotometer. The spectrum shown in Figure 4, integrates well for the expected structure.

A polarized infrared spectrum on an oriented film of the equimolar polyfluoroalcohol shows little or no parallel dichroism for OH stretching (3350 cm^{-1}), perpendicular dichroism for CH stretching (2930 cm^{-1}), perpendicular dichroism for bands at about 1225 and 1275 cm^{-1}, perpendicular dichroism for CF stretching (1100 to 1200 cm^{-1}), and perpendicular dichroism for C—C stretching at 845 cm^{-1}.

Besides being water-insoluble and soluble in dilute alkali to yield polyalkoxide type solutions, the trifluoromethyl-substituted polyvinyl alcohols show some other interesting properties. Introduction of the CF$_3$ groups has reduced the refractive index to $n_D^{25} = 1.435$, considerably below the range of 1.49–1.53 reported for ordinary PVA. Films of these fluoro polyols, when cast on glass from hexafluoroisopropanol, show such remarkable adhesion to glass that all films used in this study had to be cast on polyethylene. The films of these polyols are much harder to ignite and burn more slowly than ordinary poly(vinyl alcohol).

Efficient iodine polarizers can be prepared by treating oriented films of these polyols with aqueous KI_3 and like typical PVA–iodine polarizers they can be borated. They are slightly less neutral and more bluish in appearance than the ordinary polarizer and show maximum dichroism at about 600 mμ. Attempts to prepare polyvinylene-type polarizers by treating oriented films with moist hydrogen chloride gas, followed by baking, have been quite unsuccessful; only a very small degree of dichroic stain being obtained. These polyfluoroalcohols resist dehydration to form conjugated double-bond systems since in the equimolar copolymer, half of the hydroxyl groups are much less susceptible to oxonium ion formation and subsequent dehydration due to the electron-withdrawing effect of the α-CF_3 group. These polyfluoroalcohols readily form polyacetals and a variety of these have been prepared.

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Polymerization of Acrylonitrile by V^{5+}–Lactic Acid System in Aqueous Sulfuric Acid

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Synopsis

Kinetics of polymerization of acrylonitrile by the redox system V^{5+}–lactic acid in sulfuric acid at 20–35°C was studied. Oxidation of lactic acid by V^{5+} in the absence of monomer was also carried out under identical conditions. The rates of polymerization, V^{5+} disappearance and the chainlengths of polyacrylonitrile were measured. From the results it is concluded that the polymerization reaction is initiated by an organic free radical arising from the V^{5+}–lactic acid reaction with termination by V^{5+} ions. Mutual termination of active polymer radicals does not appear to operate under the conditions studied. The various rate parameters were evaluated.

INTRODUCTION

Vanadate (V^{5+}) in acid solutions was found to be a powerful oxidant for both organic and inorganic compounds[1–6]. It was reported that V^{5+} in presence of reducing agents such as hydroxy acids, ketones, glycols etc., initiated vinyl polymerization. V^{5+} was also employed[7–9] as initiator of graft polymerization in systems of polymer backbones containing groups such as —CHO, —CO or —NH_2 (capable of being oxidized to free radicals on the backbone) and a suitable monomer (which is grafted). No detailed kinetic study has been made so far with V^{5+} + reducing agent system as initiator of vinyl polymerization. However, we have published a preliminary report on this system.[10] The results of kinetics of polymerization of acrylonitrile by V^{5+}–lactic acid in sulfuric acid in the temperature range 20–35°C are reported in this paper. From the experimental observations a suitable reaction scheme is suggested and the kinetic parameters evaluated.

EXPERIMENTAL

Reagents

Acrylonitrile (American Cyanamid) was freed from inhibitor by treating with alkali, washed with orthophosphoric acid, washed with water, dried over anhydrous $CaCl_2$, and distilled under reduced pressure in an atmosphere of nitrogen; the middle fraction of the second distillate was collected and stored at 5°C. Ammonium metavanadate (A.R.,), lactic acid (A.R., M & B), sodium bisulfate (Riedel), sulfuric acid ($\sim 18M$; A.R., Basynth, India), and perchloric acid (60% A.R., Baker and Adamson) were used as received. Water, distilled twice over alkaline permanganate and deionized by passing through a column of Biodeminrolit resin (Permutit Co., U.K.) was used to prepare all solutions. The nitrogen (Indian Oxygen Co., Madras) used to deaerate the experimental systems was freed from oxygen by passage through five columns of Fieser's solution, a column of saturated lead acetate solution, and finally a wash bottle containing distilled water.

Preparations and Estimations

V^{5+} solution ($\sim$0.4N in $\sim$4.0M H_2SO_4) was prepared by suspending ammonium metavanadate (4.7 g) in distilled water (25 cc) and adding with stirring 75 cc of 10N sulfuric acid. The concentration of V^{5+} in the experimental systems was determined by vanadometry.[11] An aliquot (2 cc) of V^{5+} stock solution was run into a known excess of standard ferrous ammonium sulfare (0.05N, 20 cc) solution; the excess ferrous was titrated with standard V^{5+} (1×10^{-2}–2×10^{-2} N) solution using Knop's indicator [diphenylamine 0.1% in concentrated (36.0N) sulfuric acid] followed by addition of 5 cc of 80% orthophosphoric acid to a violet endpoint. The V^{5+} solution (titrant) itself was standardized by titration with standard ferrous solution (0.05N) with the use of Knop's indicator. Acidity in the V^{5+} stock solution was determined by titrating an aliquot of the former with standard sodium hydroxide (0.60N) with bromocresol green as indicator. Aqueous lactic acid ($\sim$1N) was standardized with standard sodium hydroxide solution (0.60)N, phenolphthalein being used as indicator. Sodium perchlorate (6.0N) was prepared by neutralizing sodium carbonate (6.0N; A.R., B.D.H.) with perchloric acid (6.0N).

Kinetic Measurements

The reaction tubes used for the experiments were Pyrex glass tubes (1 × 6 in.; 80 cc capacity) fitted with a B24 socket and cone and fitted with an inlet and outlet tube for nitrogen. The system (lactic acid, 0.05M; H_2SO_4, 0.5M; acrylonitrile, 0.7539M; sodium bisulfate, 0.47 M) in aqueous solution (20 cc total volume) was taken in the reaction tube and thermostatted at 30°C. A wash bottle containing an aqueous solution of acrylonitrile of the same concentration as in the reaction tube was interposed between the nitrogen train and the reaction tube (to avoid loss of monomer during deaeration). Nitrogen freed from O_2 by passage through Fieser's solution was bubbled through the solution for 20–30 min, and V^{5+} solution (0.4N, 1.5 cc) was then added. The tube was then sealed with rubber gaskets to ensure maintenance of an inert atmosphere. Polymerization as indicated by the appearance of turbidity started without any induction period. At the end of the reaction time (ca 30 min), the reaction tube was opened, and a known excess of ferrous ammonium sulfate solution (0.04N; 20 ml) was added to stop the reaction. The polyacrylonitrile was filtered from the reaction mixture by using a glass filter (I.G. 3, Jena), washed several times with distilled water, and dried at 70°C to constant weight. The rate of polymerization R_p was then computed. The filtrate was titrated with standard V^{5+} solution (1×10^{-2} N) with Knop's indicator, and the rate of V^{5+} disappearance, $-R_v$, was evaluated from the titer values. Experiments were conducted to study the effect of time, [M], [lactic acid], [V^{5+}], [H_2SO_4], [HSO_4^-], μ, ionic strength and temperature on both R_p and $-R_v$. Experiment under similar conditions was repeated in the absence of monomer with a view to study oxidation of lactic acid by V^{5+}, and $-R_v$ was determined by titrimetry. Oxidation of lactic acid by V^{5+} in perchloric acid was also carried out under the conditions reported in the literature[12] ($1M$ H^+, $3.0M$ μ, 30°C).

Molecular Weights $\bar{M}_v$

Molecular weights $\bar{M}_v$ of purified polyacrylonitrile samples were determined by viscometry. A solution of the polymer (0.1%) in dimethylformamide (Baker analyzed) filtered through a glass filter (IG_4) was placed in a suspended-level dilution viscometer (Ubbelohde type, specification D445–46T; flow time of 192 sec for dimethylformamide at 25°C), and the flow times for the polymer solution and solvent were recorded at 25°C. The corrections for shear rate and kinetic energy were not necessary. Intrinsic viscosities for the polymer solutions were determined, and the $\bar{M}_v$ values were evaluated by using the Mark-Houwink equation as given by Stockmayer and Cleland:[13]

$$[\eta] = 2.430 \times 10^{-4} \bar{M}_v^{0.75}.$$

RESULTS AND DISCUSSION

General Features

Thermal or photochemical (diffused day light) polymerization of acrylonitrile by V^{5+} alone was not observed. Oxidations of water and monomer by V^{5+} were also completely absent under experimental conditions. No induction period was observed under deaerated conditions with the V^{5+}–lactic acid initiator system, whereas in undeaerated systems an induction period (~5 min) was usually noticed; it was therefore obvious that polymerization was initiated by free radicals. The rate of polymerization as well as the rate of V^{5+} disappearance were found to be the same in the presence and absence of nitrogen, provided the period of induction was not neglected. A steady-state rate was reached within 10 min. Polymerization experiments were conducted at constant hydrogen ion concentration $[H^+] = 0.5M$ and ionic strength ($\mu = 1.0M$) and at 20, 30, and 35°C.

Rate of Polymerization

A regular increase in rate was noticed with an increase in monomer concentration (0.60 to $1.0M$), R_p versus [M^2] plots being linear with zero intercept (Fig. 1) and therefore the order of [M] was two. The rate was in-

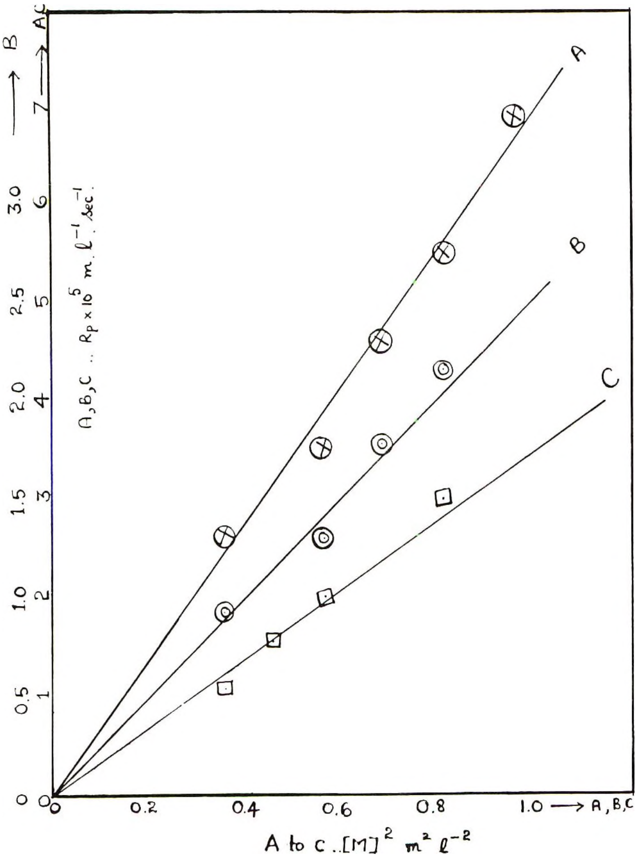


Fig. 1. Variation of R_p with $[M]^2$ at $[H_2SO_4] = 0.5M$, and $\mu = 1.0M$. (*A*) [Lac] = 0.1872*M*, $[V^{5+}] = 0.03832N$, 30°C; (*B*) [Lac] = 0.0521*M*, $[V^{5+}] = 0.05736N$, 35°C; (*C*) [Lac] = 0.0632*M*, $[V^{5+}] = 0.03479N$, 35°C.

versely proportional to $[V^{5+}]$ (3.0×10^{-2}–$9 \times 10^{-2}N$), $1/R_p$ versus $[V^{5+}]$ plots being linear with intercept on the ordinate (Fig. 2). The rate increased linearly with lactic acid concentration [Lac] (0.04 to 0.2*M*); linear plots of log R_p versus log [Lac] with unit slopes as well as R_p verus [Lac] plots with zero intercepts (Fig. 3) indicated that the order with resepct to [Lac] was unity. Dependence of R_p on $[M]^2$, $1/[V^{5+}]$, and [Lac] will be discussed later. The increase of rate with increase of $[HSO_4^-]$ (0.7 to 1.3*M*) as shown in Figure 4 may be understood in terms of the equilibrium (1),[14]

$$VO_2^+ + HSO_4^- \rightleftharpoons VO_2SO_4^- + H^+ \qquad (1)$$

the species $VO_2SO_4^-$ being less active as a terminator; this was also supported by the increase of rate with decrease of $[H^+]$. An increase in $[H_2SO_4]$ (0.2 to 1.5*M*) decreased the rate, which implied that protonated species like $V(OH)_3^{2+}$ or $VO.OH^{2+}$ or sulfate complexes may be either poor initiators or better terminators of polymer chains. The positive salt effect

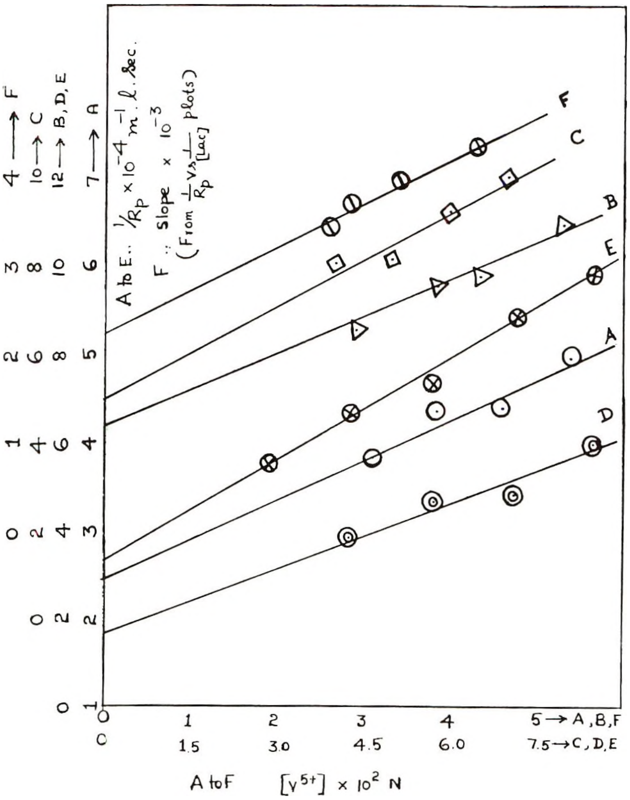
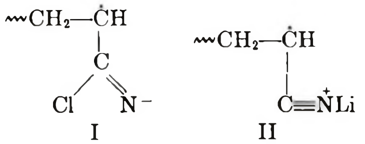


Fig. 2. Variation of $1/R_p$ with [V^{5+}] at [H_2SO_4] = 0.5*M*, μ = 1.0*M*: (*A*) [Lac] = 0.177*M*, [M] = 0.7539*M*, 20°C; (*B*) [Lac] = 0.0505*M*, [M] = 0.9036*M*, 20°C; (*C*) [Lac] = 0.08554*M*, [M] = 0.7539*M*, 20°C; (*D*) [Lac] = 0.09040*M*, [M] = 0.7539*M*, 30°C; (*E*) [Lac] = 0.06165*M*, [M] = 0.7539*M*, 30°C; (*F*) Slope (from Fig. 7. plots *A*, *B*, *D*, *E*) vs [V^{5+}], 30°C.

(4-fold increase) of ionic strength (0.5 to 1.5*M*) on the rates (Fig. 4) may be due to the catalysis of the primary oxidation step (lactic acid–V^{5+}) and or the propagation step [step III, reaction (4) below]. In the first case, as the primary radical formation is enhanced, more primary radicals may be available for initiation. Secondly the monomer (which is polar) may complex with the added salt. Bamford et al.[13] assumed that the acrylonitrile radical —CH_2—$\dot{C}H$—CN was capable of forming complexes with salts such as LiCl, $LiNO_3$, etc., and that the increase in R_p values was due to catalysis of the propagation step by both cation and anions of the salt (I and II, respectively).



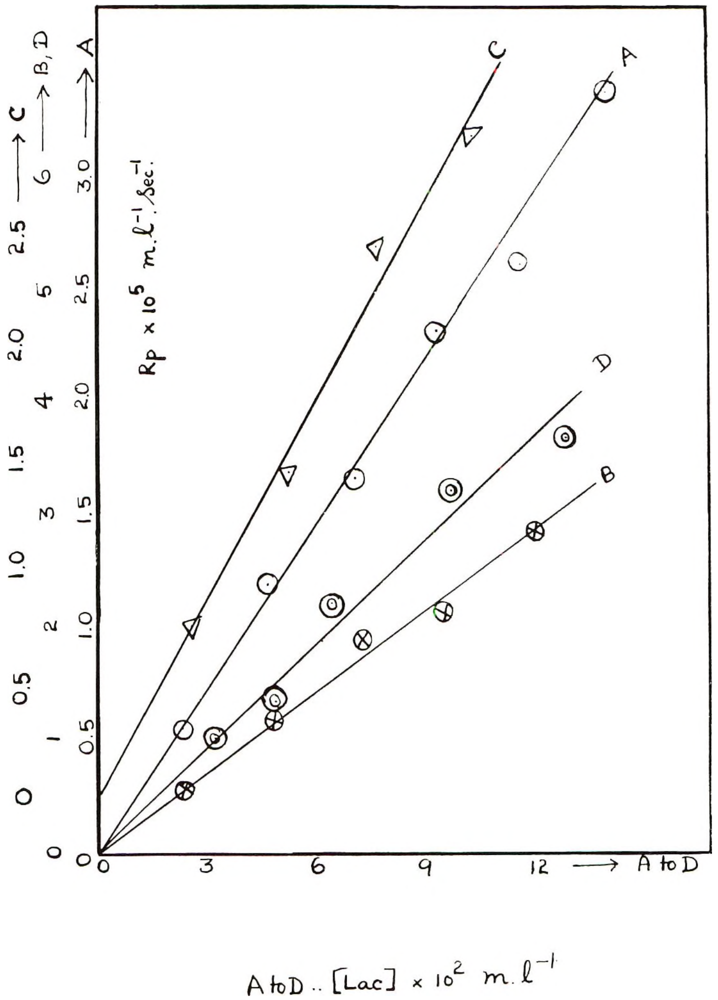


Fig. 3. Variation of R_p with [Lac] at various [V^{5+}] and [H_2SO_4] = 0.5M, μ = 1.0M, and [M] = 0.7539M, 30°C: (A) [V^{5+}] = 0.03414N; (B) [V^{+5}] = 0.04281N; (C) [V^{+5}] = 0.02633N; (D) [V^{+5}] = 0.02779N.

Rate of V^{5+} Disappearance ($-R_v$)

[M] (0.60 to 1.0M) had no effect on the rate. Increasing [V^{5+}] (0.03 to 0.09N) increased the rate, and first-order dependence of rate on [V^{5+}] was concluded from the linear plots of $-R_v$ versus [V^{5+}] (Fig. 5 and 6). An increase in [Lac] (1.5 × 10^{-2} to 20 × $10^{-2}M$) increased the rate; at high [Lac] and temperature (35°C), plots of $-R_v$ versus [Lac] were curved, and the order with respect to [Lac] varied from 0.7 to 0.9. An increase in [H_2SO_4] (0.2 to 1.5M) increased the rate, the plot of $-R_v$ versus [H_2SO_4] being linear with an intercept on the ordinate (Fig. 4). It may be that ~30% of protonated species[1,14] $-V(OH)_3^{2+}$, $VOOH^{2+}$, or sulfato complexes[16] may be reactive (as initiators). Since plots of both $-R_v$ versus

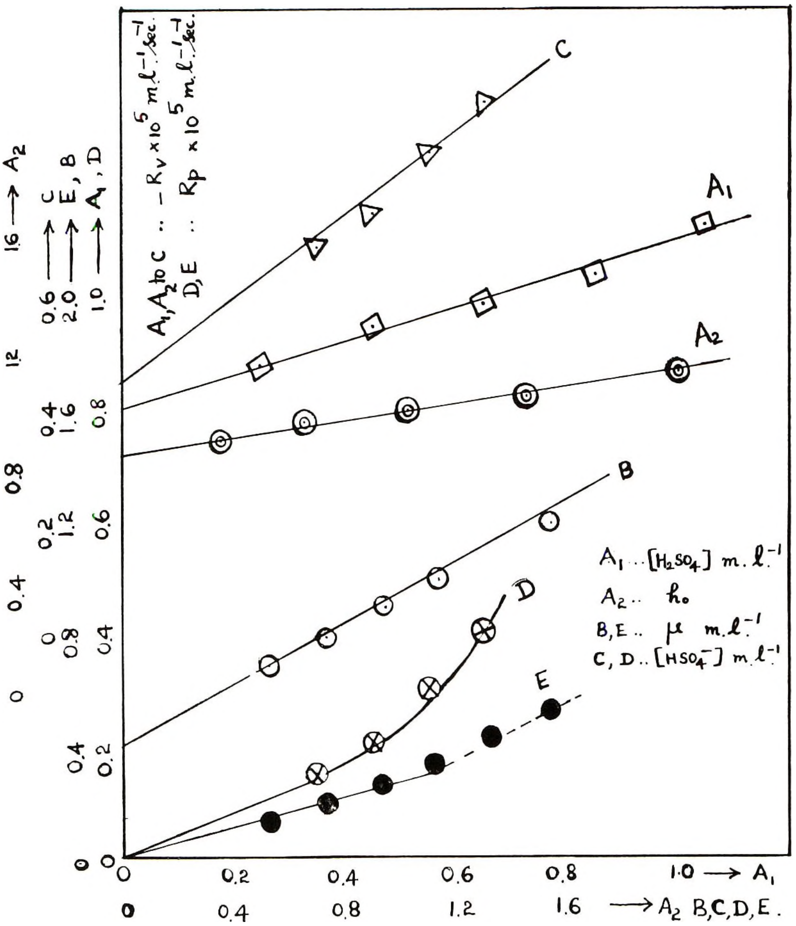


Fig. 4. Variation of rates with $[H_2SO_4]$, μ, and $[HSO_4^-]$ at $[M] = 0.7539M$, 30°C: (A_1), (A_2) variation of $-R_v$ with $[H_2SO_4]$ and with h_0, respectively, $[Lac] = 0.106M$, $[V^{5+}] = 0.02297N$, $\mu = 1.0334M$; (B), (E) $-R_v$ vs. μ and R_p vs μ respectively, $[Lac] = 0.106M$, $[V^{5+}] = 0.03226N$, $[H_2SO_4] = 0.5M$; (C), (D) $-R_v$ vs. $[HSO_4^-]$ and R_p vs. $[HSO_4^-]$, respectively, $[Lac] = 0.09311M$, $[V^{5+}] = 0.03262N$, $[H^+] = 0.5M$, $\mu = 1.33M$.

$[H_2SO_4]$ as well as $-R_v$ versus Hammett acidity function, h_0 were linear, it was not possible to differentiate between $VOOH^{2+}$ and $V(OH)_3^{2+}$ as the reactive species. (The acid-dependent rate evaluated by subtracting the acid-independent rate from the total rate was plotted against $[H_2SO_4]$ or h_0, and both the plots were found to be linear and passing through the origin.) An increase in $[HSO_4^-]$ (0.7 to 1.3M) increased the rate (~43%), indicating that bisulfate or sulfato complex was also active. Increased ionic strength (0.5 to 1.5M) also increased the rate (~2-fold).

Chainlength

The chainlengths n of the polyacrylonitrile decreased (1838 to 397) with

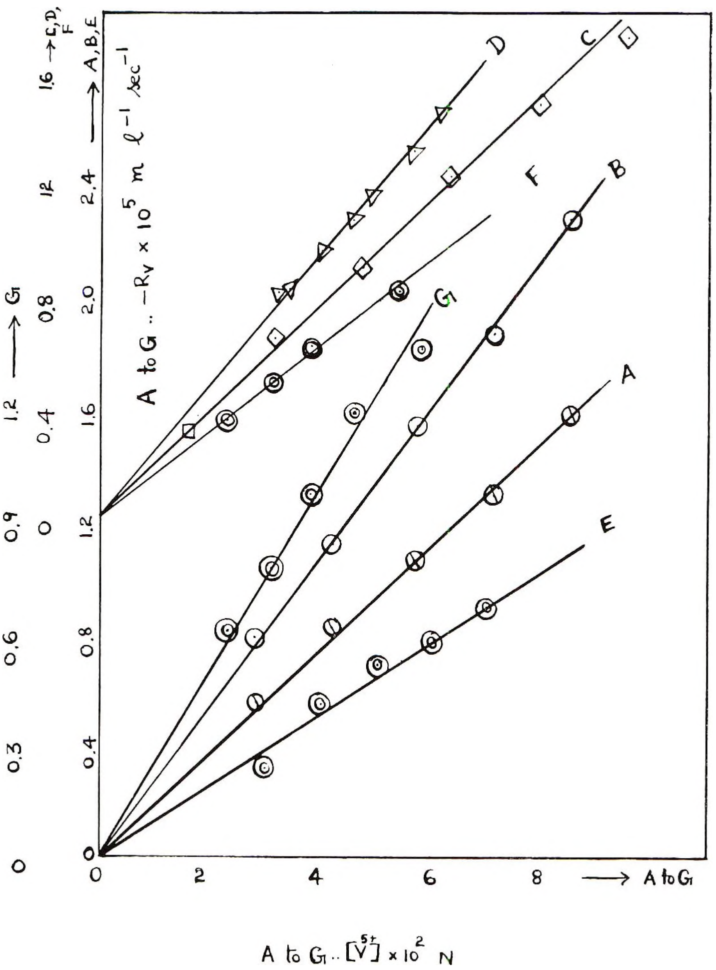


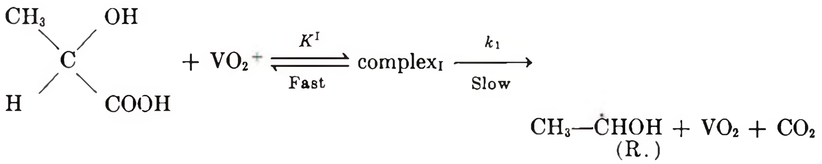
Fig. 5. Variation of $-R_v$ vs. $[V^{5+}]$ at $[H_2SO_4] = 0.5M$, $\mu = 1.0M$, $[M] = 0.7539M$: (*A*) [Lac] = 0.06165*M*, 30°C; (*B*) [Lac] = 0.09040*M*, 30°C; (*C*) [Lac] = 0.06375*M*, 30°C; (*D*) [Lac] = 0.05621*M*, 35°C; (*E*) [Lac] = 0.08554 *M*, 20°C; (*F*) [Lac] = 0.101*M*, 20°C; (*G*) [Lac] = 0.177*M*, 20°C.

increase in $[V^{5+}]$ (2.3×10^{-2} to $5.8 \times 10^{-2}N$) and n values were more or less constant when [Lac] was increased (2.5×10^{-2} to $15.0 \times 10^{-2}M$).

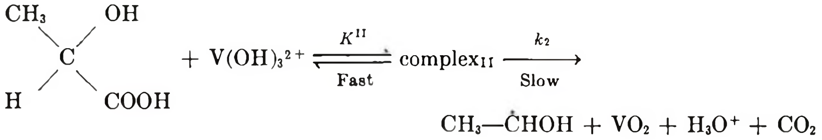
Reaction Mechanism and Rate Law

From the proportionalities obtained between the measurable parameters and the variables the following reaction scheme is suggested involving initiation by the organic free radical produced by the interaction of V^{5+} with lactic acid and termination by V^{5+} ion. Termination by metal ion, it may be mentioned, is not unusual.[17,18]

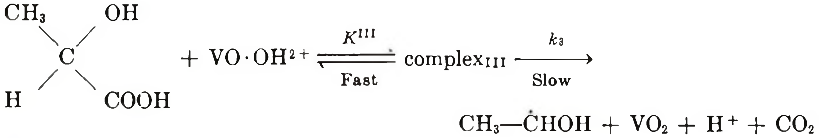
Primary radical production:



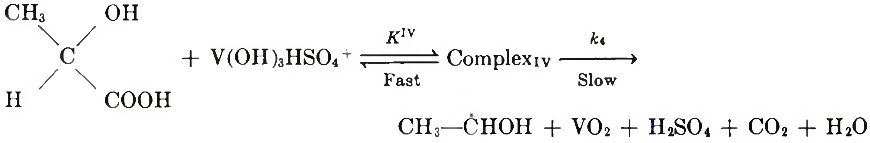
$$\mathrm{CH_3CH(OH)COOH} + \mathrm{VO_2^+} \underset{\text{Fast}}{\overset{K^{\mathrm{I}}}{\rightleftharpoons}} \text{complex}_{\mathrm{I}} \xrightarrow[\text{Slow}]{k_1} \underset{(\mathrm{R}^{\cdot})}{\mathrm{CH_3{-}\dot{C}HOH}} + \mathrm{VO_2} + \mathrm{CO_2} \quad (2)$$



$$\mathrm{CH_3CH(OH)COOH} + \mathrm{V(OH)_3^{2+}} \underset{\text{Fast}}{\overset{K^{\mathrm{II}}}{\rightleftharpoons}} \text{complex}_{\mathrm{II}} \xrightarrow[\text{Slow}]{k_2} \mathrm{CH_3{-}\dot{C}HOH} + \mathrm{VO_2} + \mathrm{H_3O^+} + \mathrm{CO_2} \quad (3)$$



$$\mathrm{CH_3CH(OH)COOH} + \mathrm{VO{\cdot}OH^{2+}} \underset{\text{Fast}}{\overset{K^{\mathrm{III}}}{\rightleftharpoons}} \text{complex}_{\mathrm{III}} \xrightarrow[\text{Slow}]{k_3} \mathrm{CH_3{-}\dot{C}HOH} + \mathrm{VO_2} + \mathrm{H^+} + \mathrm{CO_2} \quad (4)$$



$$\mathrm{CH_3CH(OH)COOH} + \mathrm{V(OH)_3HSO_4^+} \underset{\text{Fast}}{\overset{K^{\mathrm{IV}}}{\rightleftharpoons}} \text{Complex}_{\mathrm{IV}} \xrightarrow[\text{Slow}]{k_4} \mathrm{CH_3{-}\dot{C}HOH} + \mathrm{VO_2} + \mathrm{H_2SO_4} + \mathrm{CO_2} + \mathrm{H_2O}$$

where

$$\mathrm{VO_2^+} + \mathrm{H_3O^+} \overset{K_1}{\rightleftharpoons} \mathrm{V(OH)_3^{2+}} \quad (5)$$

$$\mathrm{V(OH)_3^{2+}} + \mathrm{HSO_4^-} \overset{K_2}{\rightleftharpoons} \mathrm{V(OH)_3HSO_4^+} \quad (6)$$

$$\mathrm{VO_2^+} + \mathrm{H^+} \overset{K_3}{\rightleftharpoons} \mathrm{VO.OH^{2+}} \quad (7)$$

Initiation:

$$\mathrm{R^{\cdot}} + \mathrm{M} \overset{k_i}{\rightarrow} \mathrm{R{-}M^{\cdot}} \quad (8)$$

Propagation:

$$\mathrm{R{-}M^{\cdot}} + \mathrm{M} \overset{k_p}{\rightarrow} \mathrm{R{-}M_2^{\cdot}} \quad (9)$$

$$\mathrm{R{-}M^{\cdot}_{n-1}} + \mathrm{M} \overset{k_p}{\rightarrow} \mathrm{R{-}M^{\cdot}_{n}} \quad (10)$$

Linear Termination:

$$\mathrm{R{-}M^{\cdot}_{n}} + \mathrm{VO_2^+} \xrightarrow{k_{t1}} \text{Polymer} + \mathrm{V^{4+}} \quad (11)$$

$$\mathrm{R{-}M^{\cdot}_{n}} + \mathrm{VO.OH^{2+}} \xrightarrow{k_{t3}} \text{Polymer} + \mathrm{V^{4+}} \quad (12)$$

$$\mathrm{R{-}M^{\cdot}_{n}} + \mathrm{V(OH)_3^{2+}} \xrightarrow{k_{t2}} \text{Polymer} + \mathrm{V^{4+}} \quad (13)$$

Reactions of the Primary Radical with V^{5+}:

$$\left.\begin{array}{l} \mathrm{R^{\cdot}} + \mathrm{VO_2^+} \xrightarrow{k_{01}} \\ \mathrm{R^{\cdot}} + \mathrm{V(OH)_3^{2+}} \xrightarrow{k_{02}} \\ \mathrm{R^{\cdot}} + \mathrm{VO.OH^{2+}} \xrightarrow{k_{03}} \end{array}\right\} \text{Products} + \mathrm{V^{4+}} \quad (14)$$

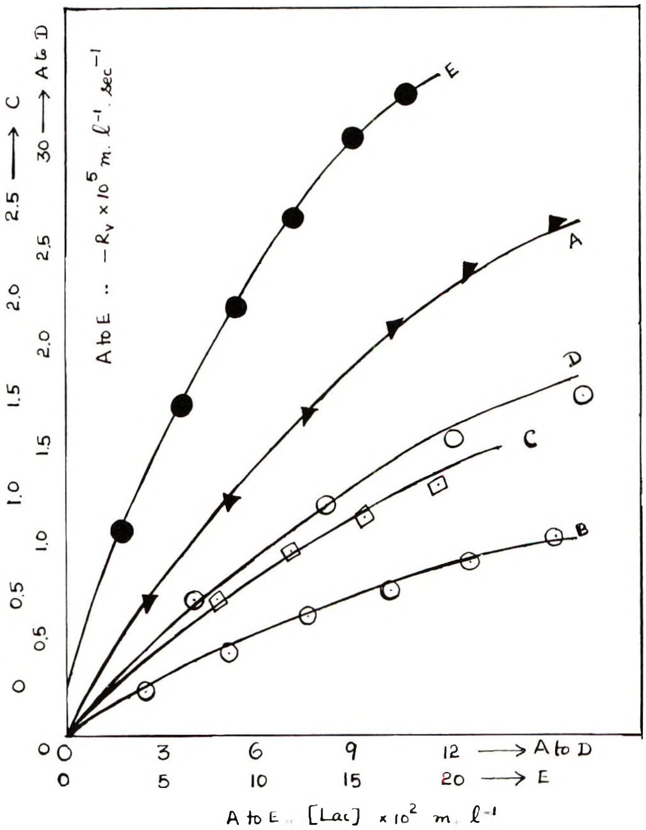


Fig. 6. Variation of $-R_v$ vs. [Lac] at $[H^+] = 0.5M$, $\mu = 1.0M$, and $[M] = 0.7539M$: (A) $[V^{5+}] = 8.090 \times 10^{-2}N$; 30°C; (B) $[V^{5+}] = 2.633 \times 10^{-2}N$, 30°C; (C) $[V^{5+}] = 7.31 \times 10^{-2}N$, 30°C; (D) $[V^{5+}] = 3.262 \times 10^{-2}N$, 35°C; (E) $[V^{5+}] = 4.044 \times 10^{-2}N$, 35°C.

Possible expressions for R_p, $-R_v$, and chainlength n were derived from the scheme presented above. In accord with the usual stationary-state principle for micro and macro free radicals and nondependence of rate constants (k_p and k_t) on chainlengths we have:

$$R_p = (k_p/k_t)\cdot k'[\text{Lac}][\text{M}]^2/\{[\text{M}] + (k_0/k_t)[\text{V}^{5+}]\} \tag{15}$$

$$-R_v = 2k'[\text{Lac}][\text{VO}_2^+] \tag{16}$$

where $k' = k_1K^{\text{I}} + K_3k_3K^{\text{III}}[\text{H}^+]$, $k_1K^{\text{I}} + K_1K^{\text{II}}k_2[\text{H}_3\text{O}^+]$, or $k_1K^{\text{I}} + K^{\text{IV}}k_4K_2K_1[\text{H}_3\text{O}^+][\text{HSO}_4^-]$; $k_t = k_{t1}$ or k_{t2} or k_{t3}; $k_0 = k_{01}$, k_{02} or k_{03}; and

$$n = (k_p/k_t)\cdot[\text{M}]/[\text{V}^{5+}] \tag{17}$$

The dependence of R_p on $[\text{M}]^2$, [Lac], of $1/R_p$ on $[\text{V}^{5+}]$ and 1/[Lac], of $-R_v$ on [Lac], $[\text{V}^{5+}]$ and not on [M], all of which were observed, favored

TABLE I

Rate Parameters for V^{5+}–Lactic acid–Acrylonitrile System in Aqueous Sulfuric Acid

	$k' \times 10^3$, l./mole-sec			k_p/k_t		k_0/k_i	
Temp, °C	From log $a/(a-x)$ vs. time	From $-R_v$ vs. [Lac]	From $-R_v$ vs. $[V^{5+}]$	From $1/R_p$ vs. 1/[Lac]	From $1/R_p$ vs. $[V^{5+}]$	From $1/R_p$ vs. 1/[Lac]	From $1/R_p$ vs. $[V^{5+}]$
20	1.425[a]	0.744	—	—	0.4053	—	13.05
30	2	1.563 4.088[a]	1.50	0.277	0.281	10.96	11.17
35	—	2.365	2.14	—	—	—	—

[a] Value obtained from oxidation experiment.

the above scheme. In the case of mutual termination, the expression for R_p would involve $[M]^{3/2}$, $[V^{5+}]^{1/2}$, and $[Lac]^{1/2}$ terms not realized by us experimentally. $-R_v$ would be dependent on both $[V^{5+}]$ and $[V^{5+}]^2$, again not realized experimentally. In the case of termination by primary radicals, expected nondependence of R_p on [Lac] and $[V^{5+}]$ was not obtained. Therefore mutual termination as well as termination by primary radicals were treated as unimportant reactions.

Evaluation of Rate Constants

The second-order rate constant k' (in the presence of monomer) was obtained from the plots $-R_v$ versus $[V^{5+}]$, $-R_v$ versus [Lac] (from the initial slopes) and log $a/(a - x)$ versus time. The values are presented in Table

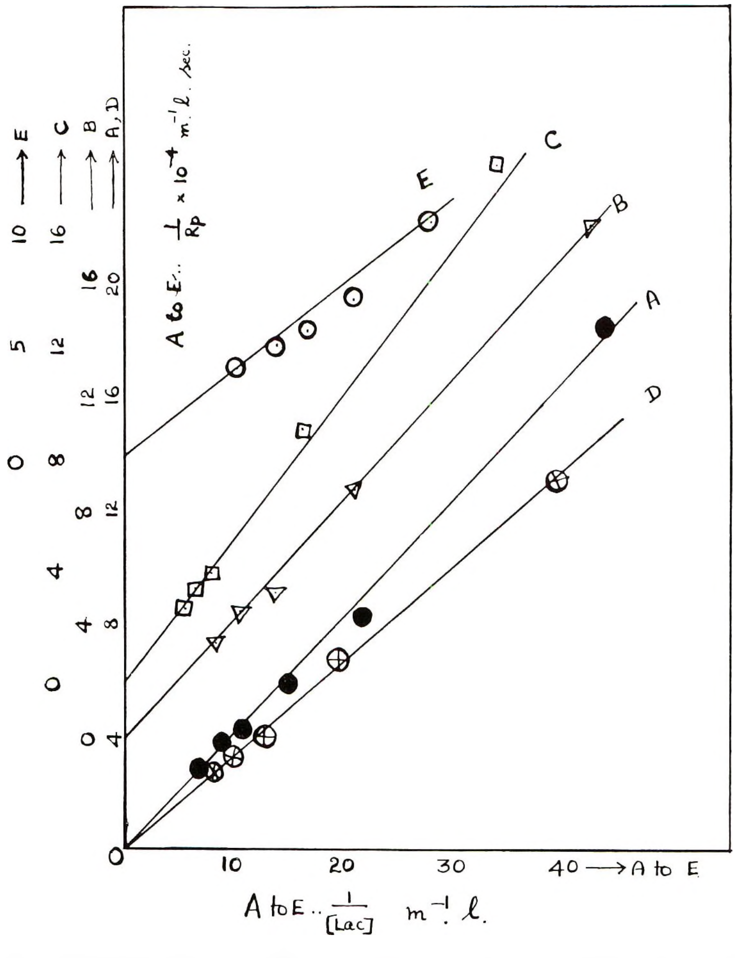


Fig. 7. Variation of $1/R_p$ vs. 1/[Lac] at $[H^+] = 0.5M$, $\mu = 1.0M$, $[M] = 0.7539M$, 30°C: (*A*) $[V^{5+}] = 3.41 \times 10^{-2}N$; (*B*) $[V^{5+}] = 4.28 \times 10^{-2}N$; (*C*) $[V^{5+}] = 8.090 \times 10^{-2}N$; (*D*) $[V^{5+}] = 2.633 \times 10^{-2}N$; (*E*) $[V^{5+}] = 2.84 \times 10^{-2}N$.

I. k_p/k_t and k_0/k_t were evaluated as follows. k_p/k_t and k_0/k_t were evaluated from the plots of $1/R_p$ versus $[V^{5+}]$. The reciprocal of the rate expression for R_p [eq. (15)] and rearranging gives eq. (18),

$$\frac{1}{R_p} = \frac{k_t}{k_p k'[\mathrm{Lac}][\mathrm{M}]} + \frac{k_t(k_0/k_i)[\mathrm{V}^{5+}]}{k_p k'[\mathrm{Lac}][\mathrm{M}]^2} \tag{18}$$

plots of $1/R_p$ versus $[V^{5+}]$ according to eq. (18) were linear (Fig. 3), and (k_0/k_i) from (slope/intercept) × [M] and k_p/k_t from reciprocal of (intercept) × k'[Lac][M] and the k' (obtained by the three methods indicated above) were obtained. Alternatively k_0/k_t and k_p/k_t values were evaluated from the linear plot of $1/R_p$ versus 1/[Lac], whose slope would be

$$\frac{k_t}{k_p}\,\frac{(k_0/k_i)[\mathrm{V}^{5+}]}{k'[\mathrm{M}]^2} + \frac{k_t}{k_p \cdot k'[\mathrm{M}]}$$

at four $[V^{5+}]$; [Lac] was varied, and hence four plots of $1/R_p$ versus 1/[Lac] were obtained (Fig. 7). The slopes of these plots were then plotted against $[V^{5+}]$ (Fig. 2*F*) to resolve the composite term into two. The slope and intercept of this latter plot were equal to $(k_t/k_p)\{(k_0/k_i)/k'[\mathrm{M}]^2\}$ and $(k_t/k_p k'[\mathrm{M}])$, respectively; k_0/k_i from plots of (slope/intercept)[M] and k_p/k_t from (1/intercept)(1/k'[M]) were evaluated, and a comparison was made between the values obtained by the two methods (Table I). The k' value obtained (1.2×10^{-3} l./mole-sec; literature value[12], 1.22×10^{-3} l./mole-sec). from the oxidation experiments were approximately twice those from polymerization experiments as expected from the reactions. ΔE values for k' (12.73 kcal/mole), k_p/k_t (−6.56 kcal/mole) k_0/k_i (−2.92 kcal/mole) and $\Delta S^*_{303.2°\mathrm{K}}$ values for k' (−29.52 eu/mole), k_p/k_t (−82.73 eu/mole), and k_0/i_i (−63.43 eu/mole) were evaluated.

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Polymerization of Perhydro-1,5-diazocine-2,6-dione

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Synopsis

Perhydro-1,5-diazocine-2,6-dione polymerized in solid state in the presence of water in vapor phase and produced poly-β-alanine almost quantitative yield. Further, this monomer was found to polymerize rapidly on heating above its melting temperature without water. The results of x-ray diffraction measurement and thermal analysis suggest that this solid-state polymerization is like partial melt polycondensation.

INTRODUCTION

Two procedures for polymerization of lactams are known, of which one is initiated by alkali and acyl compound and the other by water. Further, in both cases, polymerization is usually carried out on molten monomers if the melting points of lactams and polyamides produced are not very high. However, if the melting points of the monomers and the polymers derived therefrom are exceedingly high, polymerization in the molten state would be impossible, because of decomposition of the monomer and polymer obtained. Cyclic diamides are known to have high melting points, especially those with small rings. Few studies have been carried out on the polymerization of cyclic diamide, and details have not yet been ascertained.[1]

In the present investigation, polymerization of perhydro-1,5-diazocine-2,6-dione initiated with water was undertaken to clarify the polymerization mechanism of dilactam in the solid state.

RESULTS AND DISCUSSION

Solid State Polymerization

All polymerizations were carried out at 210°C in the glass apparatus shown in Figure 1. The reaction condition selected was polymerization in a solid state with initiation with water in the vapor phase. The results of the polymerization are shown in Table I.

No polymer was obtained at 210°C in the absence of water. However, in the presence of water polymer was obtained, and the yield of polymer increased with the reaction period, becoming almost quantitative after a long period. Plots of the yields of the polymer versus the reaction period are shown in Figure 2.

TABLE I
Solid-State Polymerization of Perhydro-1,5-diazocine-2,6-dione[a]

Water μl 10^{-3}, ml	Reaction time, hr	Yield, %	η_{inh}[b]
0	30	0	—
1	30	6.4	—
1	50	14.1	0.35
1	100	50.4	0.38
2	20	9.3	—
2	30	49.9	0.36
2	50	93.8	0.38
3	10	8.7	0.25
3	20	32.0	0.24
3	30	66.2	0.28
3	50	96.7	0.35
6	5	9.8	—
6	10	67.8	0.30
6	20	95.6	0.30
6	30	98.6	0.30
10	2	9.6	0.31
10	10	90.6	0.36
10	20	97.2	0.34
10	50	96.5	—
70	2	84.7	—

[a] Polymerization was carried out by heating 0.5 g of the monomer at 210°C in a 5-ml sealed tube in the presence of various amounts of water.

[b] Measured in a solution of sulfuric acid, 0.5 g/100 ml, 30°C.

These plots gave sigmoidal curves, and maximum slopes of these curves were found to be proportional to the amount of water used as an initiator, as shown in Figure 3. The results obtained here would indicate that the polymerization of perhydro-1,5-diazocine-2,6-dione was initiated by water.

The polymer obtained in the earlier stage of the polymerization showed a high viscosity. The viscosity of the polymer obtained was almost the same and independent of the yield and the reaction period, as shown in Table I. From studies of polymerization of vinyl compounds and trioxane in the solid state, it is well known that the molecular weight of the polymer obtained depends on the crystalline size of the monomer,[2] and this is attrib-

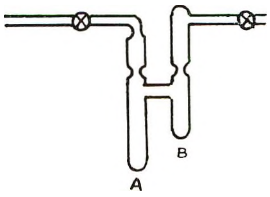


Fig. 1. Apparatus for solid-state polymerization.

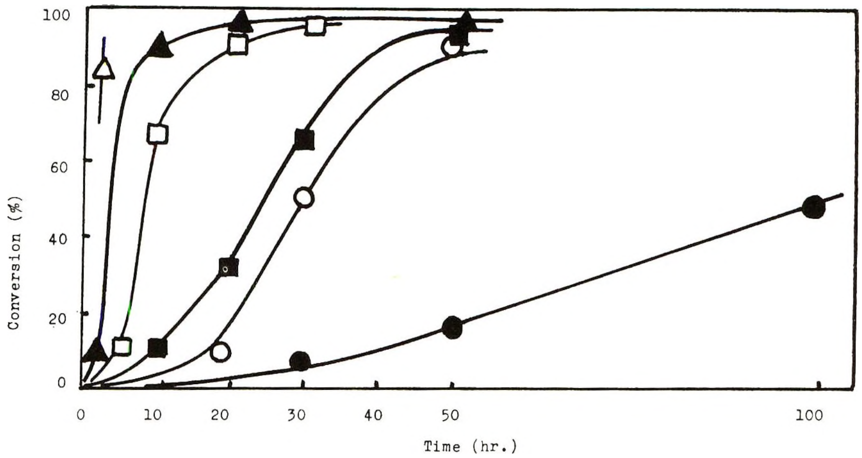


Fig. 2. Polymerization of perhydro-1,5-diazocine-2,6-dione (0.5 g) at 210°C in the presence of water: (●) 10^{-3} ml, (○) 2×10^{-3} ml; (■) 3×10^{-3} ml; (□) 6×10^{-3} ml; (▲) 10^{-2} ml; (△) 7×10^{-2} ml.

uted to disturbance of the propagation of the polymerization by defects of the crystalline lattice. Therefore, the result obtained above, would indicate that the termination of the growing polymer chain depends on the crystalline size. However, in the present study, as all the crystalline monomer used was prepared under the same conditions, the relation between polymerization behavior and the crystalline structure of the monomer or the conditions of preparing monomer crystals could not be observed.

This leads to another conclusion, i.e., that the apparent increase of the polymer yield is due to the increase of the number of the polymer chains.

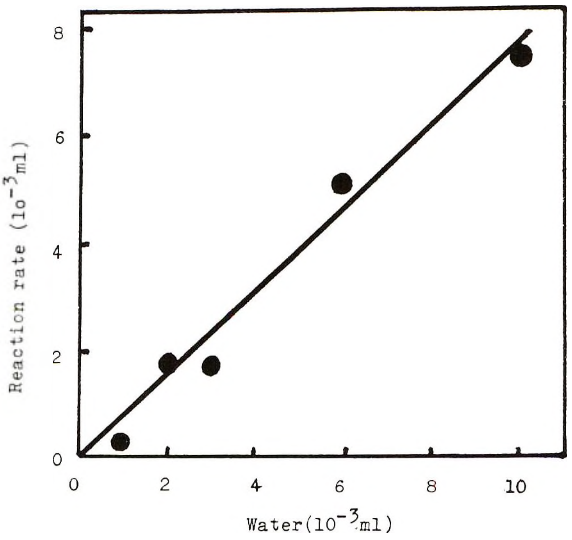


Fig. 3. Maximum rate of polymerization.

TABLE II
Solid-State Polymerization of Perhydro-1,5-diazocine-2,6-dione[a]

Heating time, hr	Yield, %	η_{inh}[b]
20	32.0	0.24
35[c]	32.2	0.24

[a] Polymerization was carried out in the same manner as described in Table I.

[b] Measured in a solution of sulfuric acid, 0.5 g/100 ml, 30°C.

[c] The polymerization was stopped after 20 hr of heating. Heating was continued again for 15 hr after removal of the water *in vacuo*.

This is supported by the fact that when the polymerization was stopped after 20 hr, about 30% of the polymer was obtained; if the water was removed under highly reduced pressure, and the reaction started again after sealing the tube, no more polymer occurred and there was no variation in viscosity, as shown in Table II. Generally, water is expected to hydrolyze amides to amine and carboxyl, which are then the propagating species. Therefore, when excess water is removed, there is no initiation. This indicates that the initiation reaction is slow, but the succeeding propagation reaction is faster than the initiation.

Melt Polymerization

Perhydro-1,5-diazocine-2,6-dione did not polymerize in the absence of water on heating it in a solid state as described above. However, it polymerized on heating above its melting temperature. The result of the polymerization in the molten state is shown in Table III. As the melting point of the monomer is high, a small amount of decomposition was observed in every case, and the resulting polymer was slightly colored. Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) of the crystalline perhydro-1,5-diazocine-2,6-dione and the polymer were carried out to follow the behavior of the polymerization. The results obtained are shown in Figure 4. The DTA curve of the monomer showed a sharp endothermic peak at 299.5°C and a subsequent large exothermic peak. Further, an endothermic peak was observed again around 320°C. For the

TABLE III
Melt Polymerization of Perhydro-1,5-diazocine-2,6-dione[a]

Monomer, g	Na salt of pyrrolidone, g	*N*-acyl compound[b] g	Polymer yield, %	η_{inh}[c]
1.00	—	—	34	—
1.00	—	0.017	56	0.23
1.00	0.03	0.016	19	0.24

[a] The polymerization was carried out by heating the mixture at 310°C.

[b] *N,N'*-Diacetyl perhydro-1,5-diazocine-2,6-dione.

[c] Measured in a solution of sulfuric acid, 0.5 g/100 ml, 30°C.

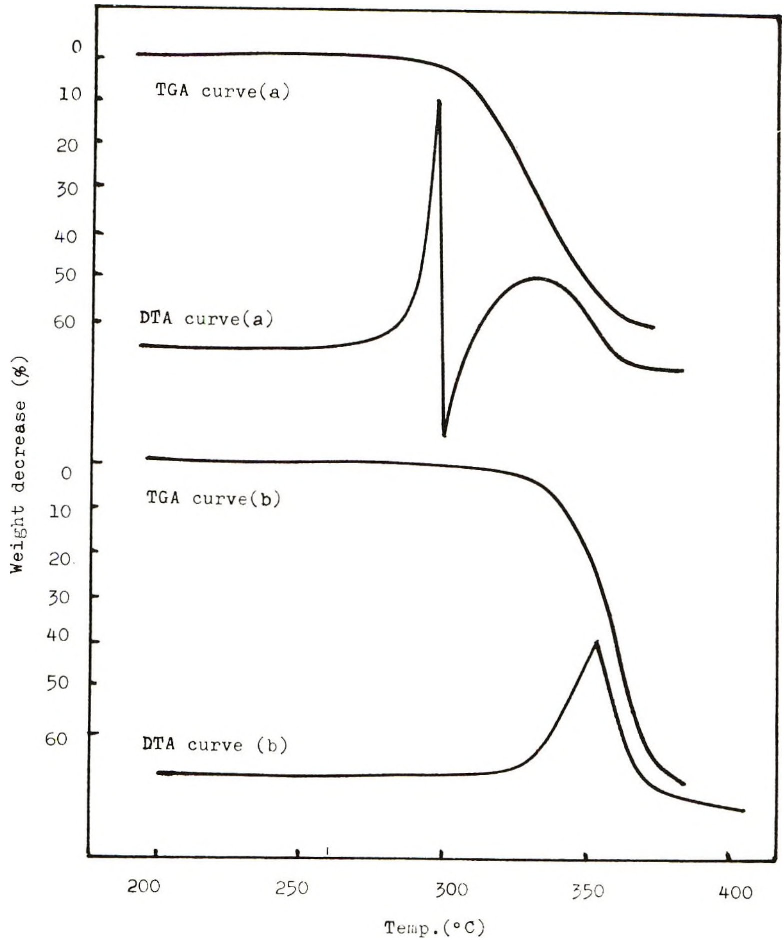


Fig. 4. TGA curves and DTA curves of (*a*) perhydro-1,5-diazocine-2,6-dione and (*b*) its polymer (nitrogen atmosphere).

polymer, only a single endothermic peak and a large weight loss due to the decomposition of the polymer were observed at 350°C. From these results, the endothermic peak at 299.5°C was attributed to the melting point of the monomer crystal. The DTA curve obtained for the monomer on keeping the temperature constant after it reached 305°C showed no effect on exothermic peak. But, the rate of the weight loss of the sample became slow, and the endothermic peak due to the weight loss became broad in comparison with that in Figure 4. However, the endothermic peak at 299.5°C and the exothermic peak unchanged. This result would suggest that the exothermic change of the sample is very fast and is already complete before the weight loss.

The monomer used here is a compound having an eight-membered ring. Such a medium-sized ring is well known to have considerable internal strain and would be considered to give an exothermic phenomenon on ring-opening reaction. Therefore, the large exothermic peak after the endothermic peak at 299.5°C appeared to be due to the ring-opening polymerization of the cyclic monomer. The driving force of the rapid polymerization of perhydro-1,5-diazocine-2,6-dione in the molten state would be attributed to the large internal strain.

Characterization of the Polymer

The infrared spectrum of the polymer is shown in Figure 5. It showed characteristic amide bands at 3300, 1650, and 1550 cm^{-1}, and the results of elementary analysis of the polymer agreed with the theoretical values for poly-β-alanine.

The x-ray diffraction patterns were obtained for powdered samples of polymer obtained in various conditions with Ni-filtered Cu$K\alpha$ radiation as shown in Figure 6. The patterns 6*a*, 6*b*, 6*c*, and 6*d* are, respectively, diagrams of the polymer obtained in the solid state, the polymer obtained by melt polymerization, the polymer reprecipitated from formic acid and methanol, and the polymer obtained by annealing the reprecipitated one. The annealing was carried out by heating the polymer *in vacuo* at 210°C for 6 hr; this condition corresponds to that in the solid-state polymerization. The patterns of the polymer prepared in the solid-state and the melt polymerization are about the same, and indicative of very high crystallinity. On the other hand, the pattern of the reprecipitated polymer was quite different from that of the polymer prepared in a solid state and showed rather low

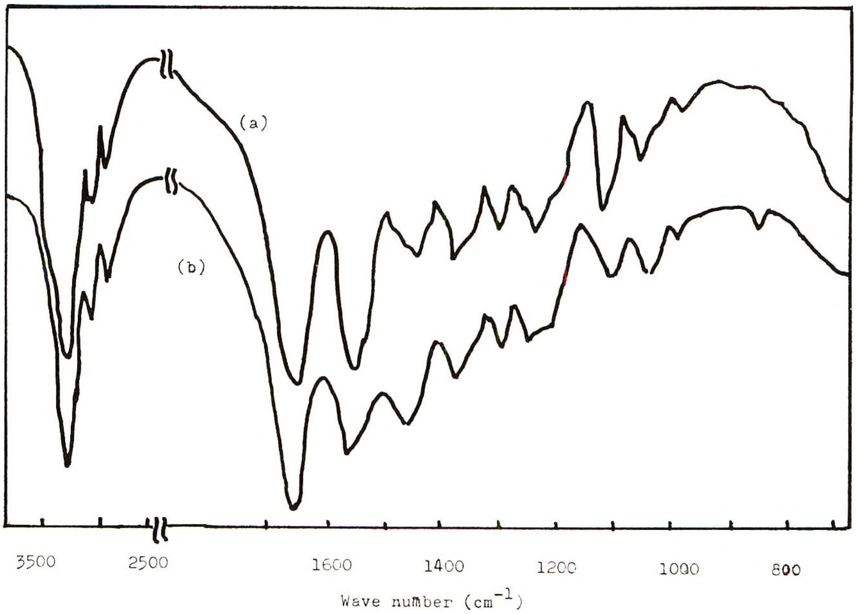


Fig. 5. Infrared spectra of (*a*) the polymer of perhydro-1,5-diazocine-2,6-dione and (*b*) poly-β-alanine obtained from acrylamide (KBr disk).

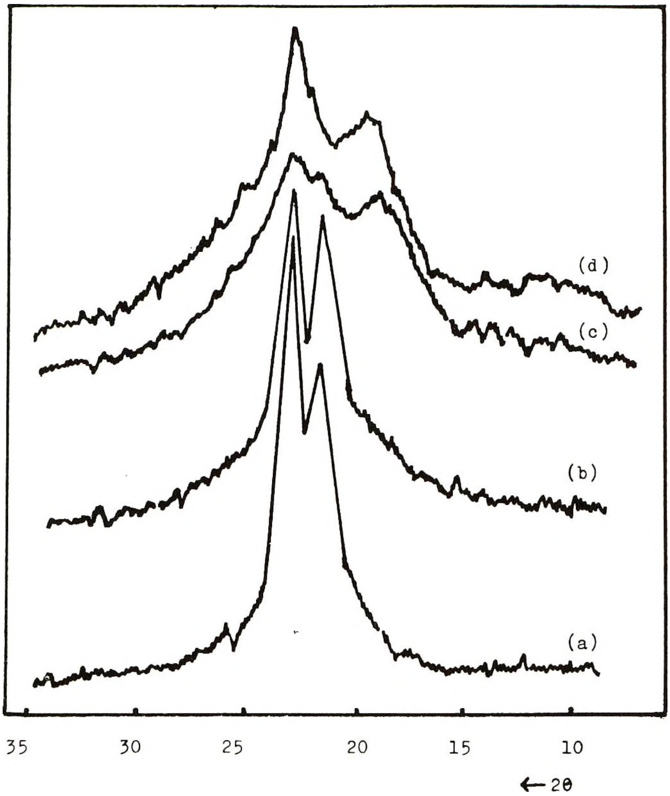


Fig. 6. X-ray diffraction patterns of powdered samples of poly-β-alanine (CuKα, Ni filter): (*a*) polymer obtained by solid-state polymerization; (*b*) polymer obtained by melt polymerization; (*c*) polymer obtined by reprecipitation of polymer (*a*), (*d*) polymer obtained by annealing of polymer (*c*).

crystallinity. Annealing the polymer hardly increased the crystallinity of the polymer. This would indicate that the thermal movement of the conformation of the polymer chain does not occur to any appreciable extent under these conditions.

Mechanism of the Solid-State Polymerization of Perhydro-1,5-diazocine-2,6-dione Initiated with Water

In this polymerization, some active centers seem to be formed by the action of water on the crystalline monomer, and the propagation proceeds from these active centers. The fact that the structure of the polymer obtained in the solid state is the same as that obtained in melt polymerization, and further, the structure of the polymer formed could not be changed under the condition corresponding to the polymerization would lead to following consideration. This polymerization proceeds in the solid state but there is no crystalline lattice control of the monomer on the structure of the resulting polymer. Therefore, in the region between the growing poly-

Fig. 7. Model for discussion of mechanism of the solid-state polymerization.

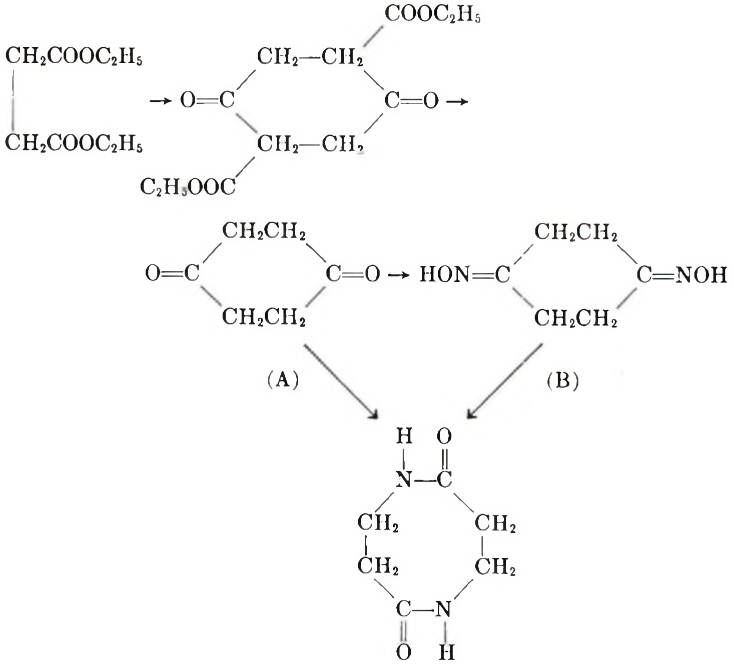
mer end and the crystalline monomer, the lattice of the crystalline monomer would be deformed, and the monomer molecules in this region are very labile just as in the melt polymerization, as shown in Figure 7.

In the earlier stage of the polymerization, the deformed region between the polymer end and the monomer crystal would increase with the degree of the reaction, and this would cause an increase in the polymerization rate. The sigmoidal curves of the polymerization shown in Figure 2 would confirm such a scheme of the reaction.

EXPERIMENTAL

Materials

Cyclohexane-1,4-dione and its dioxime were prepared by the usual methods according to the scheme shown in eq. (1).



(1)

Diethyl succinate was prepared by the usual esterification of succinic acid in 90–95% yield, bp 115°C/26 mm Hg.

Diethyl succinosuccinate was obtained by using the method of Liefrman. A mixture of diethylsuccinate (174 g) and sodium sand (46 g) was kept at room temperature for 2 hr, then heated to 100°C over a period of 6 hr, and then maintained at the same temperature for an additional 2 hr. After that, to complete the reaction, the mixture was heated to 140°C over a period of 30 hr and finally to 160°C for 5 hr. The reaction mixture was poured into a large amount of water and neutralized with HCl. The resulting precipitates were collected and dried, yielding 83 g (65%). Recrystallization of the product from ethanol gave crystals, mp 126–127°C.

Cyclohexane-1,4-dione[4] was obtained by heating 25 g of ethyl succinosuccinate with an equal weight of water at 200°C; the yields was 80–85%, bp 132°C/32 mm Hg.

Cyclohexane-1,4-dione dioxime was obtained from cyclohexane-1,4-dione by heating a mixture of dione and aqueous hydroxylamine hydrochloride in the presence of pyridine.

Perhydro-1,5-diazocine-2,6-dione[5] was prepared from cyclohexane-1,4-dione by the Schmidt reaction (A) and from dioxine by Beckmann rearrangement (B).

Schmidt Reaction. Cyclohexane-1,4-dione (30 g) was dissolved in sulfuric acid, and then 150 ml of a benzene solution of hydrogen azide (about 2*N*) was dropped slowly into the mixture at 0°C. After generation of about theoretical amount of nitrogen, perhydro-1,5-diazocine-2,6-dione was isolated from the mixture by a method described in the literature; the yield was 30%, mp 299.5°C.

Beckmann Rearrangement. A mixture of 10 g of cyclohexane-1,4-dione dioxime, 40 ml of sulfuric acid, and 60 ml of oleum (20%) was heated to 100°C. A vigorous reaction occurred when the temperature of the mixture reached 160°C. Perhydro-1,5-diazocine-2,6-dione isolated from the mixture similarly as above; the yield was 30%.

Solid-State Polymerization

All the experiments were carried out in the glass apparatus shown in Figure 1. A certain amount of the monomer was put in the tube A and dried at 100°C *in vacuo*. After filling with nitrogen, adding a given amount of water, the apparatus was sealed. The sealed apparatus was immersed in an oil bath at a definite temperature. After the polymerization, the unreacted monomer was removed by washing with water, and the residual polymer was dried; mp 350°C.

Melt Polymerization

The monomer was placed in a small tube and heated at 300°C under nitrogen. After 7 min, the melted reaction mixture was cooled, and the unreacted monomer was removed as described above. The polymer was dried and characterized.

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Reactivities and NMR Spectra of Vinyl Ethers

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Synopsis

Copolymerizations of *n*-butyl vinyl ether (M_1) with other vinyl ethers were carried out in toluene at -78°C with $EtAlCl_2$ catalyst and the monomer reactivity ratios were determined. It was found that the relative reactivity of alkyl vinyl ether $\log 1/r_1$ is higher when the alkyl group is more electron-donating and the reactivity correlates linearly with the Taft σ^* of alkyl group in the monomer. The NMR spectra of vinyl ethers and of vinyl ether–trialkylaluminum complexes were investigated. Close correlations were found between the spectral characteristics and the relative reactivity of vinyl ether in the copolymerization. The degree of resonance contribution in alkyl vinyl ether was also discussed on the basis of NMR data.

INTRODUCTION

A number of studies have been reported on the copolymerization of vinyl ether with another vinyl monomer by cationic mechanism. However, there have been few reports[1–5] on the copolymerization of a vinyl ether with other vinyl ethers. Dunphy[3] has copolymerized β-chloroethyl vinyl ether with isobutyl and octadecyl vinyl ether using stannic chloride as catalyst and determined the monomer reactivity ratios. Khomutov[5] has determined the monomer reactivity ratios in the copolymerization of *n*-butyl vinyl ether with ethyl and isopropyl vinyl ether in the presence of sulfuric acid–aluminum sulfate. Fueno[6] has copolymerized substituted phenyl vinyl ethers by stannic chloride to study the Hammett's relations in the copolymerization.

In this paper the studies on the copolymerizations of *n*-butyl vinyl ether (M_1) with other vinyl ethers with the use of $EtAlCl_2$ catalyst will be reported. It was found that there is a linear relationship between the relative reactivity of alkyl vinyl ether in the copolymerization and the Taft σ^* of the alkyl group in the monomer. The NMR spectra of vinyl ethers were also investigated, and close correlations were found between the spectral characteristics and the reactivity of vinyl ether in the copolymerization.

EXPERIMENTAL

Materials

Methyl vinyl ether and isobutyl vinyl ether were obtained from a commercial source. Other vinyl ethers were prepared by the vinyl transetherification between methyl or isobutyl vinyl ether and the corresponding alcohols, mercuric acetate being used as catalyst with[7] or without[8] molecular sieves. All the ethers were purified by fractional distillation under nitrogen pressure. The purified vinyl ethers were thoroughly dried by being refluxed over lithium aluminum hydride, followed by a distillation under high vacuum before use.

Toluene was purified in an usual manner, dried, and stored over calcium hydride; before use, it was dried further with a small amount of *n*-butyllithium and distilled under high vacuum.

Ethylaluminum dichloride was a commercial product of Ethyl Corporation and used without further purification as a 1 mole/l. solution in *n*-heptane.

Trialkylaluminum–vinyl ether complex was prepared by adding vinyl ether to an equimolar amount of trialkylaluminum in toluene.

Nitrogen gas was purified by being passed through a column of molecular sieves 4A cooled to −78°C in a Dry Ice–acetone bath.

Polymerization

A 50 ml ampoule fitted with a three-way stopcock was flushed by dry nitrogen. Toluene and monomers were added to the ampoule by hypodermic syringes through the three-way stopcock under nitrogen pressure and cooled to −78°C in an Dry Ice–acetone bath. The polymerization was initiated by introducing the catalyst $EtAlCl_2$ and stopped at a low degree of conversion by adding a small amount of methanol containing hydrochloric acid. The copolymer produced was precipitated by pouring the mixture into a large amount of methanol. After standing overnight, the polymer was collected by filtration, washed with methanol and dried to constant weight *in vacuo* at room temperature.

Determination of Monomer Reactivity Ratios

The copolymer compositions were determined by elementary analyses when the compositions of comonomers were different enough for accurate determinations. If the compositions of comonomers were very similar or the same, as in the pair of *tert*-butyl and *n*-buty lvinyl ether or *n*-propyl and *n*-butyl vinyl ether, the copolymer compositions were determined by NMR spectroscopy. For example, the composition of the copolymer of *tert*-butyl and *n*-butyl vinyl ether was calculated from the relative intensity of a singlet peak at 8.83τ and a triplet at 9.11τ, which are methyl resonances of *tert*-butyl and *n*-butyl vinyl ether units, respectively. The maximum deviations were about 3% for elementary analyses and 5% for NMR analyses. On the basis of these data, the monomer reactivity ratios, r_1 and r_2, were calculated by the graphical method of Fineman and Ross.[9]

Measurements of NMR Spectra

The spectra of copolymers were obtained on 10% solutions in CCl_4 at

60°C, tetramethylsilane being used as an internal reference. The spectra of vinyl ethers or of vinyl ether–trialkylaluminum complexes were taken as 0.5 mole/l. solutions in toluene, with reference of the chemical shifts to the methyl signal of toluene. All the spectra were measured with a JNM-4H-100 Spectrometer (Japan Electron Optics Laboratory Co.) at 100 Mcps.

RESULTS

Monomer Reactivity Ratios of Vinyl Ethers

The monomer reactivity ratios, r_1 and r_2, in the copolymerizations of *n*-butyl vinyl ether (M_1) with other vinyl ethers (M_2) are summarized in Table I, in which the monomers M_2 are arranged in increasing order of reactivity from top to the bottom.† Table I shows that the reactivity of vinyl ether is greater, when the alkyl group in the monomer is more electron-donating.

TABLE I

Monomer Reactivity Ratios in the Copolymerization of *n*-Butyl Vinyl Ether (M_1) with An Other Vinyl Ether (M_2) in Toluene at −78°C[a]

M_2 $CH_2{=}CH{-}OR$	r_1	r_2	$1/r_1$	$\log 1/r_1$
CH_3	5.67 ± 0.02	0.47 ± 0.02	0.18	−0.745
C_6H_5	2.17 ± 0.15	0.24 ± 0.17	0.46	−0.337
C_2H_5	2.05 ± 0.05	0.75 ± 0.02	0.49	−0.310
n-C_3H_7	1.35 ± 0.15	0.99 ± 0.10	0.74	−0.131
n-C_4H_9	1.00	1.00	1.00	0.00
n-C_6H_{13}	0.95 ± 0.02	1.38 ± 0.03	1.05	0.021
i-C_4H_9	0.73 ± 0.15	1.48 ± 0.10	1.37	0.137
$C_6H_5CH_2$	0.72 ± 0.05	1.61 ± 0.08	1.40	0.146
i-C_3H_7	0.38 ± 0.07	2.77 ± 0.10	2.63	0.420
C_6H_{11}	0.29 ± 0.02	3.80 ± 0.02	3.44	0.537
$C_6H_5CH(CH_3)$	0.38 ± 0.10	1.40 ± 0.10	2.63	0.420
t-C_4H_9	0.19 ± 0.02	9.67 ± 0.05	5.26	0.721

[a] Total monomer, 20 mmole; $EtAlCl_2$, 0.05 mmole; total volume of the reaction mixture, 23 ml.

In Figure 1 the relative reactivities of vinyl ethers, represented by $\log 1/r_1$, are plotted against the Taft σ^* values of the substituents. There was a linear relationship between $\log 1/r_1$ of alkyl vinyl ether and the Taft σ^* value of the alkyl group ($*\rho = -4.7$). Monomers containing a phenyl group gave another straight line for plots of $\log 1/r_1$ and the Taft σ^* ($\rho^* = -1.5$).

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† Recently Higashimura et al. have carried out the copolymerization of *n*-butyl vinyl ether with other vinyl ethers by $BF_3 \cdot OEt_2$ and found that the relative reactivities decrease in the order, *tert*-butyl- > isopropyl- > ethyl- > *n*-butyl > isobutyl- > methyl vinyl ether, which is partly different from our result.[10]

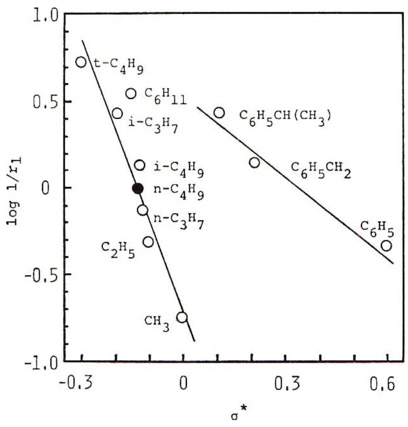


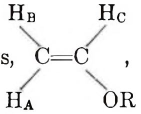
Fig. 1. Plots of log $1/r_1$ against the Taft σ^* value of R in vinyl ether (R—O—CH=CH$_2$).

The relative reactivity is smaller for larger values of the Taft steric parameters E_s of the alkyl group in the monomer, as shown in Figure 2, where the E_s values for R in the monomer used are those for RCH_2 of RCH_2COOR'. The plots of log $1/r_1$ against the E_s value for R of $RCOOR'$ were more scattered.

Relation between NMR Spectra and Reactivities of Vinyl Ethers

The parameters in the NMR spectra of vinyl ethers observed are listed in Table II; the vinyl ethers are also arranged in the order of their reactivi-

TABLE II

Chemical Shifts and Spin Coupling Constants of Various Vinyl Ethers,  , in 0.5M Toluene Solution at 21.5°C

R	Chemical shift, ppm[a]			Coupling constant, cps		
	δ_A	δ_B	δ_C	J_{AB}	J_{BC}	J_{AC}
CH_3	1.88	1.76	4.31	−2.4	7.0	14.6
C_6H_5	2.55	2.06	4.21	−1.4	6.0	13.8
C_2H_5	1.95	1.79	4.25	−1.7	6.9	14.8
n-C_3H_7	1.96	1.77	4.27	−1.7	6.9	14.5
n-C_4H_9	1.97	1.78	4.27	−2.0	7.4	13.3
n-C_6H_{13}	2.00	1.79	4.29	−1.7	6.9	14.6
i-C_4H_9	1.99	1.77	4.27	−1.8	7.4	13.3
$C_6H_5CH_2$	2.06	1.83	4.28	−1.9	6.5	13.8
i-C_3H_7	2.13	1.80	4.04	−1.3	6.8	14.1
C_6H_{11}	2.19	1.83	4.08	−1.3	6.7	14.2
$C_6H_5CH(CH_3)$	2.14	1.77	4.06	−1.3	6.5	13.8
t-C_4H_9	2.41	1.90	4.18	0.0	6.3	13.7

[a] Chemical shifts referred to the methyl signal of the solvent toluene.

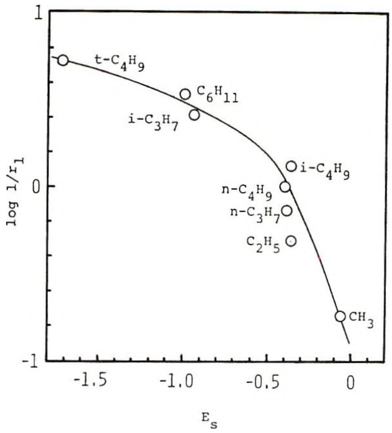


Fig. 2. Plots of log $1/r_1$ against the Taft E_s value of R in vinyl ether (R—O—CH═CH$_2$).

ties as in Table I. It can be seen that the geminal coupling constant in vinyl group, J_{AB}, is generally less negative as the reactivity of vinyl ether increases.

The increases in the chemical shifts of the terminal ethylenic hydrogens, δ_A and δ_B, generally follow the increasing order of reactivity of the monomer. As shown in Figure 3, a linear relation was found between δ_A and $1/r_1$, where δ_A is the chemical shift of a β-proton *trans* to the α-proton in the vinyl system of a monomer. No correlation was obtained between the chemical shift of the α-proton, δ_C, and $1/r_1$.

As shown in Figure 4, a fairly good linear correlation was found between the chemical shift separation, $\delta_A - \delta_B$ and $1/r_1$, although the point for phenyl vinyl ether greatly deviated from the straight line.

A similar linearity was also obtained by plotting the sum of the absolute values of three coupling constants, $\Sigma|J|$ $(= |J_{AB}| + J_{BC} + J_{AC})$ against

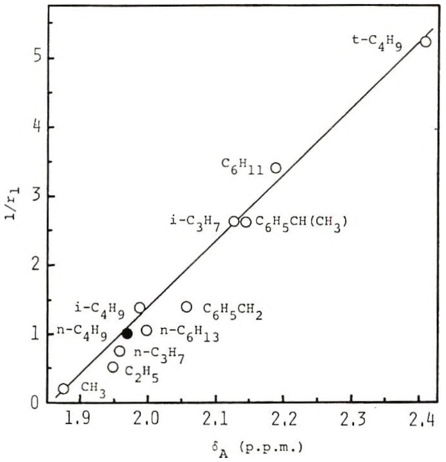


Fig. 3. Plots of $1/r_1$ against δ_A of vinyl ether.

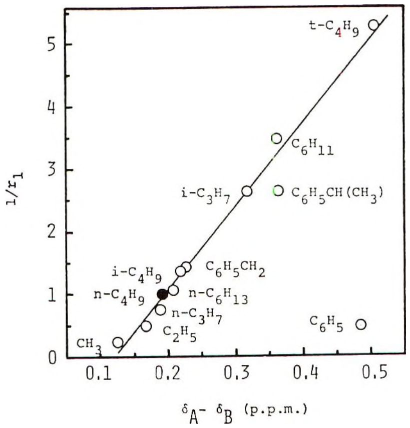


Fig. 4. Plots of $1/r_1$ against $\delta_A - \delta_B$ of vinyl ether.

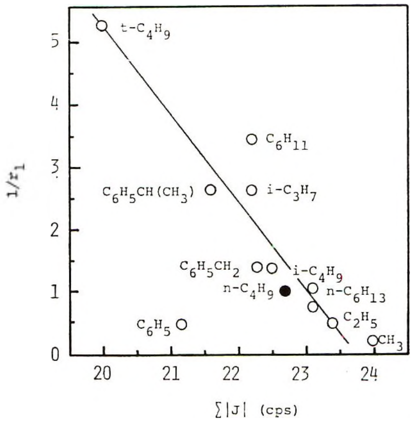


Fig. 5. Plots of $1/r_1$ against $\sum |J|$ of vinyl ether.

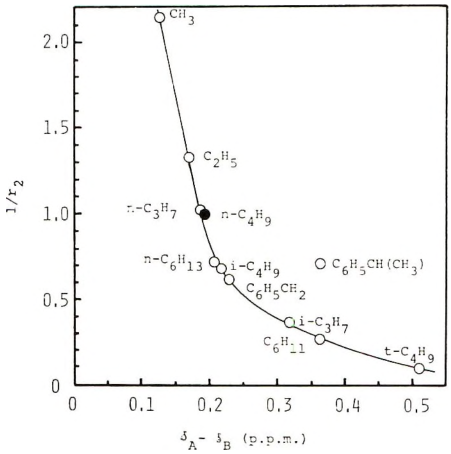


Fig. 6. Plots of $1/r_2$ against $\delta_A - \delta_B$ of vinyl ether.

$1/r_1$ as given in Figure 5, but the correlation was less satisfactory than that between $\delta_A - \delta_B$ and $1/r_1$.

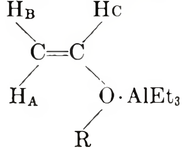
It is also observed that the value $\delta_A - \delta_B$ is correlated with $1/r_2$ as well as with $1/r_1$ (Fig. 6).

Relation between NMR Spectra of Vinyl Ether–Trialkylaluminum Complexes and Reactivities of Vinyl Ethers

The chemical shifts and the coupling constants in the NMR spectra of vinyl ether–triethylaluminum complexes are summarized in Table III. The geminal coupling constant in the vinyl system of the complex, J_{AB}, was more negative than that of the corresponding free ether. Except for the case of phenyl vinyl ether, the chemical shifts of the terminal ethylenic proton, δ_A and δ_B, were shifted to lower field and the chemical shift δ_C was shifted to higher field on the coordination of triethylaluminum to the ether.

TABLE III

Chemical Shifts and Spin Coupling Constants of Triethyl-aluminum–vinyl Ether Complexes,



$H_BH_CC{=}C(H_A)(O(R)\cdot AlEt_3)$

in 0.5*M* Toluene Solution at 21.5°C

R	Chemical shift, ppm[a]			Coupling constant, cps		
	δ_A	δ_B	δ_C	J_{AB}	J_{BC}	J_{AC}
CH_3	1.88	1.83	4.13	−3.63	6.6	14.6
C_6H_5	2.06	1.97	4.39	−2.75	6.9	12.1
C_2H_5	2.10	1.96	3.82	−3.25	6.8	14.2
n-C_3H_7	2.16	1.96	3.84	−3.10	6.7	14.2
n-C_4H_9	2.21	2.01	3.83	−3.18	6.8	13.8
n-C_6H_{13}	2.22	2.00	3.84	−3.25	6.8	14.0
i-C_4H_9	2.31	2.06	3.71	−3.13	6.8	13.8
$C_6H_5CH_2$	2.17	1.92	3.82	−3.00	6.3	13.8
i-C_3H_7	2.57	2.21	3.53	−2.10	6.1	14.1
C_6H_{11}	2.59	2.22	3.61	−2.10	6.0	13.9
$C_6H_5CH(CH_3)$	2.42	2.00	3.48	−2.12	6.3	13.8
t-C_4H_9	2.42	1.91	4.17	0.00	6.4	13.7

[a] Chemical shift referred to the methyl signal of solvent toluene.

If the $1/r_1$ values are plotted against the $\delta_A - \delta_B$ values of the complexes, a good correlation (Figure 7) is obtained, including the plot for phenyl vinyl ether which deviated greatly from the relation in the case of free ether. A good correlation was also found between $1/r_2$ and $\delta_A - \delta_B$ of the complex, except for the complex of phenyl vinyl ether. This correlation is illustrated in Figure 8.

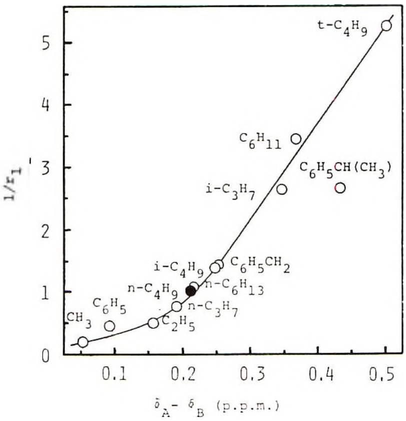


Fig. 7. Plots of $1/r_1$ against $\delta_A - \delta_B$ of vinyl ether–$(C_2H_5)_3Al$ complex.

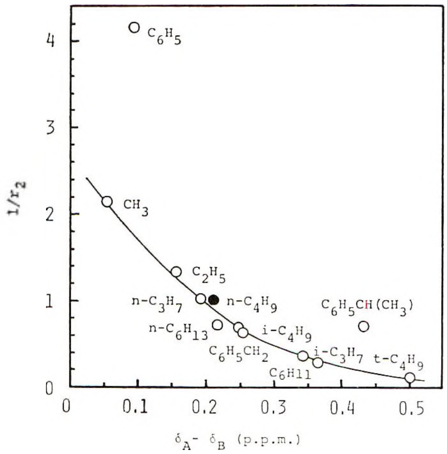


Fig. 8. Plots of $1/r_2$ against $\delta_A - \delta_B$ of vinyl ether–$(C_2H_5)_3Al$ complex.

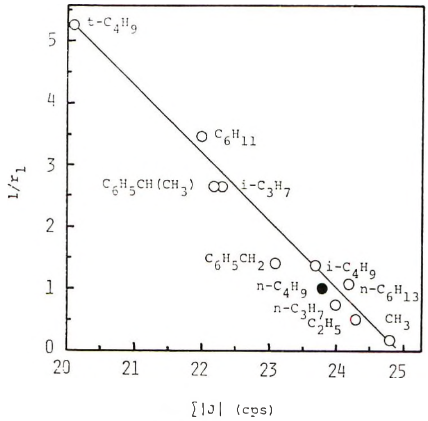


Fig. 9. Plots of $1/r_1$ against $\sum|J|$ of vinyl ether–$(C_2H_5)_3Al$ complex.

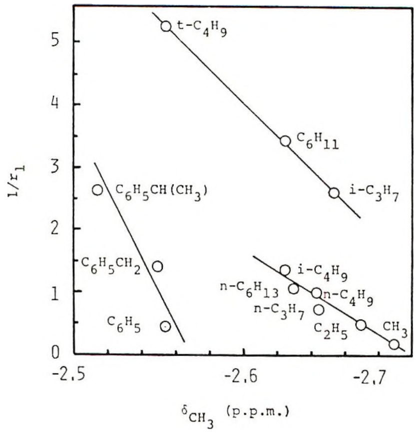


Fig. 10. Plots of $1/r_1$ against δ_{CH_3} of $(CH_3)_3Al$ in vinyl ether–$(CH_3)_3Al$ complex.

Similarly to the case of free vinyl ether, the sum of the absolute values of the three coupling constants in the vinyl system decreased linearly with increasing $1/r_1$ value in the case of complex. Figure 9 shows the graph illustrating this correlation, the linearity of which is more satisfactory than that in the case of free ether.

By plotting $1/r_1$ against δ_{CH_3}, the chemical shift of methyl proton of trimethyl aluminum in its complex with vinyl ether, three separate straight lines were obtained: one including the complexes in which the α-carbons of alkyl groups in vinyl ethers were primary, one for the complexes having secondary or tertiary α-carbons, and one for complexes having aromatic groups (Fig. 10).

In the NMR spectra of the complexes between trimethylaluminum and donor compounds, such as ether and amine, the chemical shift of methyl proton in trimethylaluminum has been found to shift toward higher field as the donor character of the coordinating compound increased.[11] This and the results shown in Figure 10 indicate that the reactivity of vinyl ether decreases as the donor character of the ether increases, the monomers being separated into three series according to their structures.

DISCUSSION

As can be seen in Table I, the reactivity of vinyl ether is higher when the substituent R is more electron-donating. This show that in the cationic polymerization of vinyl ether the reactivity of the monomer is strongly correlated with the polar character of the substituent.

It has been suggested that alkyl vinyl ethers may take a following resonance form resulting from a partial double bond character in the C—O bond:[12,13]

$$\overset{-}{C}H_2—CH═\overset{+}{O}—R$$

Pilcher[14] obtained a value for the resonance energy of ethyl vinyl ether of

2.8 kcal/mole. Pople[15] has shown that the coupling constant between geminal hydrogen atoms increases as the *s* character of the carbon atom between them increases. The J_{AB} value of alkyl vinyl ether can thus be used as an indication of the degree of resonance. As shown in Table II, the increase in J_{AB} of alkyl vinyl ether mostly follows the increasing order of its reactivity. Thus the contributions of the resonance form are greatest in methyl vinyl ether, which is least reactive, and least in *tert*-butyl vinyl ether, which is most reactive.

As the vinyl ether is more reactive, the chemical shifts δ_A and δ_B are to lower field, and the difference $\delta_A - \delta_B$ increases (Table II, Figs 3 and 4). This is also evidence for the fact that the resonance contribution of alkyl vinyl ether decreases in increasing order of its reactivity, because the resonance must lead to a reduction in the olefinic character of the vinyl group and consequently the terminal methylene protons should resonate at higher fields and, also, they will become more equivalent.

These results suggest that resonance stabilization in alkyl vinyl ether may play some important role in determining its reactivity besides the polar character of the alkyl group. The resonance will be most favorable when the olefinic π-orbital and the lone-pair *p*-orbital on the oxygen atom overlap. So the degree of this resonance contribution is considered to depend on the conformation of alkyl vinyl ether. If the oxygen atom is assumed to have essentially sp^3 hybridization and hence a tetrahedral disposition of its bonds and lone-pair electrons, the probable conformations could be represented as shown in Figure 11. By an infrared spectroscopic study Owen and Shepherd[16] showed that for methyl vinyl ether the *cis* form is more stable at room temperature, which is most favorable for the resonance, and the second form appears at elevated temperatures. The NMR spectra of alkyl vinyl ethers at various temperatures indicate that the second form in methyl vinyl ether is *gauche* and the contribution of this conformation gradually increases as alkyl vinyl ether is more reactive.[17] In the case of *tert*-butyl vinyl ether all other conformations except the *gauche* type will be sterically hindered; hence the resonance cannot occur.

Ledwith et al.[13,18] have observed that the chemical shifts of terminal ethylenic hydrogens in alkyl vinyl ethers, δ_A and δ_B, shift to lower field in the sequence methyl < isopropyl < *tert*-butyl vinyl ether and concluded that the electron density at the double bond is highest in methyl vinyl ether and least in *tert*-butyl vinyl ether, although the reverse is expected from the reactivity of the ether in cationic polymerization. However the

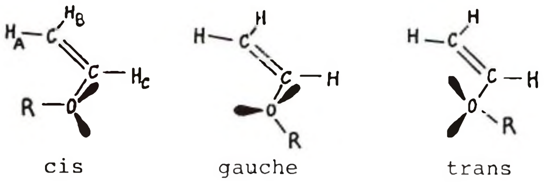


Fig. 11. Diagrammatic representation of possible conformations of alkyl vinyl ether.

chemical shifts of the ethylenic hydrogens may be controlled not only by the electron density at the double bond but also by other various shielding factors.[19] In the case of alkyl vinyl ether it seems easier to explain the δ_A and δ_B in terms of the resonance effect as mentioned above.

The results shown in Figure 2 indicate that the vinyl ether is more reactive as its alkyl group is sterically larger. On the other hand, the donor character of alkyl vinyl ether toward trimethyl-aluminum depends mainly on the steric factor of the alkyl group, and the reactivity generally decreases as the donor character of the ether increases (Fig. 10). This suggests that the reactivity of vinyl ether decreases as the ether coordinates more strongly to the catalyst $EtAlCl_2$ at the oxygen atom. By the coordination of alkyl vinyl ether to triethylaluminum δ_A and δ_B shift to lower field and δ_C shifts to higher field. This means that the electron withdrawal from the double bond through the oxygen atom occurs upon coordination. Lal[20] has reported that in the presence of aluminum hexahydrosulfate heptahydrate, alkyl vinyl ether polymerizes more rapidly as the ether coordinates more strongly to the catalyst. The opposite behavior found between these two catalyst systems may be caused by the difference in their polymerization mechanisms. In Lal's heterogeneous catalyst, vinyl ether may be activated to polymerize by the coordination on the catalyst surface. On the other hand, in the polymerization system with $EtAlCl_2$, which is soluble in the polymerization medium, the reactivity may be decreased by the coordination with $EtAlCl_2$ at the oxygen atom, probably because of the decrease of the electron density in the vinyl group.

Better correlations were observed between the spectral parameters of vinyl ether–triethylaluminum complex and the reactivity of vinyl ether (Figs. 7 and 9) compared with those observed in the case of free vinyl ether (Figs. 4 and 5). This may suggest that the electronic structure in the vinyl group of the complex resembles more closely that of the vinyl ether in the polymerization system catalyzed by $EtAlCl_2$ than does that of the free ether.

It must be noted that the interrelation between $\delta_A - \delta_B$ versus $1/r_1$ (Figs. 4 and 7) and $\delta_A - \delta_B$ versus $1/r_2$ (Figs. 6 and 8) may be used for the estimations of the monomer reactivity ratios in the copolymerization of the monomer with *n*-butyl vinyl ether.

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Salt Effect in the Base-Catalyzed Polymerization of Unsaturated Amide Compounds. IV. Polymerization of *p*-Vinylbenzamide in the Presence of LiCl/*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine*

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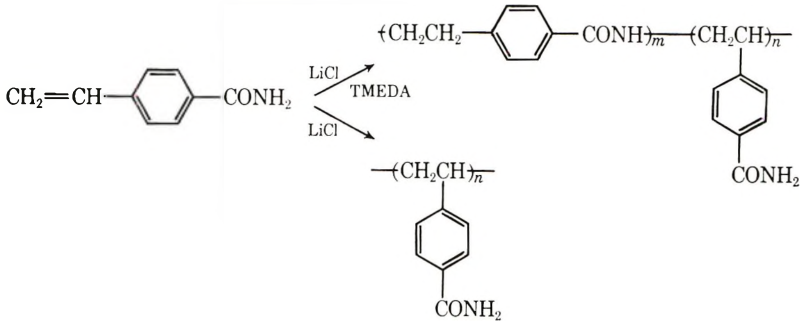
Synopsis

In the presence of lithium chloride and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, *p*-vinylbenzamide was polymerized in basic media to form a polymer with structure consisting of units due to both proton transfer and vinyl type polymerization, whereas in the presence of the salt alone the monomer underwent exclusively vinyl type of polymerization to give a polystyrene derivative:



INTRODUCTION

The salt effect in the polymerization reaction bears a close resemblance to that in catalytic organic reactions, where the reactant changes its electronic structure through interaction with a metallic compound. It is especially noteworthy in the case when the reaction proceeds through a different mechanism to give a different product by the addition of a small amount of inorganic compounds.

It was shown in the previous paper[1] that inorganic salts have a striking effect on the orientation of polymerization of *p*-vinylbenzamide (VBA) in affording different types of polymer and that coordination plays an important role in determining the course of the reaction; a lithium cation

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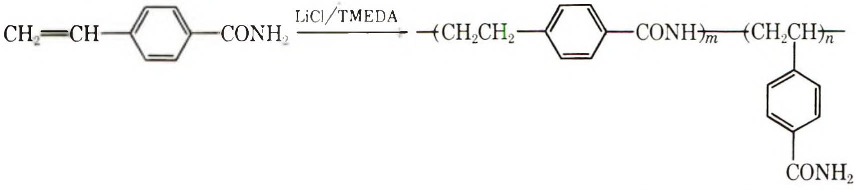
behaves as an acceptor which stabilizes the amide hydrogen atom, resulting in the inhibition of proton transfer polymerization.

An alternative reaction mechanism is possible when other components are added to the system to decrease the inhibition effect of the lithium cation on the proton transfer reaction, and only a solvating effect is maintained by coordination with functional groups of the resulting polymer. *N*,*N*,*N*′*N*′-Tetramethylethylenediamine (TMEDA) is well known as a powerful bidentate ligand to the lithium atom.[2–4]

We wish to describe the results of anionic polymerization of *p*-vinylbenzamide in the presence of both lithium chloride and TMEDA. The ratio of proton transfer to vinyl polymerizations according to eq. (1) was found to vary with changes in both the proportion and amounts of additives.



$m/m + n = 0\text{–}0.95$ (1)

RESULTS AND DISCUSSION

The Role of Initiator

In most of our experiments, *n*-butyllithium was employed as initiator to exclude the effect of a metal–metal exchange reaction. It was found previously that the catalytic activity of the lithium initiator was remarkably enhanced by the addition of TMEDA.[2–4] It is necessary to ascertain the effect of the initiator which may control the mechanism of the polymerization. The possibility that only the lithium initiator with TMEDA could cause the proton transfer polymerization through the enhancement of the catalytic activity can be ruled out by the results in Table I. Consequently, TMEDA acts as a "trapping" agent of a lithium cation of the salt.

Polymerization Solvents

The results of Table II show remarkable differences in the effect of various solvents on the mechanism of the polymerization. An interesting fact is that only hexamethylphosphoramide (HMPA) gave rise to a homogeneous system with proton transfer polymerization, while *N*-methylpyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), dimethylformamide (DMF), and pyridine lead to polymer precipitation and vinyl polymerization. In the case of *N*-methylpyrrolidone, polymer formed as transparent substance on the glass wall. This suggests that only HMPA provides good solvation of the polymer–lithium chloride system.

TABLE I

Proton Transfer Polymerization of VBA with Different Initiators

Initiator	Initiator concn, mole × 10^4	Monomer, mole × 10^3	LiCl, mole × 10^4	TMEDA, mole × 10^4	Solvent (HMPA), ml	Polymerization condition		Polymer yield, %	η_{inh}[a]	H$^+$ transfer, %[b]
						Temp, °C	Time, hr			
n-BuLi	4.74	3.34	19.4	39.3	4.5	120	4	45.0	0.252	85
t-BuONa	3.13	2.44	19.1	24.0	3.0	120	20	44.0	0.374	65

[a] In concentrated H_2SO_4, 0.50%, 25.0°C.

[b] Percentage of proton transfer units $\{[m/(m + n)] \times 100\}$ determined from the infrared spectrum ofthe polymer.

TABLE II

Anionic Polymerization of VBA in Various Solvents in the Presence of LiCl/TMEDA

Solvent	Vol solvent, ml	Monomer, mole × 10^3	Initiator,[a] mole × 10^4	LiCl, mole × 10^3	TMEDA, mole × 10^3	Polymerization conditions		Appearance of the system[b]	Polymer yield, %	η_{inh}[c]	H$^+$ transfer, %
						Temp, °C	Time, hr				
HMPA	3.0	2.44	3.13	1.91	2.40	120	5	Homogeneous	44.6	0.374	65
NMP	2.5	2.22	3.21	2.19	2.67	120	18	—[d]	17.2	—	<10
DMAc	2.5	1.84	2.83	2.16	2.59	120	18	Heterogeneous	15.5	—	0
DMF	2.5	2.10	2.61	2.34	2.60	120	18	Heterogeneous	13.6	—	0
Pyridine	2.5	2.03	3.18	2.22	2.63	120	18	Heterogeneous	12.4	—	0

[a] n-BuLi.

[b] At the end of the polymerization.

[c] In concentrated H_2SO_4, 0.50%, 25.0°C.

[d] Indistinguishable.

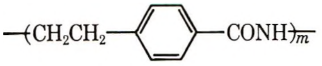
Concentrations of Monomer, Lithium Chloride, and TMEDA

The concentration of the components has a striking effect on the reaction mechanism in this polymerization. In actual runs, the amount of TMEDA was made greater than that of LiCl in order to simplify the relationship between them.

The details of the experiments are given in Table III and Figure 1.

The inhibition of the proton transfer increases with increasing concentration of the salt, in spite of the addition of TMEDA. Since it is reasonably presumed that almost all of the lithium cations have been "trapped" by TMEDA molecules, the inhibition effect in these systems must have been brought about by coordinated lithium cations and not by free lithium cations. Another possibility may be an increase in vinyl type polymerizability with increase in the polarity of the system due to increasing salt concentration.

The increase in inherent viscosities with the increasing salt concentration shown in Figure 1 is ascribed chiefly to increase of the proportion of vinyl type polymerization units. Moreover, the concentration of lithium chloride controls the relative contents of the proton transfer (I) and vinyl type(II) polymerization units, which in turn govern the solubility of the resulting polymer in the solvent used for the viscosity determination, since the solubility of the vinyl polymer is much greater than that of the proton transfer polymer.[1]



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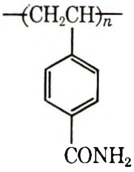

II

The polymer yield decreases with increasing salt concentration, as shown

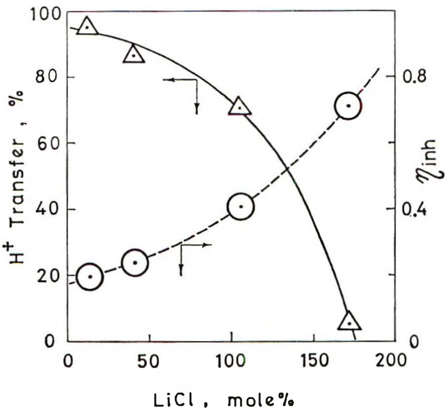

Fig. 1. Effect of amount of LiCl on the viscosity and proton transfer ratio of polymer. Viscosity measurement in concentrated H_2SO_4, 0.50%, 25.0°C.

TABLE III

Polymerization of VBA in the Presence of Greater Amounts of TMEDA than that of LiCl[a]

Monomer mole $\times 10^{-3}$	LiCl, mole $\times 10^3$	TMEDA, mole $\times 10^3$	n-BuLi, mole $\times 10^3$	Polymer yield, %	η_{inh}[b]	H^+ transfer, %
4.21	0.52	0.99	0.756	87.5	0.197	95
4.09	1.65	2.32	0.774	74.6	0.237	86
4.11	4.29	4.82	0.774	35.2	0.407	75
4.08	7.20	8.08	0.756	36.2	0.710	5

[a] Polymerization conditions: 120°C, 17.5 hr; solvent, HMPA, 5.0 ml.

[b] In concentrated H_2SO_4, 0.50%, 25.0°C.

TABLE IV

Polymerization of VBA in the Presence of Various Amounts of Lithium Chloride at a Constant TMEDA Concentration[a]

	LiCl					
Monomer, mole $\times 10^3$	Mole $\times 10^3$	Mole-% (based on monomer)	TMEDA, mole $\times 10^3$	Polymer yield, %	η_{inh}[b]	H^+ transfer, %
2.75	1.25	45.4	126.1	51.9	0.424	76
2.65	2.52	96.2	127.4	36.4	0.604	17
2.57	3.30	128.5	134.9	38.4	0.634	12
2.89	4.50	158.0	128.0	40.2	0.761	3

[a] Polymerization conditions: 120°C, 20 hr; solvent, HMPA, 3.0 ml.; initiator, n-BuLi, 0.487×10^{-3} mole.

[b] In concentrated H_2SO_4, 0.50%, 25.0°C.

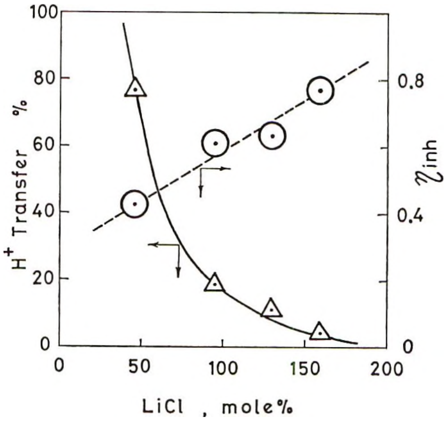

Fig. 2. Effect of amount of LiCl on the viscosity and proton transfer ratio of polymer at constant [TMEDA]. Viscosity measurement in concentrated H_2SO_4, 0.50%, 25.0°C.

in Table III. These relationships are the reverse of those observed in VBA polymerization in the presence of the salt only, where the number of active species increased with the lithium chloride concentration.[5]

The results of another experiment on the effect of the salt concentration is shown in Table IV. In this case the amount of TMEDA was kept nearly constant and only the lithium chloride concentration was varied. The results, plotted in Figure 2, show a similar phenomenon to that in Figure 1, where the proportion of proton transfer decreased as the viscosity of the polymer increased. The proton transfer polymerization was shown to occur predominantly in the presence of a considerable amount of TMEDA with smaller amount of lithium chloride added than that of the monomer.

An important result was obtained by varying the TMEDA concentrations at a constant concentration of lithium chloride. In order to decrease the effect of proton transfer inhibition caused by excess lithium chloride, the salt concentration was kept at nearly 90 mole-% relative to monomer, as shown in Table V. The proton transfer ratio was found to be almost

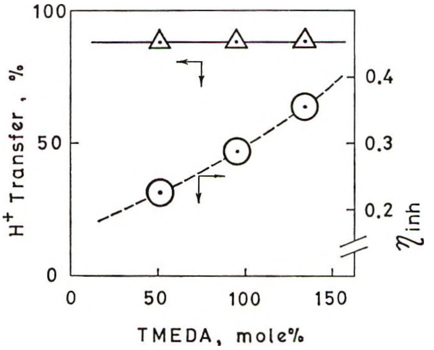

Fig. 3. Effect of TMEDA concentration on the viscosity and proton transfer ratio of polymer. Viscosity measurement in concentrated H_2SO_4, 0.50%, 25.0°C.

TABLE V

Polymerization of VBA in the Presence of Various Amounts of TMEDA at a Constant LiCl Concentration[a]

Monomer, mole × 10³	TMEDA, mole × 10³	LiCl, mole × 10³	System	Polymer yield, %	η_{inh}[b]	H⁺ transfer, %
2.97	1.51	2.67	Homogeneous	76.7	0.225	87
2.92	2.77	2.59	Homogeneous	73.0	0.286	87
2.97	3.97	2.92	Homogeneous	58.0	0.355	87

[a] Polymerization conditions: 120°C, 18 hr; solvent, HMPA, 3.0 ml; initiator, *n*-BuLi, 0.582 mole × 10³.

[b] In concentrated H_2SO_4, 0.50%, 25.0°C.

TABLE VI

Effect of the Initiator Concentration on VBA Polymerization[a]

Monomer, mole × 10³	Initiator (*n*-BuLi) concn: Mole × 10³	Initiator (*n*-BuLi) concn: Mole-% (based on monomer)	LiCl, mole × 10³	TMEDA, mole × 10³	System[b]	Polymer yield, %	η_{inh}[c]	H⁺ transfer, %
2.57	0.261	9.49	1.29	3.45	Homogeneous	41.6	0.174	82
2.79	0.457	16.4	1.28	3.49	Homogeneous	72.0	0.176	88
2.79	0.783	28.1	1.23	3.50	Heterogeneous	92.5	0.218	91
2.86	1.273	45.5	13.0	3.49	Heterogeneous	88.7	0.153	85

[a] Polymerization conditions: 120°C, 21 hr; solvent, HMPA, 3.9 ml.

[b] At the end of the polymerization.

[c] In concentrated H_2SO_4, 0.50%, 25.0°C.

constant (87%), in spite of the considerable variation in the TMEDA concentration, as shown in Figure 3. It is interesting to note that addition of 50 mole-% TMEDA to the monomer was found to be enough to produce polymer consisting mainly of the proton transfer units. It is suggested therefore that multi-coordinated lithium cations are formed under these conditions,[2] since a small amount of free lithium salt inhibits the proton transfer polymerization completely.[5]

The effect of the initiator concentration on the polymerization was studied as described in Table VI. Proton transfer ratios were found to be nearly constant over a wide range of initiator concentrations. The system changes from homogeneous to heterogeneous by the end of the polymerization as the initiator concentration increases.

Table VII shows that the proton transfer ratio is almost constant independent of the polymerization period.

Infrared Spectra of Polymers

Polymerization in the presence of LiCl/TMEDA can give polymers of various proton transfer ratios. These polymers exhibit considerable differences in the carbonyl stretching region of the infrared spectra, as shown in Figure 4. The proton transfer ratio, calculated on the basis of the spectra, is given in the figure.

EXPERIMENTAL

Materials

Monomer. *p*-Vinylbenzamide was synthesized according to the previous direction.[5]

Additives. Commercially available lithium chloride (analytical grade)

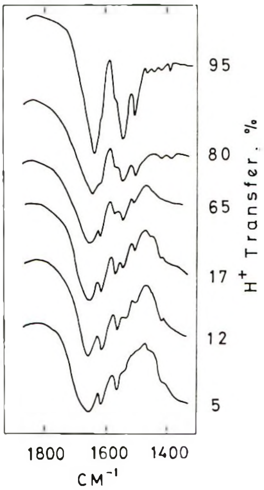

Fig. 4. Infrared spectra of the polymer of various proton transfer ratios.

TABLE VII

Effect of Polymerization Time on the Proton Transfer Ratio[a]

Time, hr	Monomer, mole × 10^3	LiCl, mole × 10^3	TMEDA, mole × 10^3	Polymer yield, %	η_{inh}[b]	H^+ transfer, %
4.0	3.34	1.94	3.93	45.1	0.252	85
8.5	3.29	1.95	3.89	61.5	0.186	87
20.5	3.35	2.00	3.92	87.2	0.163	90
30.5	3.36	1.99	3.91	87.6	0.220	91

[a] Polymerization conditions: 120°C; solvent, HMPA, 4.5 ml; initiator, *n*-BuLi, 0.474 mole × 10^{-3}.

[b] In concentrated H_2SO_4, 0.50%, 25.0°C.

was dried in a high vacuum at 200°C. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) was commercially obtained and distilled after having been dried with potassium hydroxide.

Solvents. Commercially available materials were dried with calcium hydride and distilled under reduced pressure in the presence of phosphorus pentoxide.

***n*-BuLi.** Obtained from Foote Chemicals Company as a 15% hexane solution; the concentration was determined by NaOH titration in each of the polymerization runs.

Polymerization

The same method and apparatus were used as in the previous paper,[5] except that TMEDA was used together with LiCl.

Infrared Measurement

Infrared spectra were taken on a Hitachi EPI-S spectrometer with the use of the KBr technique.

Calculation of the Proton Transfer Ratio of Polymers

The intensities of the amide II band (1545 cm^{-1}) and amide I band (1640 cm^{-1}) were measured by the symmetrical drawing of the amide I absorption as shown in Figure 5*A*. The amide II intensity was measured as shown in Figure 5*B* when the intensity of the conjugative phenylene

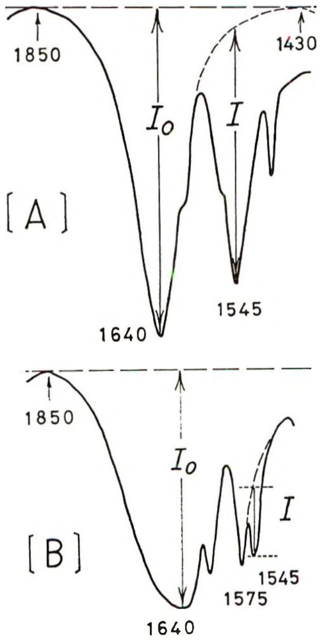

Fig. 5. Calculation of proton transfer ratio of polymer from the infrared spectra. (I_0, I denote the intensity of amide I and II absorptions, respectively.)

group absorption (1575 cm^{-1}) was stronger than that of the amide II. The amide II intensity of *N*-ethylbenzamide (as a model compound) was similarly calculated. Dividing the intensity of the amide II by that of the amide I gave the value of I/I_0, and the I/I_0 value of *N*-ethylbenzamide was 0.935. The proton transfer ratio, in short, was obtained by calculating $(I/I_0)/0.935$. The magnitude of error in these calculations was estimated to be less than about 10%. The result could be considered as a first-order approximation of the proportion of the proton transfer units in the polymer.

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Direct Metalation of Poly(2,6-dimethyl-1,4-phenylene ether)

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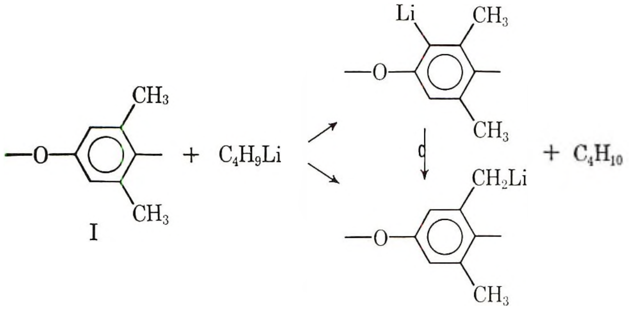
Synopsis

Poly(2,6-dimethyl-1,4-phenylene ether) (I) was metalated with butyllithium in tetrahydrofuran and with the *N,N,N',N'*-tetramethylethylenediamine complex of butyllithium in a variety of solvents. In these cases, metalation occurred at both the ring and side chain positions, the former being preferred initially. Subsequently, there was an isomerization in favor of the side chain.



At 25°C, there is no significant amount of polymer scission or crosslinking during metalation, but some crosslinking occurs on derivatizing with dimethyl sulfate and trimethylchlorosilane for high extents of ring metalation. With sodium and potassium alkyls, only side-chain metalation was observed. The metalated polymer reacts as a typical organometallic, allowing polymer modification by a wide variety of reactions.

INTRODUCTION

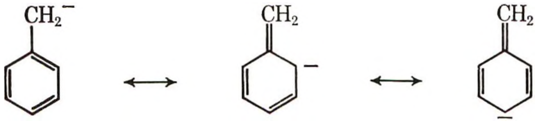
A recent communication[1] disclosed the facile metalation of polyphenylene ethers under a variety of conditions. The present paper details the metalation of poly(2,6-dimethyl-1,4-phenylene ether) (I), the isomerization of the lithiated polymer, and its reactions.

In view of the many reactions possible with lithium alkyls and aryls, metalation is a very versatile method of polymer modification. By this means, it is possible to introduce a wide variety of organic groups into the polymer and to initiate the graft polymerization of anionically polymerizable monomers at the metalation sites. This concept has been applied to metalated polystyrene which was prepared by the reaction of halogenated polystyrenes with alkali metals.[2,3] This method had the disadvantage, however, that reaction between metalated and halogenated sites could lead to crosslinking. This disadvantage is obviated if the polymer can be directly metalated with metal alkyls.

The direct metalation of polymers, however, required, until recently, fairly acidic protons, activated by some neighboring electronegative group which itself was often reactive. The polyphenylene ethers, however, may be metalated directly with butyllithium in tetrahydrofuran without side reactions.[4] While this discovery was being pursued, a report that the *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA) complex of butyllithium was capable of directly metalating benzene[5] caused us to investigate the use of alkyllithium-amine complexes for the direct metalation of polymers in hydrocarbon solvents. It was found that butyllithium-TMEDA was capable of metalating both the polyphenylene ethers[4] and the polystyrenes, the latter discovery was later reported by Yampol'skaya[6] and ourselves.[7] Recently, diene polymers have also been metalated in this way.[8]

The earlier syntheses employing halogenated polymers allowed the preparation of *o*-, *m*-, or *p*-metalated polystyrenes, but the direct metalation raised the question of orientation. We have previously discussed orientation in the metalation of polystyrene,[7] and the present paper details our results on the polymer of 2,6-dimethyl-1,4-phenylene ether (I).

Reviews[9,10] on metalation give little information of value on orientation, but more recently a number of papers have appeared on this subject.[11–13] The metalation of alkylbenzenes has thus been shown to proceed first on the ring, followed by an isomerization to the side chain. This is consistent with the greater stability of a benzyl anion over that of an aryl anion. The former is believed more stable due to resonance.



The introduction of heteroatoms can change this simple picture, however, in some cases thermodynamically favoring ring metalation. This has been ascribed to stabilization by chelate formation of the metal with the heteroatom.[14]

Of the many variables likely to affect the orientation of metalation, time was considered to be the most important in view of the earlier work. The metalation was therefore terminated after varying times with a suitable reagent such as dimethylsulfate or trimethylchlorosilane, the solvent composition examined by glpc and the polymer recovered and examined by NMR spectroscopy. The polymer was also examined for chain scission and crosslinking side reactions by molecular weight measurements.

EXPERIMENTAL

Materials

Poly(2,6-dimethyl-1,4-phenylene ether) (I) was obtained from General Electric Polymer Products Operation, Selkirk, New York. It was dried for 18 hr at 70°C *in vacuo* prior to use.

Butyllithium in hexane (1.6*M*), Foote Mineral Company, was analyzed[15] by direct titration with 0.1N HCl after hydrolysis.

N,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), Ames Laboratories, was distilled under nitrogen prior to use.

Dimethyl sulfate, Matheson, Coleman and Bell, was used without further purification.

Trimethylchlorosilane, GE Silicone Products Department, was distilled under nitrogen before use.

Tetrahydrofuran was refluxed over lithium aluminum hydride for two days and distilled from lithium biphenyl.

Benzene, toluene, and cyclohexane were dried over calcium hydride.

Metalation of I with Lithium Compounds

Solutions of I (2%) in a suitable solvent were reacted under nitrogen with butyllithium or phenyllithium. When benzene or toluene was used as solvent, TMEDA was added to the extent of one mole of amine per mole of lithium. When tetrahydrofuran was used as solvent, the polymer solution was obtained by rapidly cooling a hot solution to room temperature. After varying time intervals, samples were reacted with a small excess of a suitable reagent (dimethyl sulfate, trimethylchlorosilane, etc.). The solvent composition was then examined by glpc and the polymer recovered by precipitation into excess methanol. The polymer was then examined by NMR (Varian A-60, deuteriochloroform or carbon disulfide solvent, dioxane internal standard), gel-permeation chromatography, automatic osmometer (Hallikainen model 1361), capillary viscometer, and light-scattering photometer (Brice-Phoenix). The latter measurements were all made in benzene solution.

Metalation of I with Sodium and Potassium Compounds

Hexylpotassium and Hexylsodium. A solution of 6 g of I in 250 ml of benzene containing 4 g of solid potassium metal was heated to 72°C under a nitrogen atmosphere with vigorous stirring to produce a dispersion of the potassium metal. No reaction occurred between the metal and the polymer solution. After cooling to room temperature, 6 g of 1-chlorohexane was added over a 30-min period to produce hexyl potassium *in situ*. The solution was heated to 65°C, causing the solution to become very dark brown and very viscous. After 1 hr 7 g of dimethyl sulfate was added, causing the dark brown color to disappear and the viscosity of the solution to decrease. The polymer was isolated as described previously.

This reaction was repeated, except with the use of 2.3 g of sodium in place of potassium and with toluene instead of benzene so that the dispersion step could be carried out at 100°C. The polymers were recovered in good yield (>90%).

Potassium and α-Methylstyrene. Potassium (1 g) was dissolved with stirring in a solution of 1 g of biphenyl in 20 ml tetrahydrofuran under nitrogen. α-Methyl-styrene (3 g) dissolved in 10 ml tetahydrofuran was then added slowly over 2 hr. The resulting red solution was filtered through glass wool and a sample titrated against *n*-hexanol to give a molarity of 0.45.

An 8-ml portion of the solution was added to 2 g of I dissolved in 30 ml benzene. In 25 min, the solution set to a thick gel, and after 1 hr was reacted with 2 ml trimethylchlorosilane. The product was diluted to 100 ml with benzene, centrifuged, and the solution precipitated into methanol, washed and dried *in vacuo*. The polymer was recovered in good yield (90%).

Reactions of the Metalated Polymer

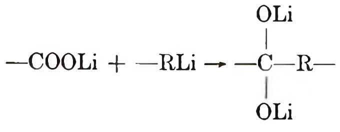
In addition to derivatization with dimethylsulfate and trimethylchlorosilane, a variety of other reactions were tried. In each case, the polymer was isolated by precipitation into methanol, and the success of the reaction assessed by suitable analysis, e.g., elemental analysis, NMR, etc. One reaction, carboxylation, required a special procedure and will be described in detail.

Carboxylation. A solution of 5 g of I in 100 ml of benzene and 25 ml of tetrahydrofuran was prepared and reacted with 36 g of butyllithium ($1.6M$ in *n*-hexane) for 1 hr and then poured into 500 ml of ether containing an excess of solid carbon dioxide.* After the suspension was warmed to room temperature, the polymer was removed by filtration and triturated with dilute hydrochloric acid and then with water. The polymer was then dried *in vacuo* at 100°C overnight. Analysis of the isolated polymer showed that it had a neutralization equivalent of 5.23 meq/g, i.e., an average of 0.82 carboxyl groups for each repeating unit of the polymer.

Hydrolysis of Trimethylsilylated Polymer

Acidic Conditions. A 0.75 g sample of polymer with repeating units substituted to the extent of 41.2% with trimethylsilyl groups (63% at 9.53 τ and 37% at 10.05 τ) was dissolved in 25 ml benzene and stirred at room temperature with 50 ml concentrated aqueous hydrochloric acid for 72 hr. The mixture was then precipitated into an excess of methanol,

* A large excess was used to avoid possible crosslinking reactions which could result from:



$$\text{—COOLi} + \text{—RLi} \rightarrow \text{—}\underset{\text{OLi}}{\overset{\text{OLi}}{\underset{|}{\overset{|}{\text{C}}}}}\text{—R—}$$

washed and dried *in vacuo.* The resulting polymer differed from the original only in its lack of the 9.53 τ peak.

Basic Conditions. A 1.0 g sample of the polymer used in the above example was dissolved in 40 ml benzene and stirred at room temperature with 1 g potassium *tert*-butoxide and 10 ml dimethyl sulfoxide. Samples were removed periodically, precipitated into excess methanol, washed, dried *in vacuo* and examined by NMR. After 5 hr, the absorption at 10.05 τ had completely disappeared without affecting the remainder of the spectrum.

RESULTS

The Reaction of I with Lithium Compounds

Hydrocarbon Solvents in the Presence of TMEDA. When the ratio of butyllithium to polymer was high as in Table I (one lithium per aromatic ring of the polymer), lithiated polymer precipitated from solution within minutes as a yellow gel. The lithiated polymer only remained in solution when the above ratio was reduced by at least a factor of $^1/_5$. Reaction of the lithiated polymer with dimethyl sulfate or trimethylchlorosilane was very exothermic, but slowed by the heterogeneous nature of the reaction when the lithiated polymer was not in solution.

TABLE I

Lithiation of Poly(2,6-dimethyl-1,4-phenylene ether) (I)
(2% in Benzene, [TMEDA] = [C_4H_9Li] = 0.17*M*, 25°C)

Time, min	Distribution of lithium, %[a]				Yield of recovered polymer, %
	LiC_4H_9[b]	LiC_6H_5	On polymer		
			Side chain (*m*)	Ring (*n*)	
0.17		11	9	15	100
1	20	18	18	27	45
2	16	18	11	33	30
4	5.5	23	20	40	15
8	5	32	18	48	50
21	1.2	36	23	50	60
42	0	50	26	37	15
198	0	57	29	11	93
360	0	53	34	15	85
1140	0	51	46	19	85

[a] Metalation terminated by dimethyl sulfate. N.B. 100% lithium corresponds to the added amount, equivalent to one lithium per oxygen of the polymer.

[b] Minimum values; see text.

Some crosslinked gel was encountered in the work up and was removed by centrifugation. This accounts for some of the lower yields.

Examination of the solvent composition by GLPC prior to workup of the polymer showed the presence of pentane and toluene when the reaction was run in benzene and terminated with dimethyl sulfate. This indicated the presence of both butyl- and phenyllithium in the amounts shown in Table I. The values for butyllithium appear to be slightly low, which would be expected in view of the volatility of pentane. When the reaction was terminated by trimethylchlorosilane, butyltrimethylsilane and phenyltrimethylsilane were identified by infrared and elemental analysis.

Figure 1 shows spectra for (*a*) I, (*b*) I methylated largely on the ring, and (*c*) I methylated largely on the side chain. A and B are due to aromatic and aromatic methyl protons respectively.

Ring substitution is shown by a new aromatic hydrogen (C) attached to a pentasubstituted aromatic ring and new aromatic methyl protons (D and E). Side chain substitution is shown by an aliphatic methyl group (G) and an aromatic methylene (F). Figure 1 *d* shows a polymer sample terminated with trimethylchlorosilane, L being proportional to ring and M to side chain silylation. Aryl methylene, although adjacent to silicon, appears to be included in peak K. This assignment is consistent with results on benzyl trimethylsilane where the aryl methylene was found to absorb from 8.0 to 8.6 τ.[17,18] Evidence for these assignments was discussed earlier.[1]

In the case of the silylated polymer, the assignments were supported by selectively cleaving aryl–silicon bonds by acid hydrolysis (removal of the 9.53 τ absorption) and benzyl–silicon bonds by base hydrolysis[19] (removal of the 10.05 τ absorption). It is of interest that the conditions previously used for the base hydrolysis of low molecular weight compounds[19] were unsuccessful with the polymer, probably due to solubility differences. Thus, 64 hr reflux in a benzene/methanol mixed solvent failed to change the polymer. Use of potassium *tert*-butoxide in a mixed benzene–dimethylsulfoxide solvent, however, accomplished the benzylic desilylation very cleanly after 5 hr at 25°C. The 9.53 τ band was untouched by potassium *tert*-butoxide until the polymer was refluxed for 16 hr in 50/50 v/v benzene–dimethylsulfoxide which gave complete desilylation.

Values from Table I are plotted in Figures 2 and 3. When the experiment was repeated, but with a solution of butyllithium in hexane, the values fell on the same set of curves, except that the curve for phenyllithium was somewhat lower (Fig. 3).

A run similar to that of Table I, but with only $^1/_5$ of the amount of butyllithium, gave a similar kinetic picture but somewhat high percentages of lithium on the polymer (up to 75%) and considerably smaller percentages of phenyllithium (maximum 10%).

The use of toluene as a solvent did not significantly change the curves for *m* and *n* in Figures 2 and 3, although here benzyllithium rather than phenyllithium was formed by solvent metalation.[17]

The reaction between the butyllithium–TMEDA complex and benzene in the absence of polymer is shown in Table II. A similar reaction was run in which at the end of the reaction, polymer was added to produce a solution

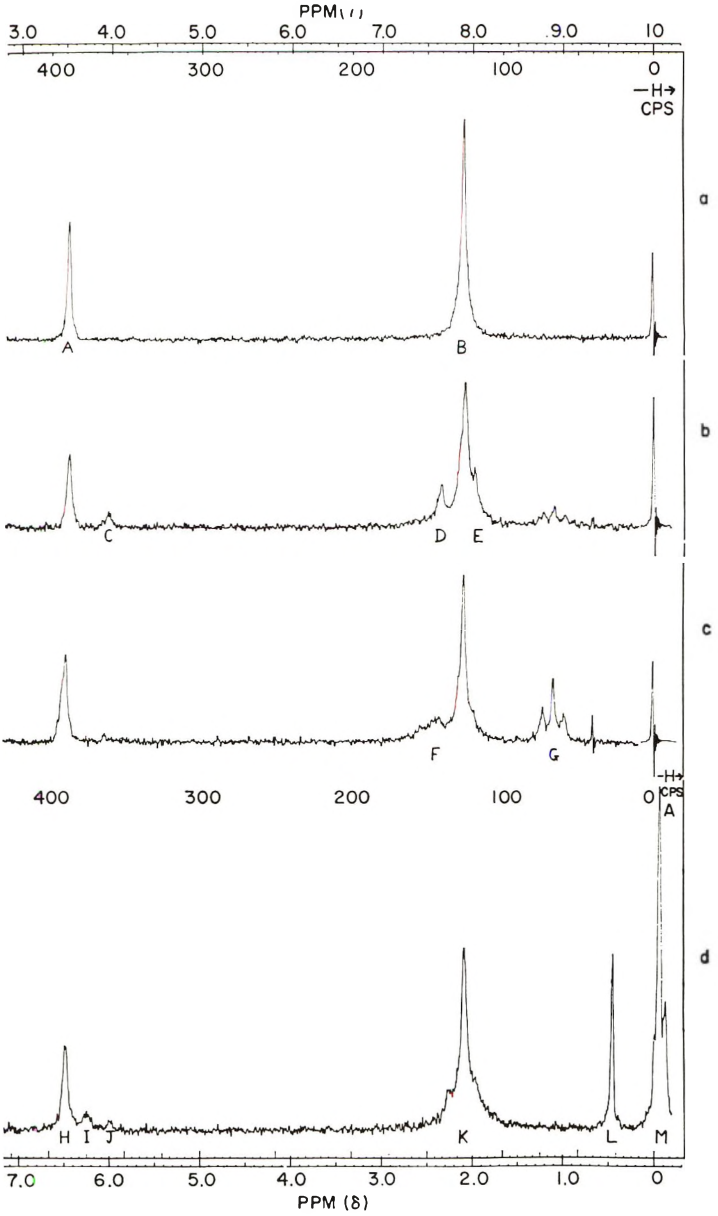


Fig. 1. NMR spectra of polymers: (*a*) I; (*b*) I methylated largely on the ring; (*c*) I methylated largely on the side chain: (*d*) polymer sample terminated with trimethylchlorosilane.

2% in polymer and 0.17M in phenyllithium. The subsequent reaction of the phenyllithium with polymer is shown in Figure 4. When the reaction was run at 70°C, a similar picture of the metalation resulted, but with 60% polymer metalation being reached after only $2^1/_4$ hr.

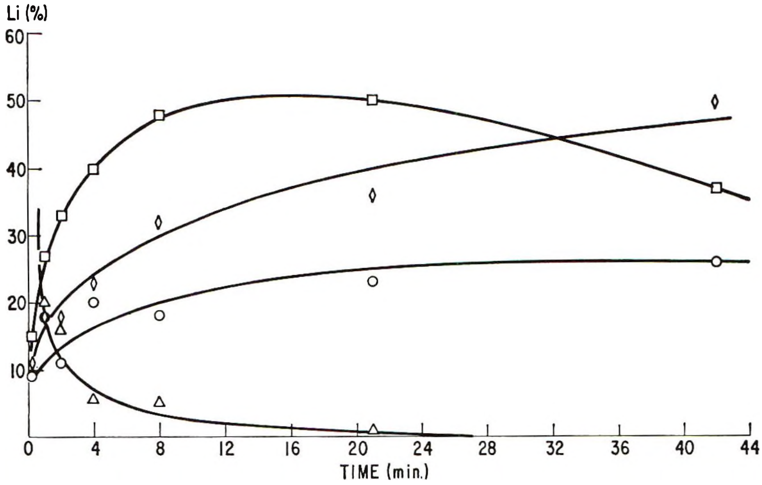


Fig. 2. Lithiation of I with butyllithium–TMEDA complex in benzene at 25°C: (Δ) LiC_4H_9; (◊) LiC_6H_5; (○) *m*; (□) *n*.

TABLE II
Lithiation of Benzene at 25°C in the Presence of TMEDA (0.17*M*)

Time, min	$[LiC_4H_9]$, *M*	$[LiC_6H_5]$, *M*	Total, *M*
0	(0.17)	0	(0.17)
3	0.086	0.055	0.141
13	0.034	0.115	0.149
33	0.010	0.141	0.151
60	0.004	0.156	0.160
1080	0	0.158	0.158

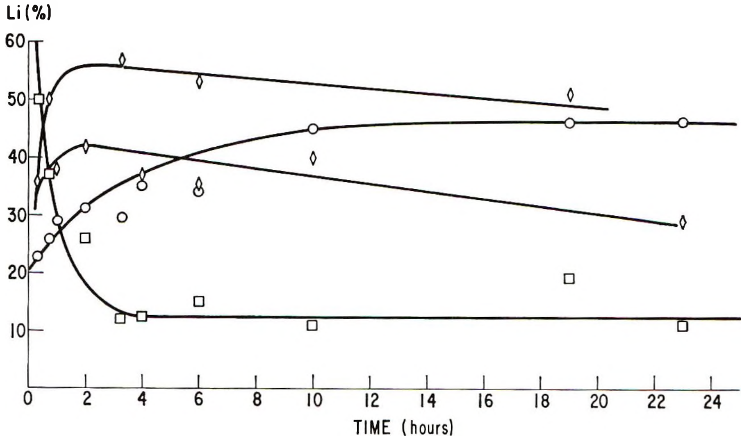


Fig. 3. Lithiation of I with butyllithium–TMEDA complex in benzene at 25°C: (◊) LiC_6H_5; (○) *m*; (□) *n*.

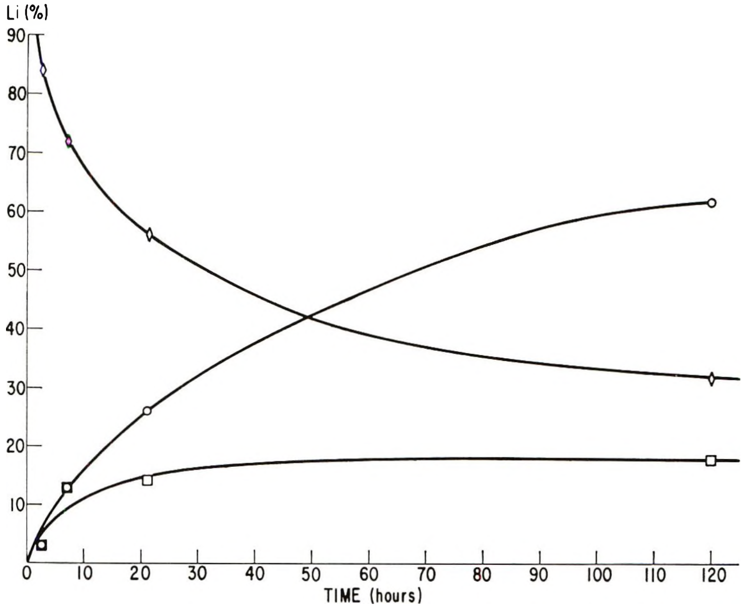


Fig. 4. Lithiation of I with phenyllithium-TMEDA complex in benzene at 25°C; (◇) LiC_6H_5: (○) *m*; (□) *n*.

Although I has little or no solubility in aliphatic hydrocarbons, metalation should be possible by a heterogeneous reaction. This possibility was examined for a 2% suspension in cyclohexane, using the same ratio of the butyllithium complex to polymer used in Table I. After 20 hr at room temperature, the amount of lithium accounted for was 26% on the polymer (5% ring, 21% side chain) and 16% as butyllithium. After a further 6 hr at 80°C, lithium was detected only on the polymer and solely on the side chain (48%). In the latter case only, there was a small decrease in molecular weight of the recovered polymer (a reduction of 30,000 to 20,000 by gel permeation chromatography).

Tetrahydrofuran as Solvent. I is metalated by butyllithium in tetrahydrofuran at a similar rate to the metalation in benzene in the presence of TMEDA. Table III also shows that the course of the metalation is very similar. As in benzene, a yellow gel was formed after about one minute. After 20 hr, the gel had changed to a deep orange, and after 2 days, had redissolved to a considerable extent. Crosslinked polymer was found throughout the reaction, but was particularly prevalent at high extents of ring metalation. This is reflected in the low yields of polymer recovered in Table III. A number of experiments were then carried out to investigate the conditions under which maximum crosslinking occurred. A number of samples were left for 30 min with butyllithium and the reaction terminated in various ways.

Water or methanol gave no crosslinking; dimethylsulfate and trimethylchlorosilane gave crosslinking when added to the mixture or when the

TABLE III
Lithiation of I (1.8% in THF) ($[C_4H_9Li] = 0.17M$, 25°C)

	Distribution of lithium, %[a]				
		On polymer			
Time, min	LiC_4H_9	Side chain (m)	Ring (n)	Total	Yield of recovered polymer, %
0.5	>35	11	20	>66	70
1	32	20	27	79	60
3	9	23	36	68	15
8	5	25	45	75	15
20	~0	28	41	69	5
47	0	24	43	67	60
123	0	25	33	58	15
360	0	35	29	64	70
2760	0	42	16	58	70

[a] n = fraction of polymer units substituted on a ring.

mixture was added to it. (The reverse addition did not work very well in view of the insolubility of the lithiated polymer.) A large excess of dimethyl sulfate was tried, added both neat and diluted with tetrahydrofuran. Only in the former case was there a significant improvement; in this case the polymer was recovered in good yield and showed a somewhat broader molecular weight distribution than the original polymer by gel permeation chromatography with a maximum at 60,000 molecular weight compared with a value of 50,000 for the original polymer.

Use of Other Amines. A variety of diamines were successfully used as alternatives to tetramethylethylenediamine. These included *N*,*N*,*N'*,*N'*-tetraamylethylenediamine, *N*-methyl-*N*,*N'*,*N'*-triethylethylenediamine, and 1,2-bis(morpholino)ethane. Monoamines such as trimethylamine were ineffective at the level of two moles/mole butyllithium. However, at this level, if as little as 2% of the trimethyllamine is substituted by TMEDA, the mixture is about as effective as 100% substitution by TMEDA. Thus, in the presence of trimethylamine, TMEDA is very effective at the catalytic level.

Molecular Weight Distribution of Recovered Polymers. The intrinsic viscosities of the recovered polymers showed no significant variation from that of the starting material (Table IV). The change of viscosity with concentration (λ) however, changed considerably, increasing markedly with the length of time of the metalation.

The molecular weight distribution profile of a number of samples was also examined by gel-permeation chromatography. The untreated polymer gave a single peak at a molecular weight of approximately 50000, the molecular weight range at half peak height being approximately 300000–10000. Polymers treated at 25°C were essentially the same, except perhaps for a slight broadening of the molecular weight range to larger values

TABLE IV
Molecular Weight Data on Recovered Polymers

Sample and conditions of metalation	$[\eta]^a$	λ^b	$\bar{M}_n{}^c$
Untreated polymer	0.55	0.132	20000
Methylated polymers			
25°C, 2 hr[d]	0.55	0.26	20000
25°C, 10 hr[d]	0.60	0.26	25000
25°C, 5 days[d]	0.515	0.396	
Trimethylsilyl polymer			
70°C, $2^1/_4$ hr[d]	0.48	0.12	

[a] Benzene, 25°C.

[b] Reduced viscosity/concentration.

[c] Benzene solution.

[d] 2% polymer in benzene, [butyllithium] = [TMEDA] = 0.17*M*.

for the longest times of metalation. Raising the temperature of the metalation, however, greatly accelerated changes in the molecular weight profile. A sample treated at 70°C for 28 hr showed a peak at a molecular weight of approximately 20000, with shoulders at 100000 and 400000 with a range of $\sim 10^6$ to 4000 at half peak height.

Reaction of I with Sodium and Potassium Compounds

In contrast to the metalations using lithium compounds, metalations by sodium or potassium compounds gave only side chain metalation. In the preparations employing hexylpotassium and hexylsodium, some heptyl groups were also incorporated.

Thus, in the example in which hexylpotassium was used, the NMR spectrum of the polymer showed that the methyl groups on 14% of the polymer repeating units had been converted to ethyl groups and 4% to heptyl groups. Similarly, the polymer obtained from the use of hexylsodium had 10% of the methyl groups converted to ethyl and 17% to heptyl groups.

In the case of the potassium dianion from α-methylstyrene, NMR showed that approximately 67% of the metal was transferred to the polymer, exclusively in the benzylic position.

Reactions of the Metalated Polymer

Some results for trimethylchlorosilane are given as a typical example. The important considerations in other reactions are given more briefly.

Trimethylchlorosilane. Some results of adding trimethylchlorosilane to polymer metalated to varying degrees are shown in Table V. As the amount of butyllithium is reduced, there is an increasingly efficient transfer to the polymer until a point is reached where the amount of butyllithium is so small that reaction with impurities competes with polymer metalation. The amount of silicon determined by NMR agreed well with elemental analysis, e.g., sample 6 gave 10.9% Si and sample 5, 4.4% Si by

TABLE V
Reaction of the Metalated Polymer with Trimethylchlorosilane[a]

Sample	Lithium added, %[b]	Si in polymer, %[c]	Yield (lithium), %[d]	T_g, °C[e]
1	0	0		220
2	5	0.38	45	218
3	10	1.45	87	212
4	20	2.40	72	196
5	40	4.80	72	187
6	100	10.70	64	170

[a] Results obtained by R. C. Gueldner.

[b] 100 × ratio of butyllithium to polymer (moles/120 g I).

[c] By elemental analysis.

[d] Percent Li effective in metalating polymer.

[e] Values on heating cycle at 80°C/min.

NMR. There was a pronounced lowering of the T_g with increasing substitution (Table V).

Carboxylation. Polymers with high degrees of carboxylation (30–100% of polymer units carboxylated) were soluble in tetrahydrofuran and pyridine, but insoluble in chloroform. There was no indication of any crosslinking. Films cast from tetrahydrofuran were tough and flexible. When heated to 300°C, they became insoluble, presumably by crosslinking via anhydride formation. The polymers were soluble in hot dilute base and heating in refluxing aniline converted them to the anilides, which were again thermoplastic.

Ketones. The metalated polymers reacted smoothly with a variety of ketones. With Michler's ketone, a polymer was obtained which on air oxidation or treatment with acid became intensely blue-green in color (polymeric triphenylmethane dye). Similarly, reaction with the bis(dihydropyranyl)ether of 4,4′-dihydroxybenzophenone gave a colorless polymer which on treatment with acid turned red. A variety of colors could also be introduced by reaction with any of the phthaleins if the phenolic hydroxyls were first blocked. Other ketones used included cyclohexanone, methylundecyl ketone, stearone, benzophenone, diisobutyl ketone, and acetylthiophene. The long-chain ketones gave polymers with greatly depressed melting points.

Organometallic Halides. The following were successfully reacted with the metalated polymer: $(C_6H_5)_2PCl$, $(C_6H_5)_3SiCl$, $(C_6H_5)_2CH_3SiCl$.

Miscellaneous. The following were also successfully reacted with metalated polymer: iodine, diphenyldisulfide, octadecylbromide. Reagents which produced insoluble gels were: sulfur, azobenzene, epichlorohydrin, carbon disulfide, 4-benzoyl pyridine, and thionylchloride.

Acid Anhydrides and Acid Chlorides. Attempts to introduce high percentages of acyl groups invariably produced insoluble gels. The ketone formed initially apparently reacts further to give a tertiary alcohol and a crosslink.

Vinyl Monomers. Anionic graft polymerization was successfully carried out with a variety of vinyl and other monomers. This will be the subject of a further paper.

DISCUSSION

Lithiation in Hydrocarbons in the Presence of TMEDA

The results shown in Table I and Figures 2 and 3 are consistent with a competitive reaction in which butyllithium attacks benzene and both side chain and ring protons on the polymer. Although substitution at a benzylic position is thermodynamically favored over the aromatic ring positions there appears to be an initial kinetic preference for the latter positions on the polymer. A less active lithiating agent would be expected to be more selective, and phenyllithium which is approximately 400 times less active in this reaction shows a greater preference for the side chain position (Fig. 4). Butyllithium rapidly disappears from the system, its disappearance coinciding with a maximum value for ring metalation (*n*) (Fig. 2). Subsequently, lithium transfers from the aromatic ring on the polymer to the side chain (*m*). Further, phenyllithium appears to be an intermediate, i.e., lithium appears to be transferred from the ring position of the polymer to benzene and then subsequently from phenyllithium to the side chain of the polymer. Thus, at one point both phenyllithium and (*m*) are growing at the expense of (*n*) (Fig. 3). Then the amount of phenyllithium reaches a maximum and declines in favor of (*m*). Phenyllithium does not appear to be essential for the isomerization from ring to side chain of the polymer, however. Thus, when the reaction was carried out in cyclohexane, there was a similar effect, although the solvent was not attacked. It seems likely, however, that the amine is attacked and subsequently transfers lithium to the polymer, since the total amount of lithium accounted for as butyllithium and polymer–lithium combined was found to increase unaccountably during the course of the reaction. Although the metalated amine could be involved in the isomerization, it is also not essential since the same reaction occurs in tetrahydrofuran. In view of the comparitively large amounts of metalation found in cyclohexane, it seems probable that the metalation occurred homogeneously due to a small solubility in the solvent.

Lithiation in toluene was very similar. The fact that the polymer continues to be metalated after the disappearance of butyllithium indicates a greater stability of lithium on the side chain of the polymer than for benzyllithium. In view of the large excess of toluene present, this metalation by benzyllithium was unexpected.

Lithiation in Tetrahydrofuran

Table III shows that a similar variation of lithium on the two sites in the polymer occurs when tetrahydrofuran is used as a solvent. As in benzene, metalation of solvent competes with metalation of the polymer. The lithiated solvent does not appear to effect any further metalation of polymer and presumably reacts further to produce lithium alkoxides. Transfer of lithium from the ring to the side chain of the polymer continues to occur, however, presumably by a reaction within or between polymer molecules.

Thus, in a variety of solvents, the lithiated polymer appears to undergo isomerization. No isomerization was previously found for the ring lithiation of toluene,[17] and such isomerizations have not previously been reported.[25]

No ring metalation was found when sodium or potassium alkyls were used. Since sodium and potassium alkaryls appear to isomerize more rapidly than the corresponding lithium compounds,[10–12] this was an expected result. The introduction of heptyl groups must have resulted from the initially metalated polymer reacting with chlorohexane. No hexyl groups were introduced into the unsubstituted 3 or 5 positions.

From the results of gel permeation chromatography, crosslinking and chain scission reactions do not appear to take place during the metalation except for prolonged reaction times at elevated temperatures (e.g., 28 hr at 70°C). Upon terminating the reaction with dimethyl sulfate or trimethylchlorosilane, however, crosslinking was sometimes found. This was most pronounced for large extents of ring metalation and was more serious in tetrahydrofuran than in benzene or toluene. It was greatly reduced by using high concentrations of the terminating reagent. Further, no crosslinking was found when methanol or water was used for termination. This suggests that with both dimethyl sulfate and trimethylchlorosilane there are side reactions in which the carbanion attacks sulfur and chlorine respectively, followed by coupling reactions. Attack at sulfur has been claimed to occur in the reaction of phenyllithium with certain alkyl sulfates.[21] Only a small percentage of such a side reaction would be necessary to result in extensive crosslinking.

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Novel Preparation of Pure β-$TiCl_3$ and Its Use in Isoprene Polymerization

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Synopsis

Treatment of the reaction product of $TiCl_4$, Al, $AlCl_3$, and an aromatic compound with an ether and subsequently with $TiCl_4$ yields very pure β-$TiCl_3$. This material, when treated with small amounts of aluminum trialkyls, is a very active catalyst for the stereospecific polymerization of isoprene. If the above reaction is stopped after the ether addition, before the addition of $TiCl_4$, the product so obtained is largely $TiCl_2$. Reaction variables in the preparation of $TiCl_3$ are described as is the effect of various organoaluminum compounds as cocatalysts for polymerization.

INTRODUCTION

It is well known that of the four crystal modifications of $TiCl_3$ presently known, only the brown (β) form polymerizes diolefins to high *cis*-1,4 polymers when treated with aluminum alkyls.[1] The other three (α, γ, and δ) yield *trans* structures preferentially. Methods reported for the preparation of β-$TiCl_3$ include the low temperature (ca. 25°C) reduction of $TiCl_4$ with hydrogen in an electric discharge or by organoaluminum compounds.[2] Only the latter process has been reported to yield a polymerization-active catalyst for diolefins. Yet another method, which has many practical advantages, was suggested by an observation,[3] several years ago, that the product formed by reacting $TiCl_4$, $AlCl_3$, Al, and benzene could be oxidized by $TiCl_4$ to give a mixed β-$TiCl_3 \cdot AlCl_3$ complex.

It had been known for several years that reaction of $TiCl_4$, $AlCl_3$, Al, and aromatic hydrocarbons under "reducing Friedel-Crafts" conditions[4] affords crystalline complexes containing Al, Cl, the aromatic hydrocarbon, and divalent Ti.[3,5] Hereinafter these are called Natta complexes. The complex formed with benzene has the empirical formula $Al_2Cl_8Ti \cdot C_6H_6$. This compound reduces $TiCl_4$ to the brown (β) form of $TiCl_3$, but the product is contaminated with an equimolar quantity of $AlCl_3$.[3] It is consequently of low activity for the high-*cis*-1,4 polymerization of isoprene.

With a view to removing the cocrystallized $AlCl_3$ from the mixed compound, thereby improving the catalytic activity of the β-$TiCl_3$, we studied the effect of ethers on the reaction between Natta complexes and $TiCl_4$.

EXPERIMENTAL

Preparation of β-$TiCl_3$

Al was from Baker and Adamson, Matheson Coleman and Bell, and Almeg. $AlCl_3$ was from Matheson Coleman and Bell. $TiCl_4$ was from Fisher Scientific. All were used without further purification. Benzene was from Matheson Coleman and Bell, Spectroquality grade. It was refluxed over and distilled from CaH_2, passed through silica gel, and stored under nitrogen. Heptane was an acid-washed commercial grade purified similarly to benzene. Toluene was acid-washed ACS reagent grade from Allied Chemical. Ethers were reagent grade from Fisher Scientific and anhydrous grade (Et_2O) from Allied Chemical. The reaction apparatus consisted of a 500-ml three-necked glass Morton flask having four sidewall indentations. This was sealed onto a sintered glass funnel of ultrafine porosity (UF series, Corning Glass Works, Corning, N. Y.). The lower stem of the funnel was bent around and upwards and a piece of glass tubing was sealed on and passed up vertically beside one indentation. A connection was then made to a reservoir and thence to a three-way stopcock one side going to vacuum, the other to a pure nitrogen system. The three-necked flask was fitted with a high-speed stirrer (Stir-O-Vac, Cole-Parmer Co., Chicago, Ill.), a large serum cap, and a pure nitrogen inlet system.

A typical $TiCl_3$ preparation involved loading the reactor with Natta complex in an inert atmosphere. Then solvent was added. The stirrer was started and a cooling bath was arranged around the apparatus. The calculated amount of ether was now added slowly. A black precipitate formed. In some runs the solvent was removed by filtration at this stage. The black solid was resuspended in fresh solvent and then $TiCl_4$ was added slowly. The black color was gradually replaced with the brown color of β-$TiCl_3$. The solvent was removed by suction and the solid was rewashed with more solvent. Finally, the β-$TiCl_3$ was made up as a suspension in heptane.

Polymerizations

Organoaluminum compounds were from Texas Alkyls and were used without further purification. The following organoaluminum compounds were used: triethylaluminum (TEA), tri-*n*-propylaluminum (TNPA), tri-*n*-butylaluminum (TNBA), triisobutylaluminum (TIBA). All were of typical commercial purity.[6] Polymerization experiments were performed in 4-oz bottles at 50°C as previously reported.[7] Isoprene, distilled under nitrogen, and pentane, dried over Drierite, were combined to give a 20% premix. The premix was then passed through a fresh column of silica-gel prewetted with pentane. A 90-ml portion of the purified premix was dispensed into each bottle. The bottle was then placed on a hot sand bath and vented until about 80 ml of premix remained. At that point the catalyst components were syringed into the still-boiling premix, the aluminum compound first, then the titanium compound. A catalyst level of 1.32 mmole

$TiCl_3$/100 g isoprene was used throughout. The polymerizations were terminated by the addition of isopropanol (containing 2,5-di-*tert*-amyl hydroquinone as antioxidant). Polymers were precipitated in isopropanol, and finally dried under vacuum. Yields were determined after the stated times.

RESULTS AND DISCUSSION

Preparation of β-$TiCl_3$

The reaction of the Natta complex with $TiCl_4$ can be written

$$Al_2TiCl_8 \cdot \text{Arene} + TiCl_4 \rightarrow 2TiCl_3 \cdot AlCl_3 + \text{Arene} \qquad (1)$$

In the presence of ether, the reactions (2) and (3) can be expected for one and two moles of ether/mole of Natta complex, respectively.

$$Al_2TiCl_8 \cdot \text{Arene} + TiCl_4 + R_2O \rightarrow (TiCl_3)_2 \cdot AlCl_3 + AlCl_3 \cdot R_2O + \text{Arene} \qquad (2)$$

$$Al_2TiCl_8 \cdot \text{Arene} + TiCl_4 + 2R_2O \rightarrow 2TiCl_3 + 2AlCl_3 \cdot R_2O + \text{Arene} \qquad (3)$$

Table I shows the results of various reaction variables on these reactions. Increasing amounts of ether results in increased removal of aluminum (40-series). However, some $AlCl_3$ is still bound up in the $TiCl_3$. By using an excess of ether and varying the order of addition of components it was found that the greatest removal of $AlCl_3$ occurred when all the ether was added before the $TiCl_4$ (12-1). Adding half the ether before the $TiCl_4$ and half after (12-2) gave good removal of $AlCl_3$ too, but adding all the ether after the $TiCl_4$ addition was not so effective (12-3). It was therefore considered to be desirable to remove $AlCl_3$ from the Natta complex (presumably to leave $TiCl_2$) before addition of the $TiCl_4$. When the reaction was performed in two separate steps

$$Al_2TiCl_8 \cdot \text{Arene} + nR_2O \rightarrow TiCl_2 \cdot (n\text{-}2)R_2O + 2AlCl_3 \cdot R_2O \qquad (4)$$

$$TiCl_2 \cdot (n\text{-}2)R_2O + TiCl_4 \rightarrow 2TiCl_3 + (n\text{-}2)R_2O \qquad (5)$$

with repeated washing of the intermediate $TiCl_2 \cdot (n\text{-}2)R_2O$ by solvent, much greater removal of $AlCl_3$ was achieved (93-1). The traces of $AlCl_3$ still remaining in the final $TiCl_3$ are not injurious to the subsequent polymerization, since treatment with aluminum alkyls, even at low levels, overcomes any poisoning effect.

Most of our efforts were concentrated on aromatic ethers because they exert less inhibiting effect on the subsequent polymerization of isoprene than aliphatic ethers.[8] In the series 93-1, 95-1, and 114-2 the type of ether was varied. $(C_2H_5)_2O$ offered the greatest potential for removal of $AlCl_3$ since it could be expected to form the strongest complex. It also has economic advantages. However, the catalyst made with diethyl ether had poorer activity compared to those made with $(C_6H_5)_2O$ and $C_6H_5OCH_3$. It is possible that some $(C_2H_5)_2O$ remained in the catalyst, since a large excess of ether was used. The poor catalytic activity is unlikely to be due to residual $AlCl_3$ since 95% of the $AlCl_3$ had been removed by washing.

TABLE I
Catalyst Preparation Variables

Catalyst	Arene[a]	Ether	Ether, moles/mole complex	$TiCl_4$, moles/mole complex	Catalyst preparation temperature, °C	Number of washes and solvent[b]		Final diluent[b]	Al removed, %	Yield of solid polyisoprene in $2^1/_2$ hr, %[c]
						Before $TiCl_4$ addition	After $TiCl_4$ addition			
12-1[d]	Benzene	Anisole	3	1	25	0	3B	B	91	60
12-2[d]	Benzene	Anisole	3	1	25	0	3B	B	90	37
12-3[d]	Benzene	Anisole	3	1	25	0	3B	B	83	—
40-5	Benzene	Diphenyl ether	1	1	10	0	4B	B	54	80
40-6	Benzene	Diphenyl ether	2	1	10	0	4B	B	70	88
40-7	Benzene	Diphenyl ether	3	1	10	0	4B	B	86	87
73-1	Benzene	Diphenyl ether	2	2	10	0	4B	B	ND[e]	30
74-1	Toluene	Diphenyl ether	2	2	10	0	4T	T	ND	76
85-1	Toluene	Diphenyl ether	5	1	25	3B	5 (4B, 1H)	H	ND	91
93-1	Toluene	Anisole	8	2	5	3B	2 (1B, 1H)	H	98	89
95-1	Toluene	Diethyl ether	8	2	5	3B	2 (1B, 1H)	H	95	—
104-1	Toluene	Diphenyl ether	8	1	5	0	3T	H	ND	87
112-1	Benzene	Diphenyl ether	8	1	5	0	3B	H	ND	89
114-1	Benzene	Diphenyl ether	8	2	5	3B	3B	H	ND	76
114-2	Benzene	Diphenyl ether	8	2	5	3B	3B	H	ND	89

[a] In the Natta complex.

[b] B = benzene, T = toluene, H = heptane.

[c] 0.05–0.5 mole AlR_3 used per mole $TiCl_3$.

[d] Order of addition varied (see text).

[e] ND = not determined.

The Intermediate $TiCl_2 \cdot (n\text{-}2)R_2O$

The black precipitate formed on addition of ether to the Natta complex appears to be essentially $TiCl_2$ with small amounts of $AlCl_3$ and free organic material, bound in some unknown manner, in the molecule. Tables II and III detail the results obtained in several experiments. It can be clearly seen in Table III that after removing residual Al as $AlCl_3$, the resulting stoichiometry is $TiCl_2$. In his initial work, Natta[5] treated the Natta complex with a deficiency (for total Al removal) of tetrahydrofuran (THF) and isolated a product which he formulated as $AlTiCl_5 \cdot C_6H_5$, i.e., one mole of $AlCl_3$ had been removed. Martin and Vohwinkel[3] subsequently performed a similar experiment using two moles of THF and isolated a product whose analysis indicated it contained largely $TiCl_2$ together with some aluminum and organic material. Practically all the $AlCl_3$ was removed as the corresponding etherate. Heating this product in a vacuum or heating the Natta complex in a vacuum gave pure $TiCl_2$.[3]

TABLE II

Analytical Data on Products Obtained by Treating the Natta Complex with Ethers

Run	Arene in Natta complex	Ether	Ether, moles/mole complex	Wt. product used, g	Found wts, g Ti	Al	Cl	Balance
66-3	Mesitylene	Anisole	30	2.182	0.315	0.056	0.675	1.130
83-1	Toluene	Diphenyl ether	9	1.338	0.324	0.046	0.672	0.296
83-2	Toluene	Anisole	10	1.747	0.415	0.017	0.700	0.615
86-1	Toluene	Diethyl ether	6	2.110	0.584	0.009	0.897	0.620

TABLE III

Analytical Data after Normalization to Remove Al as $AlCl_3 \cdot$Ether

Run	Found wts, g Ti	Cl	Balance	Molar ratio Ti:Cl
66-3	0.315	0.454	0.909	1.00:1.96
83-1	0.324	0.490	0.113	1.00:2.04
83-2	0.415	0.633	0.547	1.00:2.06
86-1	0.584	0.862	0.584	1.00:2.00

Hydrolysis of the product formed by treating $Al_2TiCl_8 \cdot$toluene with anisole, thought to be $TiCl_2(C_6H_5OCH_3)_n$, yielded H_2, CH_4, CH_3Cl, $C_6H_5OCH_3$, C_6H_5OH, and toluene together with, presumably, HCl.[9] It is obvious that the oxygen atom of the anisole is very much influenced by the $TiCl_2$ and that the CH_4 and C_6H_5OH are formed by the $TiCl_2$-promoted action of H_2 on the anisole cleavage products. The CH_3Cl is probably formed by a Cl atom migration during hydrolysis.

It is not known, at present, why this $TiCl_2$ compound is able to reduce $TiCl_4$ to $TiCl_3$ quantitatively while the purely inorganic $TiCl_2$[10] (even in mixtures with $AlCl_3$) is unable to do so.[11] Possibly this $TiCl_2$ is of a less stable type (cf. β vs. α $TiCl_3$).

Polymerization

Table IV lists polymerization results on selected catalysts in which the type and amount of added organoaluminum compound was varied. The organoaluminum requirement is reduced as the amount of $AlCl_3$ left in the $TiCl_3$ decreases (40-5 and 40-7, Table IV). Optimum yields are obtained only at 0.5/1 Al/Ti for 40-5, with only a trace of polymer at 0.1/1. In contrast, above a ratio of 0.1/1 (40-7), yields begin to decrease markedly, so that at 0.5/1 only a minute amount of polymer is obtained. This is undoubtedly due to reduction of $TiCl_3$ to lower valency species. The polyisoprenes all showed properties typical of high-*cis*-1,4 structure. They were, in general, identical with polymers obtained by aluminum alkyl reduction of $TiCl_4$.

TABLE IV
Effect of Various Organoaluminum Compounds on Polymerization Activity of $TiCl_3$ (as Yield of Solid Polymer)

		Yield of solid polymer, % with varying moles of organoaluminum compound/mole $TiCl_3$					
Organoaluminum compound	Catalyst	0.05 mole	0.10 mole	0.15 mole	0.20 mole	0.30 mole	0.50 mole
TIBA	40-5	Tr	Tr		2	12	20
TNPA	40-5	Tr	1		2	6	11
TIBA	40-7	7	65		41	10	4
TNPA	40-7	Tr	69		28	3	2
TIBA	93-1	0	17		86	63	
TNPA	93-1	Tr	9		89	66	
TIBA	112-1	38	84	86	70		
TNPA	112-1	15	80	84	82		

CONCLUSION

β-$TiCl_3$ has been prepared from $TiCl_4$ without the use of metal alkyls to effect the reduction. This material is a very active catalyst for isoprene polymerization when combined with minute amounts of organoaluminum compounds. A new form of $TiCl_2$, prepared as an intermediate, is discussed.

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Photo and Thermal Polymerizations Sensitized by Donor–Acceptor Interaction. II. Photopolymerization and Electronic Spectroscopy of the Isobutyl Vinyl Ether–Acrylonitrile System

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Synopsis

Photopolymerization of acrylonitrile (AN), an acceptor monomer, was found to be accelerated in the presence of isobutyl vinyl ether (IBVE), a donor monomer. The propagation is completed by a radical mechanism as judged by copolymer compositions; in contrast to the *N*-vinylcarbazole–AN system studied previously. This photopolymerization system is entirely stable if kept in the dark. The comparison of the relation between R_p and [IBVE]/[AN] ratio in the monomer feed found for the spontaneous photopolymerization with that for radical polymerization initiated by azobisisobutylonitrile in the dark leads to the conclusion that the rate of photoinitiation is enhanced by the interaction between AN and IBVE, whereas the propagation step by a radical mechanism is retarded by increasing concentration of IBVE. The contact charge-transfer complex between IBVE and AN was confirmed by electronic spectroscopy of the polymerization system, which showed photosensitization by charge-transfer interaction. The spectroscopic study of other weak donor–weak acceptor systems is also discussed.

INTRODUCTION

In the previous reports,[1,2] the multimode polymerization of *N*-vinylcarbazole–acrylonitrile (AN) was discussed. The initiation of the polymerization is very likely to be a charge-transfer interaction between electron donor and electron acceptor. Of those so far examined, all electron donor–electron acceptor combinations in which at least one component of the pair is a vinyl compound, exhibit considerable photosensitization of polymerization. The photosensitivity seems to be consequently a general property of charge-transfer pairs. The irradiation of charge-transfer complexes does not, however, necessarily lead to the initiation of polymerization. The formation of small molecules such as dimers or cyclic condensates might be detected besides polymerization. A solid monomer such as vinylcarbazole (VCZ) is not suitable to study these side reactions, because of the experimental difficulties of purification and analysis.

We have found that the photopolymerization of AN is greatly enhanced in the presence of a small amount of isobutyl vinyl ether (IBVE). In the present system both electron-donating monomer (IBVE) and electron-accepting monomer (AN) are liquid at room temperature and distillable. This permits us to work under absolutely anhydrous conditions and to examine the formation of by-products other than polymer. Electron spectroscopy of the donor–acceptor system in the quartz ultraviolet region, which was not possible for the system containing VCZ, provided additional information to elucidate the phenomena of photosensitization.

EXPERIMENTAL

Materials

Acrylonitrile was washed with sodium hydroxide solution, phosphoric acid, and repeatedly with water, dried by partial freezing and then over calcium hydride, and distilled twice under nitrogen. Isobutyl vinyl ether was washed with alkaline solution until no color was observed in the aqueous layer, then with water; it was distilled under nitrogen over calcium hydride. Azobisisobutyronitrile(AIBN) was recrystallized twice from methanol. Other reagents used for spectroscopic measurement were all purified by accepted procedures.

When photopolymerization was to be carried out under absolutely dry conditions, the two monomers, purified as mentioned above, were put in separate vessels connected to a vacuum line. After degassing by several freeze–thaw cycles, the monomer was transfered into a vessel containing barium oxide which had been previously baked for 24 hr at 360°C under high vacuum and was left in contact with the drying agent for at least 24 hr. This drying procedure was repeated again and finally the required amounts of the two monomers were distilled into reaction vessels. All operations were conducted under reduced pressure (10^{-5} mm Hg).

Polymerization

Photopolymerization was carried out at 50°C in a glass tube of 12mm outside diameter at a distance of 5 cm from a 300-W high-pressure mercury lamp. Thermal polymerization systems in the dark were wrapped with aluminum foil to protect them from diffused light. The polymerization mixture was poured into methanol and the precipitated polymer was collected.

The copolymer compositions were determined by elemental analysis.

Spectroscopy

Electronic spectra of donor–acceptor systems were measured at room temperature as *n*-hexane solutions with the use of a quartz cell of 1 mm thickness. The continuous variation method was conveniently carried out by means of a spectrocell so devised that the solution of donor or acceptor could be diluted continuously with additional acceptor or donor solution respectively.

RESULTS AND DISCUSSION

Polymerization of AN-IBVE System

Radical polymerization of AN is considerably retarded in the presence of IBVE, whereas the spontaneous photopolymerization is strongly accelerated by the addition of IBVE, as shown in Figures 1 and 2 and Table I. As will be discussed later, since the photopolymerization proceeds by a radical mechanism alone, the different dependence of R_p on the monomer feed ratios as observed for thermally catalyzed and photopolymerizations must be interpreted in term of the initiation process. The enhanced rate of photoinitiation in the AN-IBVE system would therefore be due to the photoexcitation of the weak donor-acceptor pair. The AN-IBVE pair is quite stable at 50°C if the mixture is kept in the dark.

TABLE I
Spontaneous Photopolymerization and Thermally Catalyzed Polymerization of the Acrylonitrile-Isobutyl Vinyl Ether System at 50°C *in Vacuo*

VE, ml	AN, ml	Time, min	Yield, mg	Polymer, mg/min
0	2.0	153	71.0	0.465
0.2	1.8	209	178.0	0.861
0.4	1.6	212	391.5	1.85
0.7	1.3	175	122.0	0.697
1.0	1.0	212	166.6	0.786
1.3	0.7	356	150.0	0.422
1.6	0.4	681	21.1	0.031
1.85	0.2	635	30.5	0.047
2.0	0	635	0	0.000
Thermal Polymerization in the Dark ([AIBN] = 10^{-2} *M*)				
0	1.50	23	159.9	6.95
0.25	1.25	54	104.3	1.93
0.45	1.05	110	111.3	1.00
0.75	0.75	208	174.2	0.838
0.90	0.60	259	156.1	0.603
1.25	0.25	646	203.0	0.315
1.40	0.10	646	90.9	0.141
1.50	0	646	0	0

The compositions of polymer obtained by photopolymerization and thermally catalyzed polymerization agree very well, as shown in Figure 3 and Table II. On expectation of observing ionic propagation by analogy to that in radiation-induced polymerization,[3,4] the absolutely dry system was studied. However, no ionic propagation could be detected.

The photochemistry of charge transfer pairs is not at all a single process and at least the following five modes of initial acts must be taken into account.

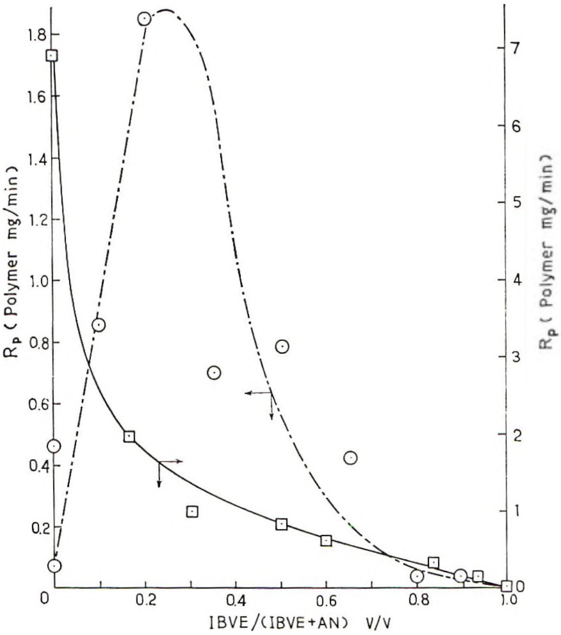

Fig. 1. Polymerization of AN–IBVE system at 50°C *in vacuo*: (○) photopolymerization (absolutely dry system) IBVE + AN = 2 ml; (□) catalyzed polymerization in the dark [AIBN] = 10^{-2} *M*, IBVE + AN = 1.5 ml.

$$D + A \leftrightarrow (\overset{+}{D}\cdots\overset{-}{A}) \xrightarrow{h\nu} (\overset{+\delta}{D}\cdots-\overset{-\delta}{A})^*, \overset{+}{D}\cdot + \overset{-}{A}\cdot, \cdot D—A\cdot, +D—A^-, DA$$

The contribution of ionic species is unlikely in the present system, and radical active species alone have to be considered. The aftereffect of photopolymerization of the donor–acceptor system does not differ much from that

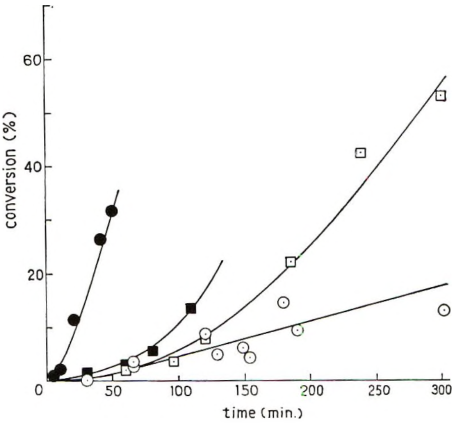

Fig. 2. Time–conversion curves of AN–IBVE system at 50°C *in vacuo*: (○) AN alone, photoirradiated; (●) AN alone, [AIBN] = 10^{-2} *M*, in the dark; (□) AN + IBVE (20 vol-%), photo-irradiated; (■) AN + IBVE (20 vol-%), [AIBN] = 10^{-2} *M* in the dark.

TABLE II
Copolymerization of Acrylonitrile—Isobutyl Vinyl Ether (M_1) at 50°C

M_1 in feed, mole fraction	N in copolymer, %	M_2 in copolymer, mole system
Photopolymerization (Absolutely Dry System)		
0.053	23.12	0.927
0.112	23.20	0.930
0.214	18.08	0.803
0.335	16.23	0.750
0.483	14.69	0.703
0.670	12.81	0.640
Photopolymerization (Ordinary Dry System)		
0.053	24.03	0.951
0.112	22.84	0.924
0.178	19.56	0.843
0.291	16.09	0.747
0.380	14.87	0.708
0.604	12.87	0.642
Thermal Polymerization Initiated by AIBN		
0.086	22.59	0.915
0.189	19.64	0.845
0.335	16.24	0.749
0.430	15.15	0.718
0.715	12.70	0.637
0.875	10.45	0.552

of photopolymerization of pure AN, as shown in Figure 4. In the case of biradical propagation, the aftereffect would be larger than that for the ordinary monoradical process unless termination by disproportionation or spontaneous linear termination predominates. Direct determination of biradical propagation by measuring the change in molecular weight during

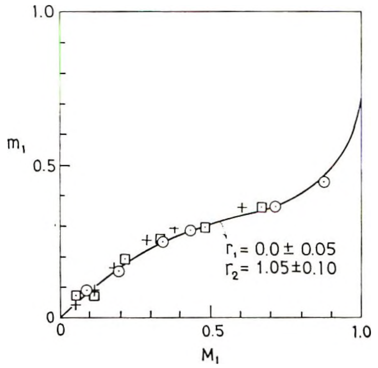

Fig. 3. Copolymer composition curve of AN–IBVE (M_1) system at 50°C: (○) thermal polymerization catalyzed by AIBN (10^{-2} *M*); (□) photopolymerization (absolutely dry system); (+) photopolymerization (ordinary dry system).

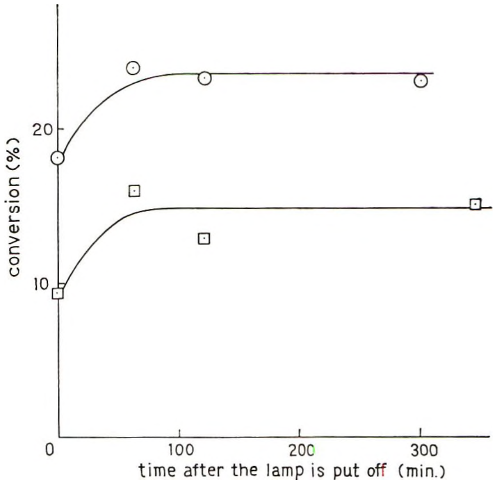

Fig. 4. Post polymerization at 50°C in the dark: (○) AN/IBVE = 4/1 (v/v), irradiated for 120 min. at 50°C *in vacuo*; (□) AN alone, irradiated for 150 min *in vacuo* at 50°C.

the post polymerization could not be done because of crosslinking of polymer.

Possibility of Side Reactions

Photosensitized reactions other than polymerization are possible. For example, cyclic dimerization of ethylenic donor–aceptor systems is known.[5] Also, homocyclic dimerization can be induced by photoirradiation under appropriate conditions as reported for AN.[6]

In the present reaction system, evidence of dimerization or of formation of small molecules could not be obtained, at least within the limit of accuracy of gas chromatographic determination. The mixture of AN–IBVE at mixing ratios varying from 1/10 to 9/10 was placed in one arm of a Y-type reaction vessel and sealed off after degrassing. After irradiating for a required time, another arm of the reaction vessel was cooled to liquid nitrogen temperature to transfer all volatile materials from the irradiated arm. The solid residue was a copolymer of AN with IBVE. The volatile material was analyzed by gas chromatography at 130°C with the use of a 3 m column packed with poly(ethylene glycol) 4000 supported on celite. Two peaks corresponding to unreacted AN and IBVE were the only ones recorded, and no other substance could be detected in the retention time of 30 min.

Spectroscopy

Although coloration was not observed visually when AN and IBVE were mixed, a clear shift of absorption spectra was detected in the ultraviolet region. The continuous variation method was applied to the mixture of AN and IBVE diluted by *n*-hexane. As shown in Figure 5, the optical absorp-

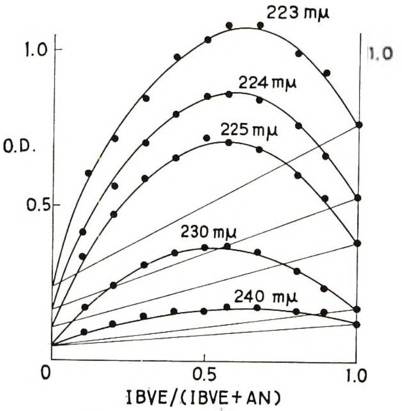

Fig. 5. Optical absorption of AN–IBVE in *n*-hexane; [IBVE] + [AN] = 0.3M.

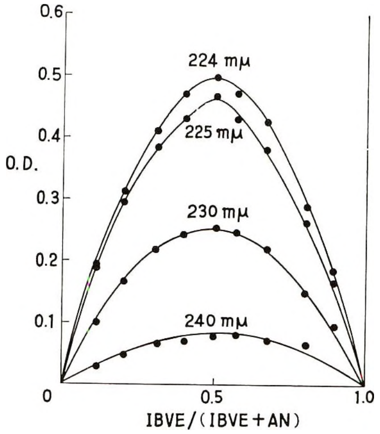

Fig. 6. Continuous variation method of AN–IBVE; [IBVE] + [AN] = 0.3 M, in *n*-hexane.

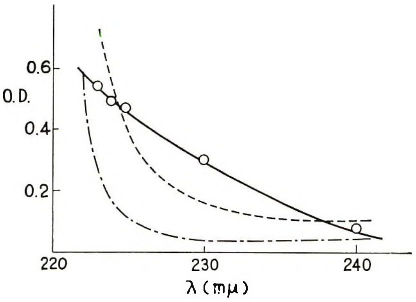

Fig. 7. Absorption spectra of AN, IBVE, and AN–IBVE complex. IBVE–AN complex [IBVE] = [AN] = 0.15 M (the absorptions of uncomplexed IBVE and AN are subtracted); (-·-) [IBVE] = 0.3M; (—) [AN] = 0.3M. (optical length = 0.10 cm, solvent = *n*-hexane).

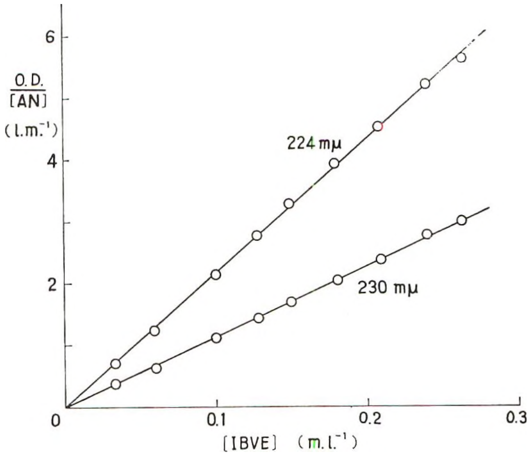

Fig. 8. Confirmation of contact charge-transfer complex formed between IBVE and AN. Data are taken from Fig. 6.

tion of the mixture does not obey the Beer's law. The additional absorptions after subtracting the absorptions of isolated AN and IBVE from the observed values are plotted in Figure 6. The formation of 1:1 complex is confirmed. The spectrum of the complex can be separated by plotting the optical density at various wavelengths, as shown in Figure 6, although the concentration of the complex could not be determined. Figure 7 indicates that the spectra due to the interaction between AN and IBVE are quite different from those of monomers. One may suspect that simple solvation might cause the change in absorption spectra. However, the definite 1:1 relation between components as shown in Figure 6 could not be expected in the case of solvation.

Interpretation of spectroscopic data on the basis of the Benesi-Hildebrand equation is not possible. As shown in Figure 8, this system is a good example of contact charge transfer complex. The data in Figure 8 are

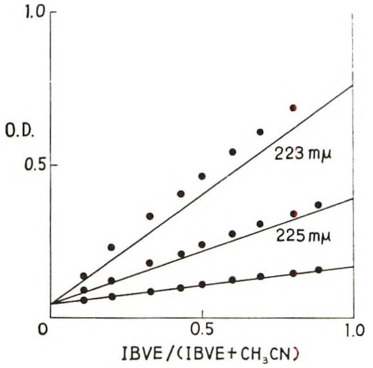

Fig. 9. Optical absorption of IBVE-acetonitrile in *n*-hexane. [IBVE] + [CH_3CN] = 0.3*M*.

derived from Figure 6 using the following equation where ϵ is the average molar absorption coefficient of the complex and γ is the probability of formation of the complex.[7]

$$OD/[AN] = \overline{\epsilon\gamma}\ [IBVE]$$

The presence of a vinyl group seems to play an important role. When acrylonitrile is replaced by acetonitrile, the charge transfer interaction is very weak (Fig. 9). Also no interaction is observed between AN and tetrahydrofuran (THF), which is an saturated ether (Fig. 10). The combinations AN–THF or IBVE–acetonitrile are thermally as well as photochemically stable.

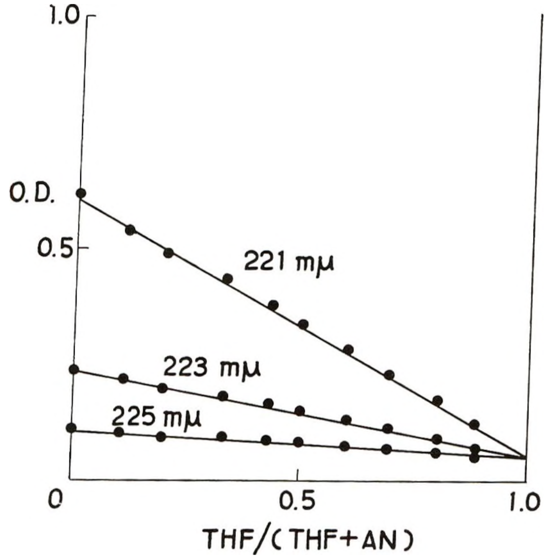

Fig. 10. Optical absorption of AN–tetrahydrofuran (THF) in *n*-hexane. [THF] + [AN] = 0.3*M*.

Comparison of the Present System with the VCZ–AN System

The major difference between the present system and the VCZ–AN system[1,2] is the absence of ionic propagation in the present system. Both VCZ and IBVE are easily polymerized by cationic mechanism. The ion-radicals, if formed by the charge-transfer process, would have higher stability for VCZ than for IBVE. The different contribution of conjugation in these two monomers would reflect on the choice of reaction path. Although the interaction between AN and VCZ is certain, at least in the excited state, from the results of polymerization, the complex formation in the ground state could not be confirmed by spectroscopy, since the strong absorptions of VCZ nearly up to the visible region disturb the measurement. In the region of measurable wavelength, the absorptions of VCZ–AN or VCZ–acetonitrile obey Beer's law, as shown in Figure 11.

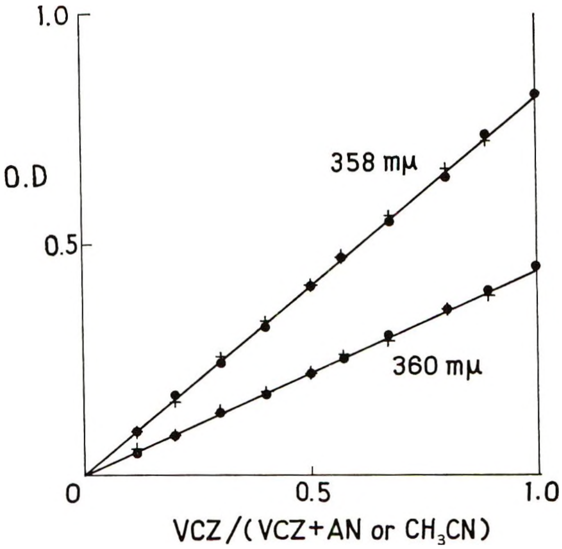

Fig. 11. Optical absorption of VCZ–AN or acetonitrile in benzene, [VCZ] + [AN] or [CH$_3$CN] = 0.3*M*: (●) [VCZ] + [AN]; (+) [VCZ] + [CH$_3$CN].

CONCLUSION

The confirmation of a contact charge-transfer complex between AN and IBVE shows that the spontaneous photopolymerization is initiated by the interaction of two monomers. The absorption of a charge-transfer band is possible only when the charge-transfer band does not overlap with the original absorptions of components. The photoexcitation of AN–IBVE system leads exclusively to radical polymerization; no other reactions were detected.

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Polymerization Behavior of *N*-(*p*-Vinyl) phenylacrylamide

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Synopsis

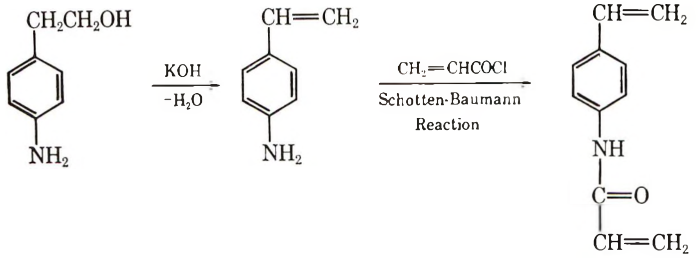
The polymerization behavior of *N*-(*p*-vinyl)phenylacrylamide, synthesized from *p*-aminostyrene and acryloyl chloride by means of the Schotten-Baumann reaction was studied. Due to a marked difference in electron density between the two double bonds, this monomer provided soluble polymers by both cationic and anionic polymerization procedures, the cationic and anionic polymers mainly carrying, as side chains, the acrylamide and styrene moieties, respectively. The polymerization behavior of the residual double bonds was also investigated for both polymers, leading to crosslinked, insoluble products.

It is well known that difunctional vinyl-type monomers usually undergo free-radical polymerizations to crosslinked, insoluble polymers. Under ionic polymerization conditions, however, either cationic or anionic, uncrosslinked, soluble polymers are obtained when the electron densities of the two double bonds are entirely different.

Thus, β-vinyloxyethyl methacrylate has been reported to respond differently to cationic and anionic polymerization catalysts, each yielding soluble polymers of different structures.[1,2] Similarly, it has been shown that allyl methacrylate and acrylate are polymerized with typical anionic initiators[3–5] and with lithium dispersion in tetrahydrofuran[6] to provide soluble polymers having essentially the same structure, comprising a polymethacrylate or polyacrylate backbone with pendent allyl groups. Anionic polymerizations of styrenes substituted at the *para* position with nucleophilic unsaturated groups were also reported to lead to linear polymers.[7]

In view of the different behaviors of the double bonds of styrene and acrylamide for nucleophilic and electrophilic attack, it appeared interesting to synthesize a difunctional vinyl monomer, *N*-(*p*-vinyl)phenylacrylamide (VPAM) and to investigate its polymerization behavior as well as the potential uses of the resulting polymers as intermediates for synthesizing responsive polymers. H. Morawetz and his co-workers appear also to have prepared this monomer,[8] but no experimental details were given.

VPAM was synthesized by the route shown in eq. (1).



(1)

Although free-radical polymerization afforded only crosslinked insoluble polymers, this monomer was found to be susceptible to both cationic and anionic initiators, each providing soluble polymers. The soluble polymers with pendent vinyl groups thus obtained indicate excellent reactivities towards free-radical, electrophilic, and nucleophilic attack.

EXPERIMENTAL

Materials

***p*-Aminostyrene.**[9] A mixture of 10 g of β-(4-amino)phenethyl alcohol and 30 g of potassium hydroxide pellets was heated to ca. 220–240°C under 10 mm Hg to distil 9 g of crude *p*-aminostyrene. A colorless liquid was obtained in approximately 70% yield by redistillation (81°C/25 mm Hg), which solidified upon standing in a refrigerator (λ_{max}, 280 mμ (chloroform)].

***N*-(*p*-Vinyl)phenylacrylamide(VPAM).** *p*-Aminostyrene (1.19 g, 0.01 mole) was dissolved in 10 ml of acetonitrile, and to this solution was added, dropwise, 1.8 g (0.015 mole) of acryloyl chloride at 0°C with stirring. The resulting white suspension was made basic with aqueous ammonia; the precipitate formed was collected by filtration and rinsed with water; recrystallization from ethanol–water afforded white crystals, mp 128–130°C, in 69% yield.

ANAL. Calcd for $C_{11}H_{11}NO$: C, 76.30%; H, 6.36%; N, 8.09%. Found: C, 76.18%; H, 6.51%; N, 8.07%.

The infrared spectrum indicated a strong C=O absorption at 1670 cm^{-1}, which is attributable to the acrylamide moiety, together with a 1610 cm^{-1} band due to the benzene ring; λ_{max} in ethanol, 295 mμ.

Polymerization

Cationic polymerizations were carried out by injecting catalysts through serum-type rubber stoppers into flasks containing monomers and solvents. After polymerization, polymer solutions were precipitated into petroleum ether, followed by dissolution in ethanol and subsequent reprecipitation into aqueous ammonia.

Lithium-initiated polymerizations were effected in sealed ampules with exclusion of oxygen, carefully purified tetrahydrofuran being used as solvent. The resulting polymer solutions were quenched with methanol and precipitated into water.

RESULTS AND DISCUSSION

Free-radical solution polymerization of VPAM with azobisisobutyronitrile as initiator leads to an insoluble three-dimensional network, the gel point occurring at a relatively low conversion.

As in the case of styrene and its derivatives, however, this monomer polymerizes readily with cationic initiators, such as boron trifluoride etherate and stannic chloride, to provide soluble polymers (Tables I and II).

TABLE I
Homopolymerization with Cationic Catalyst[a]

Polymer no.	Monomer concn, %	Catalyst Type	Catalyst %[b]	Solvent	Conversion, %	$[\eta]$[c]
I	8	BF_3	10	CH_2ClCH_2Cl	100	0.11
II	11	"	4	CH_2Cl_2	90	0.06
III	7	"	10	CH_2Cl_2	50	0.07
IV	4	"	10	Toluene-$C_2H_4Cl_2$ $^1/_1$ vol/vol	60	0.04
XIII	8	$SnCl_4$	10	CH_2ClCH_2Cl	80	0.03
XIV	8	"	10	CH_2Cl_2	70	0.05

[a] Polymerization condition: 5 hr at − 40°C.
[b] Based on the monomer.
[c] Intrinsic viscosity in dimethylformamide, 20°C.

TABLE II
Copolymerization with Cationic Catalyst[a]

Polymer no.	Second monomer	Total monomer concn, %	Catalyst Type	Catalyst %[b]	Solvent	Conversion, %	$[\eta]$[c]
V	Ethyl vinyl ether	9	BF_3	10	$C_2H_4Cl_2$	67	0.09
VI	Styrene	10	"	10	$C_2H_4Cl_2$	62	0.17
VII	"	16	"	2	CH_2Cl_2	29	Very low
XV	"	20	$SnCl_4$	10	CH_2Cl_2	60	0.07
XVI	Ethyl vinyl ether	19	"	10	CH_2Cl_2	70	0.02

[a] Polymerization conditions: monomer ratio, $^1/_1$ mole/mole; 5 hr at −40°C.
[b] Based on the total monomers.
[c] Intrinsic viscosity in tetrahydrofuran, 20°C.

Furthermore, it polymerizes with the lithium–tetrahydrofuran combination, which is considered to be an anionic initiator system, also to provide soluble polymers, although not of high molecular weights (Table III).

TABLE III
Polymerization with Lithium Dispersion[a]

Polymer no.	Monomer	Total monomer concn, %	Catalyst, %[b]	Conversion %	$[\eta]$[c]
VIII	VPAM	10	10	100	0.04
IX	"	20	"	80	0.04
X	"	50	"	80	0.07
XI	VPAM–styrene (1:1 mole/mole)	40	"	100	0.05

[a] Polymerization condition: 72 hours at 30°C.
[b] Based on the total monomers.
[c] Intrinsic viscosity in tetrahydrofuran, 20°C.

These soluble polymers in solid states are fairly stable under ambient conditions. Cationic polymers, for instance, maintain their solubilities at least for three months.

Comparisons among infrared spectra for the monomer and cationic and anionic polymers give interesting results (Fig. 1). Thus, two absorption peaks unrecognized in the monomer and generally ascribable to the $—CH_2—$ bonding in vinyl polymers are recognized at 2970 and 2900 cm^{-1} for both polymers.

The C=C stretching presumably caused by the styrene moiety of the monomer at 1640 cm^{-1} disappears in the cationic polymer; vinyl absorptions around 1300 and 1200 cm^{-1} in the monomer also decrease in both polymers. The acrylic double bond around 950 cm^{-1} and the styryl one

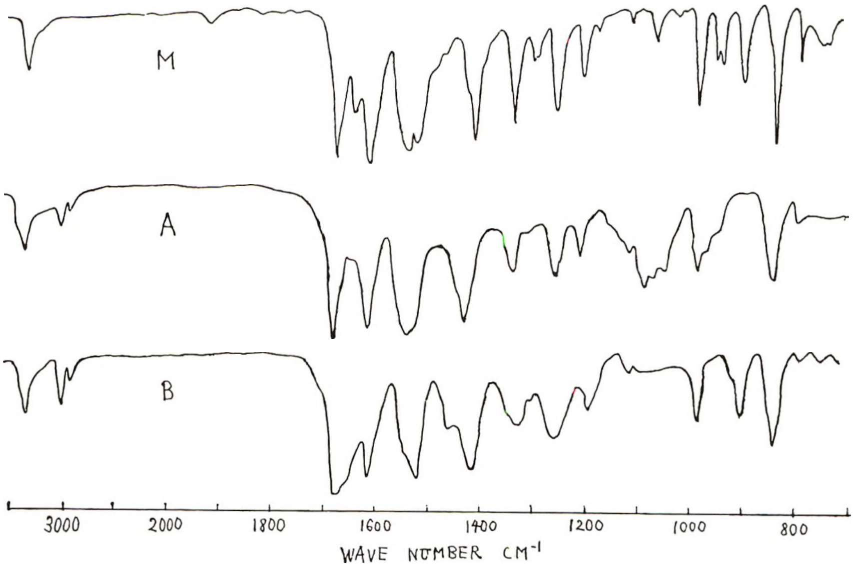
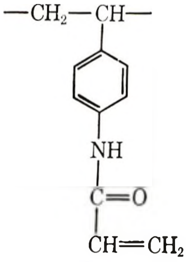


Fig. 1. Infrared spectra: (*M*) monomer, and (*A*) cationic polymer (No. I); (*B*) anionic polymer (no. IX).

near 910 cm^{-1} in the monomer disappear in the anionic and cationic polymers, respectively.

These infrared evidences strongly support the polymer structures I and II for cationic and anionic polymer, respectively.



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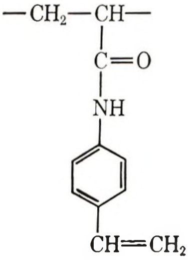


II

These structures are also supported by their solubility characteristics. The cationic polymers are readily soluble in dimethylformamide, moderately soluble in acetone and ethanol, swell in tetrahydrofuran and dioxane, and are insoluble in acetonitrile, benzene, and chlorinated hydrocarbons. The anionic polymers are soluble in tetrahydrofuran and benzene–ethanol and insoluble in ethanol, dimethylformamide, and benzene. These solubility characteristics indicate that the former carries more polar side groups than the latter, thereby denoting the appropriateness of the structures I and II.

As expected, furthermore, the ultraviolet spectra for both polymers shift towards lower wavelengths as compared with the monomer, their absorption maxima being different from each other (Fig. 2).

In order to obtain quantitative evidence for the structures of the cationic and anionic polymers, the contents of the acrylic and styrenic double bonds in the polymers were determined by conventional procedures for acrylic esters[10] and by means of infrared spectroscopy, respectively. Mercaptans are widely known to add readily to electron-poor double bonds such as those in acrylics, whereas they are expected to be entirely inert to electron-rich double bonds such as that in styrene. This relationship is well recognized in Table IV. Thus, both *N*-(*p*-methyl) and *N*-(*p*-vinyl)phenylacrylamides afforded the same double bond content within experimental error, thereby indicating that the vinyl(styrenic) group in the latter was kept intact during this analytical procedure. The fairly good agreement with

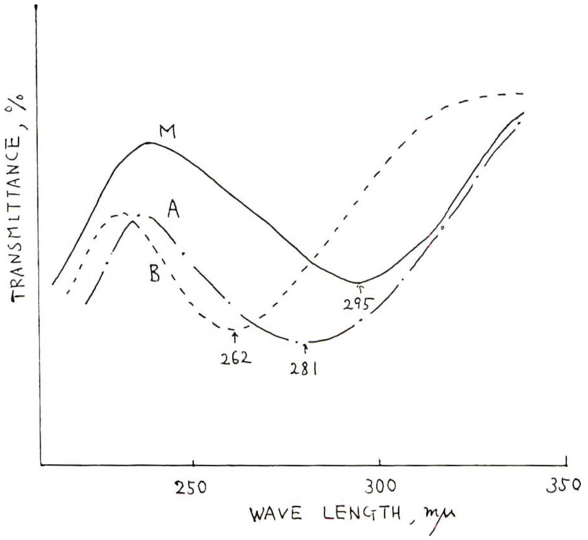


Fig. 2. Ultraviolet spectra: (*M*) monomer; (*A*) cationic polymer (No. I); (*B*) anionic polymer; (No. IX); ethanol solutions.

TABLE IV
Residual Double Bonds in Polymers as Determined by Mercaptan Addition (—SH) and Infrared (IR) Methods

	Acrylic double bond, %			Styrene double bond, %	
Sample	Theoretical value[a]	SH method	IR method 944 cm^{-1}	Theoretical value[a]	IR method (914 cm^{-1})
N-(*p*-Methyl)phenylacrylamide	100	99.8	—	0	—
N-(*p*-Vinyl)phenylacrylamide	100	101.3	—	100	—
Polymer I (cationic homopolymer)	100	91.7	95.2	0	0.2
Polymer VIII (anionic homopolymer)	0	9.4	0.8	100	90.9
Polymer V (cationic copolymer)	50	24.5	25.2	0	8.2
Polymer VI (cationic copolymer)	50	31.0	33.3	0	1.5
Polymer XV (cationic copolymer)	50	71.6	70.5	0	7.3
Polymer XVI (cationic copolymer)	50	88.2	85.4	0	10.5
Polymer XI (anionic copolymer)	0	11.5	8.2	50	74.3

[a] For pure structure I or II.

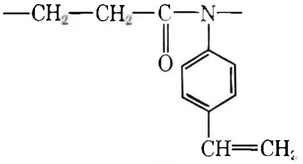
the results of infrared determinations of unsaturation also indicate the appropriateness of this procedure.

For the determination of acrylic double bonds, dodecylmercaptan was employed as mercaptan and a small amount of tetrahydrofuran was used for dissolution of copolymers and anionic homopolymers.

Infrared spectral analysis was carried out by comparing absorption intensities of the two double bonds (944 and 910 cm^{-1}), of the polymers with that of the monomer as the standard, as in the case of S-vinyl-*N*-vinyl thiocarbamates polymers.[11]

The data in Table IV indicate that more than 90% of the acrylic and styrenic double bonds of the monomer remain unaffected during cationic and anionic polymerizations, respectively, whereas less than 10% of the styrenic and acrylic double bonds remain in cationic and anionic homopolymers, respectively. In the case of copolymers, the contents of the remaining double bonds are dependent upon the kinds of catalyst as well as comonomer. However, the same tendencies as for the homopolymers are clearly recognized.

The formation of substituted poly-β-alanine (II) based upon the Michael-type addition, another possibility in the case of the anionic polymers



III

is not considered to be important, since, in their infrared spectra (Fig. 1) the band assigned to NH— stretching in the 3300 cm^{-1} region remains unchanged in intensity during polymerization and there is no evidence for the disappearance of the amide II band around 1500–1550 cm^{-1}.

These analytical, infrared, ultraviolet, and solubility characteristics might indicate that the major portions of the cationic and anionic polymers assume structures I and II, respectively.

To investigate the reactivities of the residual vinyl groups in the polymers, the polymerization characteristics of both soluble polymers as judged by crosslinking ability were examined briefly.

Thus, polymer solutions containing catalysts were evaporated on glass plates to form thin transparent films. Upon drying, they were subjected to heat treatment, after which they were immersed in solvents to determine their solubilities. The results thus obtained are summarized in Table V. It is well known from this that pendent vinyl double bonds in the polymers are fairly reactive even in the solid states.

The cationic polymer films were also subjected to light irradiations from a tungsten lamp, instead of heat treatment (Table VI).

Catalysts which had been verified to be effective for acrylic photopolymerizations[12,13] were also effective in this case.

It is interesting to note that stannous chloride is markedly more effective than other catalyst systems. Since this catalyst possesses an electron-

TABLE V
Crosslinking of the Polymer Films with Free Radical Catalyst by the Application of Heat[a]

		Immersion of the cured film in solvent		
Polymer	Catalyst[b]	Weight loss, %	Solvent	Appearance
Cationic (no. I)	None	46.4	Ethanol	Soluble to some extent
	Benzoyl peroxide	7.2	"	No swelling
	Azobisisobutyronitrile	30.7	"	Soluble to some extent
Lithium-initiated (no. X)	None	100	THF	Soluble
	Benzoyl perioxide	33.0	"	Swelling
	Azobisisobutyronitrile	61.9	"	Soluble to considerable extent

[a] 15 min. at 100°C.
[b] 5% based on polymer.

TABLE VI
Crosslinking of the Polymer Films (Cationic) by Light Irradiation[a]

Polymer no.	Catalyst		Immersion of the irradiated film in ethanol	
	Type	%[b]	Weight loss, %	Appearance
I	None		100	Soluble
I	Rose bengal Phenylhydrazine	0.5 5	72.2	Soluble to considerable extent
I	Methylene blue Phenylhydrazine	0.5 5	75.0	"
I	Fluorescein Ascorbic acid	0.5 5	81.3	Almost soluble
I	Ceric ammonium nitrate	5	54.2	Soluble to some extent
VI	Stannous chloride	5	18.8 2.7[c] 0.0[d]	Green fluorescence

[a] 2 min.-irradiation at 30 cm from a 500 W spot reflector tungsten lamp.
[b] Based on polymer.
[c] Irradiation time 5 min.
[d] Irradiation time 10 min.

donating ability for the electrophilic acrylic double bond, its action might involve some complex polymerization mechanism.

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Generation of Free Radicals at Subzero Temperatures. III. Polyamine–Hydroperoxide–Iron System.

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Synopsis

The mechanism of the reaction of tetraethylenepentamine (TEPA) with cumene hydroperoxide (CHP) and iron ions was investigated. It was found that (1) TEPA did not reduce Fe(III); (2) TEPA was consumed by this reaction; (3) both Fe(II) and Fe(III) were effective for this reaction. It was shown that though the O—O bond of a hydroperoxide could be cleaved only at elevated temperatures, it could be easily cleaved by the reaction with the iron–TEPA complex. The function of this iron–TEPA complex is discussed.

INTRODUCTION

The generation of free radicals at low temperatures appears to be of great interest from various viewpoints, and a systematic investigation has been carried out in our laboratories in recent years.[1]

One of the methods for generating free radicals at low temperatures is the use of so-called redox systems. The redox systems applicable at low temperatures usually consist of a hydroperoxide, iron ions, and a strong reducing agent, and the reactions involved are:

$$\mathrm{Fe(II)} + \mathrm{ROOH} \rightarrow \mathrm{Fe(III)} + \mathrm{RO}\cdot + \mathrm{HO}^- \tag{1}$$

$$\mathrm{Fe(III)} + \text{reducing agent} \rightarrow \mathrm{Fe(II)} + \text{oxidized product} \tag{2}$$

However, the system consisting of polyamine–iron–hydroperoxide appears to be an exceptional case, since a polyamine does not seem to be a strong reducing agent.

The effectiveness of the polyamine–hydroperoxide reaction as a source of free radicals was first observed by Whitby, et al.[2] in the course of a general survey of the decomposition of peroxygen compounds by catalysts and reducing agents. This effectiveness was confirmed in the use of this system for initiating the emulsion polymerization of vinyl monomers by various investigators,[2–6] but the mechanism or the nature of the reaction was not investigated in detail.

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Orr and Williams[7–9] investigated this system, and proposed two mechanisms, eqs. (3) and (4):

$$RNH_2{:}Fe^{2+} + ROOH \rightarrow RO\cdot + H_2O + RNH\cdot + Fe^{2+} \qquad (3)$$

$$ROOH + RNH_2Fe^{2+} \rightarrow RO\cdot + HO^- + RNH_2Fe^{3+} \qquad (4a)$$

$$RNH_2Fe^{3+} + ROO^- \rightarrow ROO\cdot + RNH_2{:}Fe^{2+} \qquad (4b)$$

They agreed with Baxendale's suggestion[8] that mechanism (3) was energetically unfavorable, and preferred mechanism (4). However, they did not attempt to make a choice between these two.

Besides mechanisms (3) and (4), another mechanism should be examined, in which polyamines reduce Fe(III) into Fe(II), and the Fe(II) thus produced reacts with hydroperoxides to form free radicals [eqs. (5)].

$$RNH_2 + Fe^{3+} \rightarrow Fe^{2+} + (\text{oxidized } RNH_2) \qquad (5a)$$

$$Fe^{2+} + ROOH \rightarrow Fe^{3+} + RO \quad + HO^- \qquad (5b)$$

The present investigation was undertaken in order to elucidate the mechanism of the polyamine–iron–hydroperoxide reaction.

RESULTS AND DISCUSSION

Tetraethylenepentamine (TEPA) was used as a polyamine, and cumene hydroperoxide (CHP) was used as a hydroperoxide.

In order to check whether or not mechanism (5) was the correct mechanism for this reaction, the reaction between TEPA and Fe(III) was examined. When the mixtures (*1*) [TEPA] = $1.8 \times 10^{-4}M$ and [Fe^{3+}] = $1.7 \times 10^{-4}M$ in a pH 4 buffer, (*2*) [TEPA] = $2.5 \times 10^{-2}M$, [Fe^{3+}] = $5.0 \times 10^{-4}M$, [EDTA] = $5.0 \times 10^{-4}M$ in a pH 11 buffer, or (*3*) [TEPA] = $1.3 \times 10^{-2}M$, [Fe^{3+}] = $6.7 \times 10^{-4}M$ in a pH 11 buffer, were allowed to stand at 20°C for 25 hr, no decrease of ultraviolet absorption of Fe(III) was observed, and the TEPA was quantitatively recovered from the solution. These findings show that TEPA is not able to reduce Fe(III), and that the mechanism (5) cannot represent the reaction of the polyamine–hydroperoxide-iron system.

The choice between mechanisms (3) and (4) can be made from the product studies; the mechanism (3) requires consumption of TEPA whereas the mechanism (4) does not. The mixtures of CHP and TEPA with or without Fe(III) and EDTA at pH 11.3 were allowed to stand at 20°C for 24 hr, and the consumptions of TEPA and CHP were determined. The results are shown in Table I. The consumption of TEPA is clearly shown.

However, it is possible that the free radicals produced by mechanism (4) could react with TEPA, causing consumption of TEPA. Therefore, in order to reject mechanism (4), consumption of TEPA must be shown in the presence of some good radical scavengers.

When an aqueous solution $0.01M$ in CHP, $0.01M$ in TEPA, $1.0 \times 10^{-5}M$ in ferric chloride, and $2.0M$ in acrylic acid was allowed to react for 4 hr at

TABLE I

Reaction in CHP–TEPA–Iron System (20°C, pH 11.3, 24 hr)

Run	CHP, mole/l.	TEPA, mole/l.	Fe(III), mole/l.	TEPA consumed, %	CHP consumed, %	C_6H_5Ac found, %
1	1.0×10^{-2}	1.0×10^{-2}		46.8	44.4	20.1
2	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-5}	95.7	100	50.4

30°C, 97% of the TEPA was decomposed. When this reaction was applied to styrene with addition of an emulsifier, it was found that 98% of TEPA disappeared. Mechanism (4) is not compatible with these findings, and thus it is highly likely that the mechanism (3) represents the reaction of the TEPA–CHP–iron system.

Styrene was then polymerized by the TEPA–CHP system for 1 hr at 10°C with Fe(II) or Fe(III) and in the absence and presence of EDTA. Results are summarized in Table II. Results in Table II show that: (1) Fe(II) and Fe(III) are equally effective; (2) in the absence of iron, the conversion was much smaller and not reproducible; this polymerization may arise from the catalytic action of trace amount of iron ions which might be present as impurities in potassium dihydrogen phosphate and sodium hydoroxide used as the buffer; (3) in the presence of iron, the conversion was almost quantitative after 1 hr at 10°C; (4) EDTA failed to suppress the polymerization; this is understandable because the formation constant of Fe(II)-TEPA complex is very large and is $10^{11.40}$ at 25°C.[10]

TABLE II

Emulsion Polymerization of Styrene by CHP–TEPA–Fe[a]

Run	CHP, mole/l.	TEPA, mole/l.	Fe(III), mole/l.	Fe(II), mole/l.	EDTA, mole/l.	Polymer yield, %
5	1.0×10^{-2}	—	—	—	—	0.7
6	1.0×10^{-2}	—	—	—	—	1.4
7	1.0×10^{-2}	1.0×10^{-2}	—	—	—	10, 25, 28, 60
8	1.0×10^{-2}	1.0×10^{-2}	—	—	1.0×10^{-3}	11, 12
9	1.0×10^{-2}	1.0×10^{-2}	—	1.0×10^{-5}	—	98
10	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-5}	—	—	91
11	1.0×10^{-2}	1.0×10^{-2}	—	1.0×10^{-5}	1.0×10^{-3}	87, 96
12	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-5}	—	1.0×10^{-3}	94

[a] Styrene, 30 g; water, 100 ml; sodium laurate, 2.0 g; pH 11.3; 10°C; 1 hr.

Since it is known that Fe(II) quickly reacts with a hydroperoxide to produce Fe(III), RO·, and HO^-, the iron species present in the solution are probably Fe(III)-TEPA even when only Fe(II)-TEPA is used in the beginning.

Thus it was shown that though the thermal cleavage of the O—O bond of CHP occurs only at elevated temperatures, this O—O bond is easily cleaved at very low temperatures when Fe(III)-TEPA complex is present in the system. This easy cleavage of the O—O bond at low temperatures is very unusual, and some explanation seems to be desirable. The phenomenon may be explained as follows.

In the Fe(III)–TEPA complex, six ligands are accepted, probably in 4*s*, three 4*p* and two 4*d* orbitals of the iron atom, and five unpaired electrons are in d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2} of the 3*d* orbitals. When the Fe(III)–TEPA complex reacts with a hydroperoxide ROOH, RO·, H_2O, and Fe-(III)–TEPA complex radical will be produced, as illustrated in Figure 1. The facile cleavage of the O—O bond may be due to resonance stabilization of this radical. The odd electron on the nitrogen atom could form a $p\pi$–$d\pi$ bond with an odd electron in the d_{xz} or d_{z^2} orbitals of iron atom.

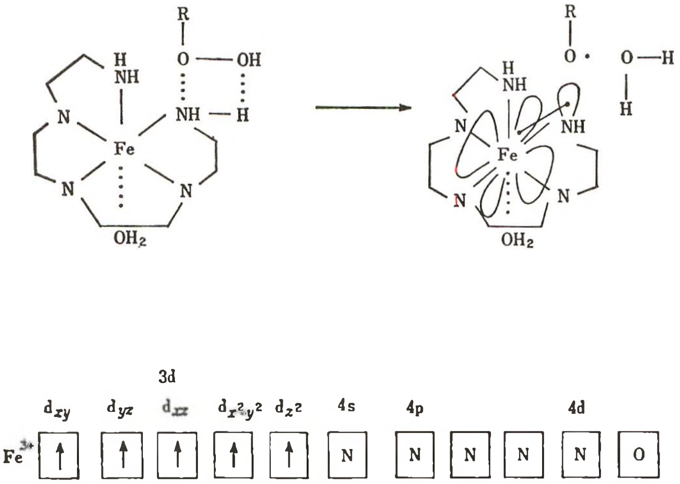
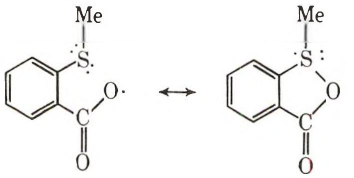


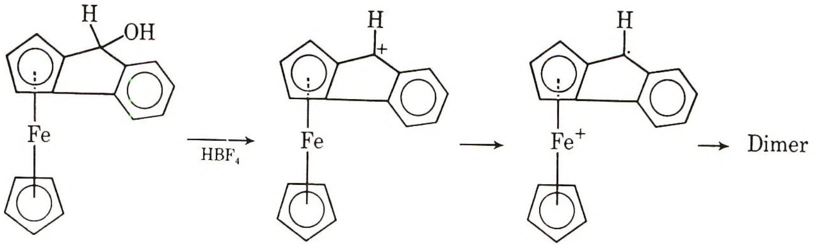
Fig. 1

The rate of decomposition of *tert*-butylperoxy *o*-methylmercaptobenzoate is reported to be 14100 times that of *tert*-butyl perbenzoate, and this rate enhancement is attributed to the resonance stabilization of the carboxy radical by use of a 3*d* orbital of sulfur.[11]



(6)

A benzopentaleneironcyclopentadienyl π-complex obtained as a transient cation from the acid hydrolysis of 2,3-ferrocoindenol undergoes an extremely fast internal oxidation-reduction process, resulting in the formation of a cation radical which then dimerizes.[12]



(7)

The explanation proposed above seems to be related with these two cases of the one-electron type interaction of the *3d* orbitals of iron and sulfur.

EXPERIMENTAL

Materials

Tetraethylenepentamine, obtained from Tokyo Kasei Co., was distilled under reduced pressure, and the fraction boiling at 157–159°C/1.5 mm Hg was collected and used.

Cumene hydroperoxide was synthesized by the method of Armstrong[13] and purified by distillation. The fraction boiling at 52.5–53.5°C/0.1 mm Hg was collected for use.

Styrene, obtained from Iwai Chemical Co., was distilled, and the fraction with bp 42.5–43.0°C/18 mm Hg was collected for use.

Acrylic acid, obtained from Tokyo Kasei Co., was distilled, and the fraction boiling at 48.0–49.0°C/16 mm Hg was collected for use.

All other chemicals were those of the best grade commercially available and were used without further purification. As the sources of ferrous and ferric ions, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ were used. A mixture of potassium dihydrogen phosphate and sodium hydroxide was used as a buffer solution.

Reaction between CHP and TEPA in the Presence or Absence of Iron

Purified nitrogen gas was bubbled through a buffer solution to which a TEPA stock solution was added. After 15 min of further nitrogen bubbling iron stock solution (if used) was added to the solution. After a further 15 min of nitrogen bubbling the CHP stock solution was added, and the reaction mixture was allowed to stand at room temperature in a nitrogen atmosphere for 24 hr. Then the mixture was divided into two portions, and one was used for the determination of residual CHP by iodometric titration. The other portion was distilled at 15 mm Hg to remove water, and the residue was dissolved in chloroform. The chloroform solution was dried and subjected to the infrared determination of TEPA. The distillate, which was mainly water, was extracted five times with ether; evaporation of the ethereal extracts yielded acetophenone, which was determined by infrared spectrophotometry.

Reaction between CHP and TEPA in the Presence of Monomers

The procedure was essentially the same as that described above for the case without monomers.

A deaerated solution which was $0.01M$ in TEPA, $0.01M$ in CHP, $1.0 \times 10^{-6}M$ in ferric chloride, and $2.0M$ in acrylic acid monomer was prepared. The pH of the solution was adjusted to 11.2 by use of sodium hydroxide. The mixture was allowed to react for 4 hr at 30°C under nitrogen atmosphere. Acrylic acid polymerized almost quantitatively in 4 hr. Then concentrated hydrochloric acid was added to precipitate poly(acrylic acid), and the precipitates were redissolved in an alkaline solution. Purification by means of dissolution and reprecipitation was repeated two more times. The combined filtrate and washings were concentrated to about 50 ml by vacuum distillation. The residual solution was extracted five times with chloroform. The chloroform solution was dried, concentrated by evaporation, and the amount of TEPA was determined by infrared spectroscopy. Two experiments showed that 97.2% and 97.8% of TEPA initially present were decomposed. The accuracy of this analysis was checked by the analysis of an aqueous poly(acrylic acid) solution containing a known amount of TEPA. TEPA was recovered quantitatively by the above procedure.

A similar experiment was carried out with styrene in the presence of sodium laurate as the emulsifier. It was found that 98.1% of TEPA decomposed.

Polymerization of Styrene

A buffer solution was added to a reaction vessel placed in a constant temperature bath at 10°C, and purified nitrogen was bubbled through the solution. Then sodium laurate, a TEPA solution, an iron solution (or iron–EDTA solution), styrene, and finally a CHP solution was added while nitrogen was bubbled through the mixture. When all the ingredients were added, the mixture was composed of 30 g of styrene, 100 ml of water, 2.0 g of sodium laurate, and the redox initiating system. Polymerization was stopped by addition of methanol containing a small amount of sulfuric acid. Polystyrene precipitated was collected, dried and weighed.

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Four-Center Type Photopolymerization in the Solid State. I. Polymerization of 2,5-Distyrylpyrazine and Related Compounds

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Synopsis

Crystalline 2,5-distyrylpyrazine (DSP) was found to polymerize into a linear high polymer with extremely high crystallinity by the action of sunlight or ultraviolet light. Based on this discovery, photopolymerizability of the related diolefins having the general formula, *trans,trans*-Ar′—CH═CH—Ar—CH═CH—Ar′ was surveyed. As a result, 1,4-bis[β-pyridyl-(2)-vinyl]benzene (P2VB) was found to polymerize in the same way as DSP. The polymers as polymerized, showed a high melting temperature (>330°C) and were soluble only in strong acids. The structure of the polymers was investigated by means of several customary methods involving infrared and NMR spectrum studies. It was concluded that both poly-DSP and poly-P2VB consist of a linear structure having a recurring cyclobutane ring in the main chain. General properties of this novel polymer were studied.

INTRODUCTION

2,5-Distyrylpyrazine was initially prepared by Frank in 1905[1] and, in 1958 Koelsch reported briefly[2] that the compound was converted in the solid state into a colorless polymeric substance by the action of ultraviolet light. We independently made the same observation, that 2,5-distyrylpyrazine is polymerized on irradiation with sunlight during storage, in the course of a preparative study of pyrazine-2,5-dicarboxylic acid from 2,5-distyrylpyrazine.[3]

Recently this phenomenon has been reinvestigated in this laboratory, and it was found that a linear high molecular weight polymer with recurring cyclobutane units in the main chain was obtained from crystalline 2,5-distyrylpyrazine by the action of ultraviolet light or sunlight.[4]

There have been so far no investigations in which diolefinic compounds such as 2,5-distyrylpyrazine were considered as promising monomers for linear high polymers. This discovery has led us to study the photopolymerization of other diolefinic compounds. Several compounds related to 2,5-distyrylpyrazine, having a structure consisting of three aromatic rings and two olefinic double bonds arranged alternately, have been synthesized and studied with respect to their photopolymerizability in the solid state.

As a result, another monomer, 1,4-bis[β-pyridyl-(2)-vinyl] benzene has been found to photopolymerize to the same type of polymer.

Both poly-2,5-distyrylpyrazine and poly-1,4-bis[β-pyridyl-(2)-vinyl]-benzene have high melting temperatures and are highly crystalline.

In this paper, the preparation of the monomers, the polymerization procedure, the study of the polymer structure, and the general properties of this novel type of polymer are described.

EXPERIMENTAL

Monomers

Preparation of 2,5-Distyrylpyrazine (DSP). A mixture consisting of 39.0 g (0.361 mole) 2,5-dimethylpyrazine, 163.0 g (1.537 mole) benzaldehyde, and 194 g (0.858 mole) benzoic anhydride, was refluxed for 15 hr. The precipitated yellow crystalline product was collected and washed with ethanol and ether.

The yield of DSP recrystallized from xylene, was 81.0 g (79.1% based on 2,5-dimethylpyrazine), mp 223–224°C (lit.[1] mp 219°C).

Preparation of 1,4-Bis[β-pyridyl-(2)-vinyl] benzene (P2VB). The yield is low according to the known procedure,[5] thus P2VB was prepared by a convenient new route. A mixture of 5.07 g. (0.038 mole) terephthaldehyde, 10.89 g (0.117 mole) α-picoline, and 24.63 g (0.109 mole) benzoic anhydride, was refluxed for 8 hrs. The precipitated greenish-yellow crystalline product was collected and washed with ethanol and ether. The yield of P2VB recrystallized from xylene, was 8.0 g (74.7% based on terephthaldehyde); mp 231–232°C(lit[5] mp 231–232°C).

Other Diolefinics. All other diolefinic compounds employed in the present paper were prepared according to one of three general procedures.

In procedure 1, 2,5-dimethylpyrazine was condensed with excess amount of aromatic aldehyde at reflux temperature in the presence of zinc chloride or benzoic anhydride.

In procedure 2, terephthalaldehyde was condensed with an excess of N-containing 2-methyl aromatic derivative at reflux temperature in the presence of benzoic or acetic anhydride.

Procedure 3 consisted of condensing *p*-xylenebis(triphenylphosphonium chloride) with aromatic aldehyde by the Wittig reaction. The product was recrystallized from benzene or xylene containing a trace of iodine in order to facilitate isomerization to the *trans*-configurations.

All these compounds are tabulated in Table I, and the analytical data on new compounds are in Table II.

Polymerization

Polymerization of DSP with Dispersant. Fine crystals of DSP (0.7 g) were dispersed in 125 ml of cyclohexane and, with stirring, irradiated with a 100-W high-pressure mercury lamp at the center of the reaction flask

TABLE I
Diolefinic Compounds

No.	Compound, Ar′—CH=CH—Ar—CH=CH—Ar′	Preparative method	Dehydrating agent	Mp, °C	λ_{max}, mμ (ϵ)[a]	Reference
I	Ar: 2,5-pyrazylene Ar′: phenyl	Procedure 1	Benzoic anhydride	223–224	384 (55,100) 305 (26,000)	1
II	Ar: *p*-phenylene Ar′: 2-pyridyl	Procedure 2	Benzoic anhydride	231–232	357 (62,000)	5
III	Ar: 2,5-pyrazylene Ar′: *p*-tolyl	Procedure 1	Zinc chloride	231	390 (48,600)	1
IV	Ar: 2,5-pyrazylene Ar′: *p*-anisyl	Procedure 1	Zinc chloride	235	400 (51,500)	1
V	Ar: *p*-phenylene Ar′: 3-pyridyl	Procedure 3		195–196	354 (55,400)	New compound
VI	Ar: *p*-phenylene Ar′: 4-pyridyl	Procedure 3		271	330 (39,800)	5
VII	Ar: *p*-phenylene Ar′: 2-pyrazinyl	Procedure 2	Benzoic anhydride	263–264	343 (45,400)	New compound
VIII	Ar: *p*-phenylene Ar′: 2-quinolyl	Procedure 2	Acetic anhydride	242	375 (58,300)	New compound
IX	Ar: *p*-phenylene Ar′: phenyl	Procedure 3		266	356 (60,600)	6
X	Ar: *p*-phenylene Ar′: *p*-tolyl	Procedure 3		307–308	360 (71,000)	6
XI	Ar: *p*-phenylene Ar′: *p*-nitrophenyl	Procedure 3		290–292	395 (62,200)	6
XII	Ar: *p*-phenylene Ar′: 1-naphthyl	Procedure 3		231–232	370 (35,700)	New compound
XIII	Ar: *p*-phenylene Ar′: 9-anthryl	Procedure 3		315	404 (32,600)	6
XIV	Ar: *p*-phenylene Ar′: 2-furyl	Procedure 3		216	340 (26,200)	New compound

[a] Measured in dioxane.

TABLE II
Analytical Data on New Compounds

	Calculated			Found		
Compound	C, %	H, %	N, %	C, %	H, %	N, %
V	84.48	5.67	9.85	83.78	5.74	9.89
VII	75.50	4.93	19.57	75.54	5.13	19.77
VIII	87.47	5.24	7.29	86.50	5.33	7.59
XII	94.20	5.80		94.07	5.71	
XIV	82.42	5.38		82.66	5.50	

(Ushio Electric Inc., capacity 300 ml), for 2 hr at room temperature. The sparkling yellow color of the starting compound gradually changed into the white of the polymer. The product was collected, washed with acetone to remove the monomer, and dried *in vacuo*. The reduced viscosity of poly-2,5-distyrylpyrazine (poly-DSP) (0.35 g polymer in 100 ml CF_3COOH, 30°C) was 3.08, and the yield is nearly quantitative. The polymer melts at 339–343°C with considerable decomposition.

ANAL. Calcd for $C_{20}H_{16}N_2$: C, 84.48%; H, 5.67%; N, 9.85%. Found: C, 83.31%; H, 5.74%; N, 9.35%.

Polymerization of DSP without Dispersant. Fine crystals of DSP in the rotary flask (Pyrex) were exposed to sunlight for 10 hr. The product was treated in the same manner as before.

The yield was 89%; η_{red} 1.31 (0.31 g. polymer in 100 ml. CF_3COOH).

Polymerization of P2VB. P2VB(0.125 g) was dispersed in 50 ml of water–ethanol (5:1 in volume) and irradiated with a 500-W xenon lamp (Ushio Electric Inc.) through a Pyrex flask at room temperature for 9 hr. The light source was 70 cm from the center of the flask. The white powdery product was collected, refluxed with acetone to remove the monomer, and dried *in vacuo*. The poly-1,4-bis[β-pyridyl-(2)-vinyl]benzene (poly-P2VB) was obtained in 90% yield and the reduced viscosity was 1.19 (0.36 g polymer in 100 ml CF_3COOH, 30°C). The polymer melted at 340°C with considerable decomposition.

ANAL. Calcd for $C_{20}H_{16}N_2$: C, 84.48%; H, 5.67%; N, 9.85%. Found: C, 82.53%; H, 5.75%; N, 9.70%.

Polymer Reactions

Thermal Depolymerization of Poly-DSP. Poly-DSP (0.103 g) was placed in a sublimation apparatus and heated at 300–345°C for about 1 hr under reduced pressure (3.5 mm Hg). Yellow, needlelike crystals of DSP with scalelike crystals sublimed, and the total yield of DSP was 0.092 g (89.3%).

Attempted Hydrolysis of Poly-DSP. A 0.0783 g portion of poly-DSP (η_{red}, 3.1, 0.35 g polymer in 100 ml CF_3COOH, 30°C) was dispersed into 50 ml of 10% aqueous sodium hydroxide and boiled for 12 hr.

The reduced viscosity of the polymer thus treated was 2.0 (0.33 g polymer in 100 ml CF_3COOH, 30°C).

Attempted Bromination of Poly-DSP. Poly-DSP (0.101 g) in 20 ml of trifluoroacetic acid solution containing 0.675 g of bromine, was refluxed for 13 hr. No bromination had occurred. Under the same reaction conditions DSP was brominated into the corresponding tetrabromide. Tetrabromo-DSP recrystallized from xylene is a colorless, scalelike crystal (0.08 g) and decomposes at 205°C.

ANAL. Calcd for $C_{20}H_{16}N_2Br_4$: C, 39.77%; H, 2.67%; N, 4.63%. Found: C, 39.93%; H, 2.96%; N, 4.57%.

Oxidation of Poly-DSP. Poly-DSP (3.7 g) was dispersed into 220 ml of aqueous solution containing 11.1 g of potassium permanganate and kept at 70°C for 10 hr, with gentle stirring; 0.71 g of poly-DSP was recovered after the reaction and 2,5-pyrazinedicarboxylic acid was identified as one of the products (0.31 g).

RESULTS AND DISCUSSION

Monomers

DSP was prepared by Frank[1] from 2,5-dimethylpyrazine and benzaldehyde in presence of zinc chloride, but the yield was very poor.

After trying the reaction under various conditions, the yield of DSP was raised to 81% based on 2,5-dimethylpyrazine by the above method[3] but the process was still troublesome. A modified procedure was developed in which zinc chloride was replaced with benzoic anhydride; this was successful, as described in the experimental part.

Benzoic anhydride was also employed in the preparation of P2VB and found to be a very potent dehydrating agent for the condensation of terephthalaldehyde with α-picoline to yield P2VB, which had been synthesized by the method of Wittig only in low yield.[5]

A *trans,trans* configuration was confirmed by the infrared and NMR spectra for all the monomers. For example, *trans,trans*-P2VB has an infrared peak near 970 cm^{-1} and NMR doublet peaks near 2.3τ with a coupling constant of 18 cps which corresponds to *trans* HC=CH bonding.

Polymerization

Polymerizable monomers were screened by prolonged irradiation (100 hr, 500-W xenon or 450-W high-pressure mercury lamp); the monomers which were found to photopolymerize into linear high polymer were DSP and P2VB. These two monomers polymerize in a similar way, except that P2VB polymerizes more slowly than DSP.

Unexpectedly, quite a high molecular weight of linear polymer was produced by the spontaneous reaction of four olefinic carbon atoms between two monomers. The reduced viscosity of poly-DSP (0.35 g polymer in 100 ml CF_3COOH) is more than 10, and the polymer is never crosslinked.

The other two monomers, compounds VI and XIV, showed some chemical changes by spectroscopy, and another monomer (XIII) has already been suggested by Campbell[6] to isomerize photochemically. However, further studies on these three compounds have not been performed.

Since the polymerizability of the monomer in the present work has been found to depend primarily on its crystal structure, the nonpolymerizable monomers may polymerize in other crystal modifications as shown for DSP in the previous paper.[7]

Polymer Structures

NMR spectra of poly-DSP and poly-P2VB showed a broad band at 4.9–5.0τ (4H) which is characteristic of protons bonded to a 1,2,3,4-tetraarylated cyclobutane ring[8] and quantitative considerations are consistent with this assignment (Fig. 1). Other peaks, at 2.9, 2.8, and 1.3τ for poly-DSP are assigned to the 3,3′-protons (4H), 2,2′- and 4,4′-protons (6H) of benzene, and protons (2H) at the 3- and 6-positions of pyrazine. The 2.8, 2.2, and 1.5–1.6 τ peaks of poly-P2VB correspond to the 4H protons of benzene, protons (4H) at 3,3′- and 5,5′-position of pyridine and protons (4H) at the 4,4′- and 6,6′-position of pyridine.

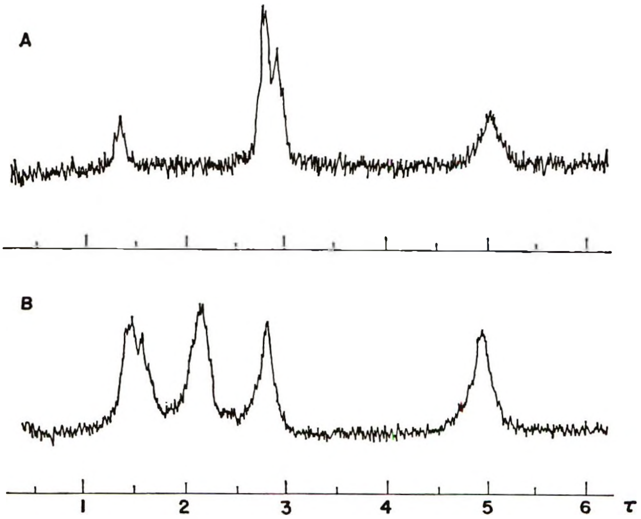
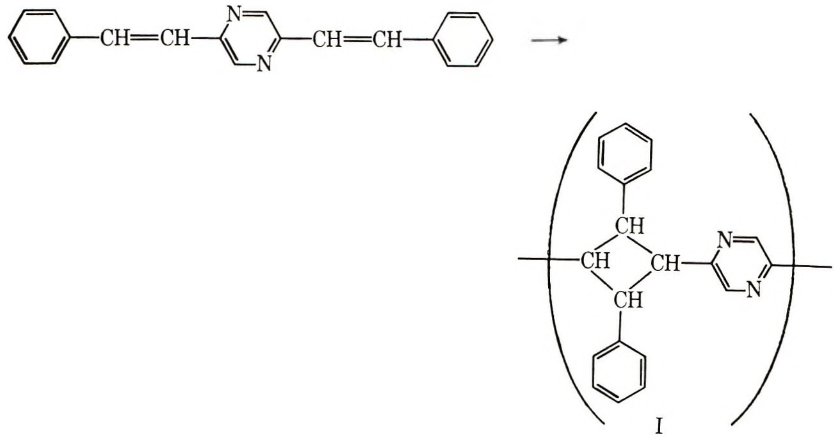
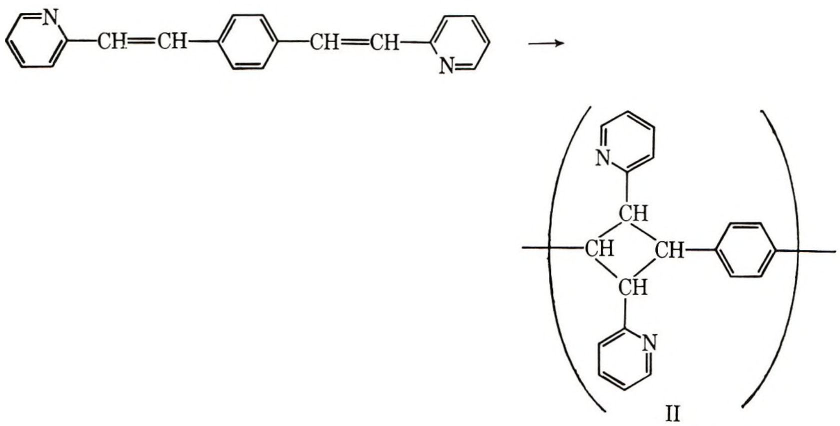


Fig. 1. NMR spectra of (*A*) poly-DSP and (*B*) poly-P2VB in trifluoroacetic acid (100 Mcps).

As a result, poly-DSP and poly-P2VB are concluded to be linear polymers with recurring cyclobutane and aromatic rings alternating in the main chain, as shown in structures I and II.



I
poly-DSP



II
poly-P2VB

However, the absolute configuration of the polymer, including the distinction between head-to-tail and head-to-head structures, has not been established at present. Williams obtained two kinds of dimers from a solid-state photoreaction of styrbazol[9] which is presumed to be a typical model reaction pertinent to the present work, but the absolute configuration has not been established on these photodimers.

The infrared spectra of poly-DSP and poly-P2VB also support a polymer structure containing cyclobutane rings (Fig. 2); the poly-DSP contains neither peaks at 1630 cm^{-1} ($\delta_{C=C}$ aliphatic) nor at 976 cm^{-1} ($\nu_{C=C}$ *trans* HC=CH) which are intense in the monomer.

The corresponding peaks in P2VB are at 1640 and 970 cm^{-1}, respectively, and these also disappear in the polymer. Disappearance of olefinic double bonds is confirmed by the fact that these two polymers were inert to bromine. A weak peak at 930 cm^{-1} in both polymers is attributable to cyclobutane.[10]

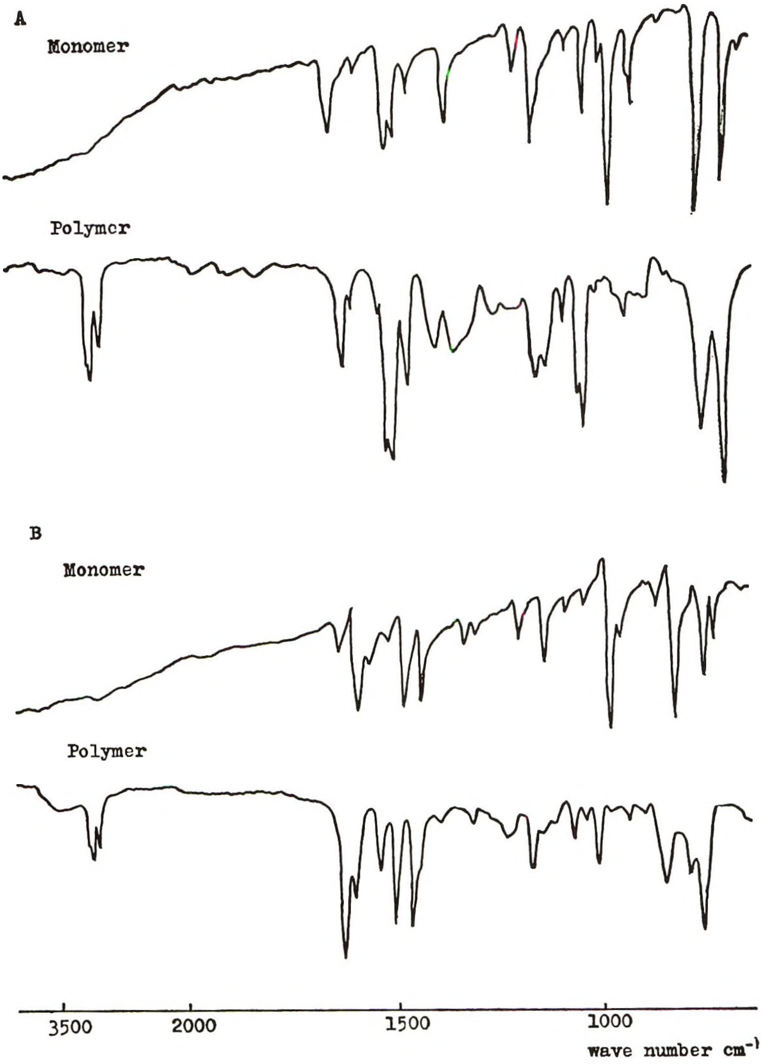


Fig. 2. Infrared spectra of (A) DSP and poly-DSP, and (B) P2VB and poly-P2VB.

Polymer Properties

Some properties of poly-DSP and poly-P2VB are shown in Table III. Melting points of these two polymers are high. However, slight decomposition is observed before the melting points are reached, and some monomer crystals are recovered; this is attributed to the pyrolytic degradation of the cyclobutane residues.

Both polymers are insoluble in ordinary polymer solvents except strong acids such as concentrated sulfuric, trifluoroacetic and dichloroacetic acids, where the polymer exists in the salt form. Although amorphous polymer film cast from trifluoroacetic acid is yellowish due to the residual solvent,

TABLE III
Properties of Polymers

	Poly-DSP	Poly-P2VB
Yield, %	95	85–90
Appearance	White powder	White powder
Crystallinity	Extremely high	Extremely high
Mp, °C	339–343	340
η_{red}[a]	1.0–10.0	0.3–1.2
Elementary analysis, calcd		
C, %	84.48	84.48
H, %	5.67	5.67
N, %	9.85	9.85
Elementary analysis, found		
C, %	83.31	82.53
H, %	5.74	5.75
N, %	9.35	9.70
Solvents	Conc. H_2SO_4 CF_3COOH $Cl_2CHCOOH$	Conc. H_2SO_4 CF_3COOH $Cl_2CHCOOH$ HCOOH

[a] 0.35 g polymer in 100 ml of CF_3COOH at 30°C.

Fig. 3. X-ray diffraction pattern of poly-DSP.

the film treated with triethylamine is colorless and transparent, and has high tenacity.

The polymer is highly resistant to alkali but not to oxidants, as described in the experimental part. Poly-DSP and poly-P2VB are crystalline polymers. The x-ray diffraction pattern of poly-DSP is shown in Figure 3. Two monomers (DSP and P2VB) or two polymers (poly-DSP and poly-P2VB) are very closely related to each other with respect to their crystal structures.[7]

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Four-Center Type Photopolymerization in the Solid State. II. Polymerization Mechanism of 2,5-distyrylpyrazine

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Synopsis

The polymerization mechanism of *trans,trans*-2,5-distyrylpyrazine (DSP) has been investigated and some crystal changes along with the polymerization process have been observed through polarizing microscope and x-ray diffraction pattern. Information has been obtained on the active species, polymerization reaction type, and other factors such as light intensity, reaction temperature, or crystalline state. The polymerization of DSP occurs only in the solid state by photoirradiation. Reduced viscosity increases gradually with the increase of conversion and increases sharply above 80% conversion. Polymerization rate increases with the increase of light intensity and temperature. On the other hand, reduced viscosity decreases with the increase of temperature but does not depend on light intensity within the range investigated. The polymer obtained at low conversion as well as at high conversion has high crystallinity, and the direction of polymer axes is simply related to that of monomer crystal. It was concluded that the four-center type polymerization of DSP proceeds topochemically by a photochemically induced stepwise mechanism.

INTRODUCTION

In previous papers[1–4] it was reported that *trans,trans*-2,5-distyrylpyrazine, *trans,trans*-1,4-bis[β-pyridyl-(2)-vinyl]benzene, and various *p*-phenylene diacrylic derivatives polymerize in the solid state to give a highly crystalline polymer containing cyclobutane in the main chain. There have been few reports of kinetic studies of solid-state photopolymerization.[5] The reaction is unique, in that olefinic double bonds react at four points to result in a highly crystalline linear polymer with very high molecular weight.

In the present work the polymerization mechanism of 2,5-distyrylpyrazine has been studied, and information has been obtained on the active species, polymerization reaction type, and other factors such as light intensity, reaction temperature, or crystalline state of the monomer which influence the polymerization rate or reduced viscosity.

It is concluded that the four-center type photopolymerization of *trans,trans*-2,5-distyrylpyrazine proceeds topochemically by a photochemically induced stepwise mechanism.

EXPERIMENTAL

Monomers

2,5-Distyrylpyrazine (DSP) and 1,4-bis[β-pyridyl-(2)-vinyl]benzene (P2VB) were prepared as described in the preceding paper.[3] The crude DSP was recrystallized twice from benzene. Recrystallization was repeated to obtain uniform crystals under the conditions described in Table I. DSP from a single recrystallization batch was employed for the whole series of kinetical experiments in order to avoid variations of the data attributable to the crystalline state of the monomer. The method of preparation of the monomer and the experimental results for each monomer are listed in Table I.

TABLE I
Conditions for Polymerization

	Condition I	Condition II
Dehydrating agent employed for preparation of DSP	Zinc chloride	Benzoic anhydride
Final crystallization condition of DSP (from benzene)	10 g per 1.5 liter	10 g per 1.0 liter
Light source	500-W xenon (Fig. 1)	100-W high-pressure mercury lamp
Reaction scale	0.125 g DSP in 50 ml. cyclohexane	0.250 g DSP in 100 ml cyclohexane
Data to which conditions pertain	Table II, Fig, 2, Fig. 3, Fig. 5, Fig. 6, Fig. 12	Fig. 4, Fig. 7, Fig. 8, Fig. 9, Fig. 10, Fig. 11

Polymerization

Two types of apparatus for photopolymerization, were used, depending on the requirement of individual polymerizations.

In one apparatus in which the light source, a 500-W xenon lamp (Ushio Electric Inc.), is 70 cm from the center of the reaction flask through a quartz flask (Fig. 1), 0.125 g of crystalline DSP was dispersed in 50 ml of cyclohexane and stirred with a magnetic stirrer at constant speed.

In another apparatus, the light source, a 100-W high-pressure mercury lamp (Ushio Electric Inc.) is at the center of the flask; in this series of experiments 0.250 g of crystalline DSP was dispersed in 200 ml of cyclohexane and stirred as before.

In these two procedures the light source was stabilized before the irradiation was initiated.

Cyclohexane, was used as a dispersing medium to give homogeneous irradiation to the monomer surface in the solid-state polymerization. Ordinary vacuum line equipment was used to charge the reagents when the catalytic polymerizability was examined.

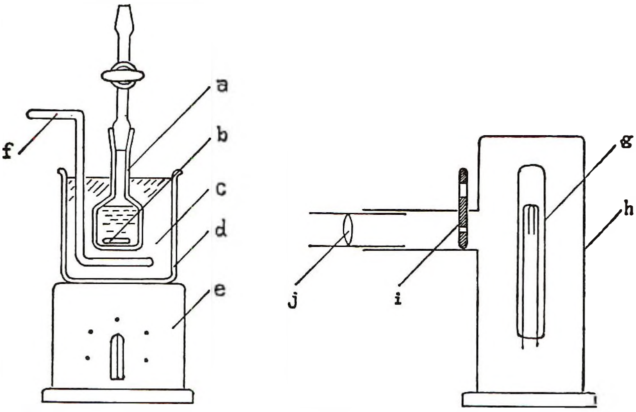


Fig. 1. Irradiation apparatus: (*a*) quartz reaction tube; (*b*) stirrer; (*c*) heat transfer medium; (*d*) quartz beaker; (*e*) magnetic stirrer; (*f*) thermoregulator; (*g*) lamp house (*h*) xenon lamp; (*i*) diaphragm; (*j*) lens.

As poly-DSP in trifluoroacetic acid solution depolymerizes readily under fluorescence light, the intrinsic viscosity in the above solvent (0.36 g polymer/dl) was measured at 30°C in the dark.

RESULTS AND DISCUSSION

Active Species

Preliminary observation indicated that the most effective wavelength for the polymerization of DSP was in the range 400–415 mμ.

The effect of inhibitors on this photopolymerization was examined and a polymerization of crystalline DSP was attempted in the presence of such initiators as benzoyl peroxide (BPO), azobisisobutyronitrile (AIBN), or boron trifluoride etherate. Solution polymerization of DSP in tetrahydrofuran was also attempted in the presence of BPO, AIBN, $BF_3 \cdot OEt_2$ and sodium naphthalate, or by the irradiation of light. However, none of these methods produced polymer (Tables II and III).

TABLE II
Effect of Inhibitors on the Photopolymerization of DSP[a]

Additives	Dispersant	Time, min	Conversion %	η_{red}, dl/g
None	Cyclohexane	60	60.0	0.70
Hydroquinone (0.133 g)	Cyclohexane	30	15.6	—
“	“	45	51.0	0.51
“	“	60	65.8	0.69
“	“	90	81.7	1.06
	“			
	Water–methanol (20/30 v/v)	60	99.5	2.40

[a] 0.125 g DSP in 50 ml cyclohexane at 30°C; light source, 500-W xenon lamp (Fig. 1).

TABLE III
Polymerization of DSP Using Various Catalysts.[a]

Catalyst	Dispersant	Solvent	Time, hr	Temperature, °C	Observation
BPO	Cyclohexane	—	10.5	81	No reaction
AIBN	"	—	22.5	81	"
$BF_3 \cdot OEt_2$	"	—	24	30	Changed
BPO	—	THF	24	64	No reaction
AIBN	—	"	24	64	"
$BF_3 \cdot OEt_2$	—	"	24	30	Changed
Naphthalene + Na	—	"	—	30	"
Light[b]	—	"	24	30	"

[a] 0.125 g DSP in 50 ml dispersant or solvent.
[b] Light source; 450-W high-pressure mercury lamp.

The photopolymerization was carried out under oxygen in a separate experiment. Neither oxygen nor hydroquinone in cyclohexane had an effect on the reaction rate. Crystalline DSP photopolymerizes in water–methanol mixture as well as in cyclohexane, whereas it does not polymerize by the action of any of the initiators tested.

DSP dissolves in cyclohexane at concentrations of 0.006 g/50 ml, and the dissolved DSP absorbs a certain amount of the effective light in the solid-state polymerization while it is entirely insoluble in methanol–water mixture. The accelerated rate in methanol–water only reflects this insolubility and is not a solvent effect on the reaction rate.

When boron trifluoride etherate was employed, the crystal surface became purple or orange, indicating electron-donor exchange of boron trifluoride from ether to DSP.

In the sodium naphthalate–THF system, a purple color, different from the green of the naphthalene radical anion, was observed; it disappeared rapidly in air. As the solution shows ESR activity, the purple color is probably caused by the DSP radical anion.

DSP in the molten state does not polymerize on prolonged irradiation at 250°C, but poly-DSP has been observed to depolymerize appreciably to the monomer at the same temperature. γ-Irradiation was also ineffective in the polymerization of crystalline DSP.

Trioxane or *N*-vinylcarbazole were reported to polymerize with cationic catalysts in the solid state as well as in solution or the molten state.[6–9] However, DSP has been confirmed to polymerize by photoirradiation only in the solid state.

Polymerization

Several plots of reaction time versus conversion, reaction time versus reduced viscosity, and conversion versus reduced viscosity were obtained by the standard procedure, as shown in Figures 2 and 3.

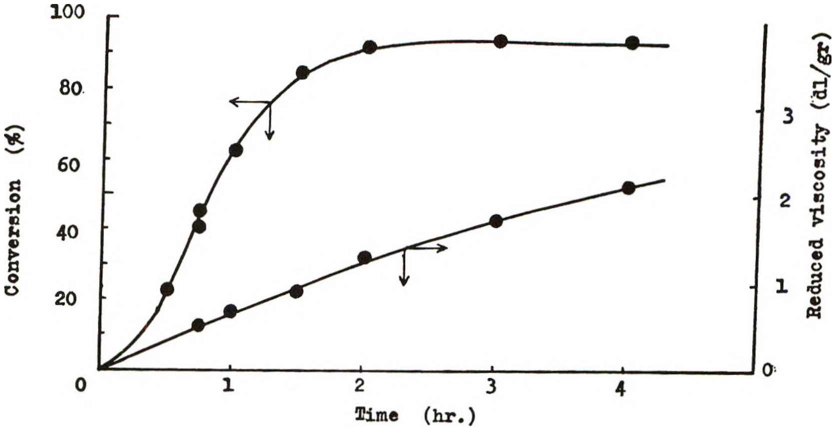


Fig. 2. Plot of conversion and reduced viscosity vs. time. Polymerization conditions: 30°C; 0.125 g DSP/50 ml cyclohexane.

The reduced viscosity increases gradually with increasing conversion and increases sharply above 80% conversion. Conversion appears to reach a limiting value around 95% (Fig. 3) but it becomes quantitative if the dissolved DSP is taken into account.

The reduced viscosity of the polymer increases with the reaction time and continues to rise on irradiation, even after the conversion is complete. It was also confirmed that the polymerization proceeded only during irradiation.

In another series of experiments (Fig. 4) a polymer with 38% conversion was reirradiated after the monomer and oligomers had been removed: the reduced viscosity was found to increase on reirradiation.

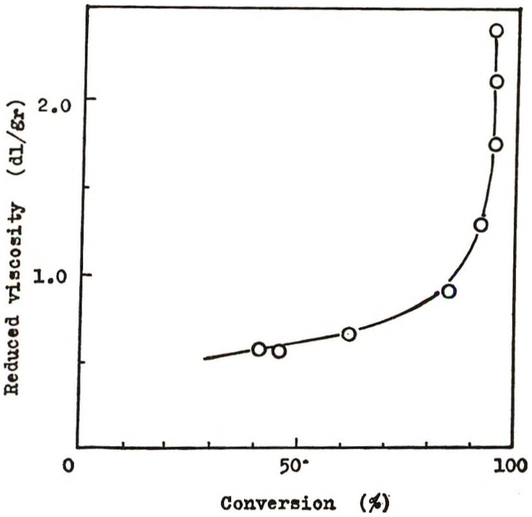


Fig. 3. Plot of reduced viscosity vs. conversion. Polymerization conditions: 30°C; 0.125 g DSP/50 ml cyclohexane.

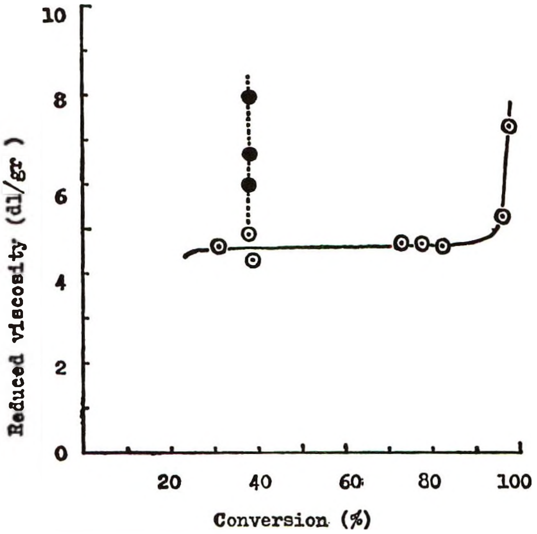
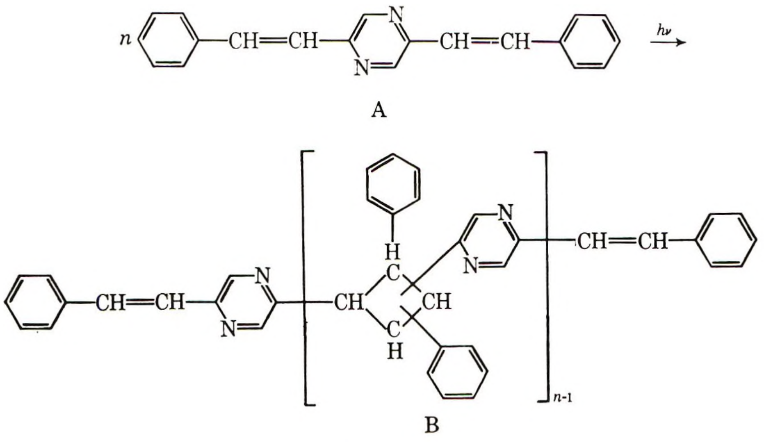


Fig. 4. Plot of reduced viscosity vs. conversion. Polymerization conditions: 100-W high-pressure Hg lamp; −25°C; 0.25 g DSP/200 ml *n*-hexane.

A wide molecular weight distribution of the polymer at low conversion is inferred from the fact that considerably less polymer is recovered from a specimen if it is treated with tetrahydrofuran, a better solvent for DSP, rather than acetone.

These features are the same as those of a typical polycondensation reaction and suggest that the solid-state photopolymerization of DSP follows the stepwise mechanism.

The reaction scheme may be represented as shown in eqs. (1)–(4).



(1)

$$A + A \longrightarrow B \quad (2)$$

$$A + B \longrightarrow B \quad (3)$$

$$B + B \longrightarrow B \quad (4)$$

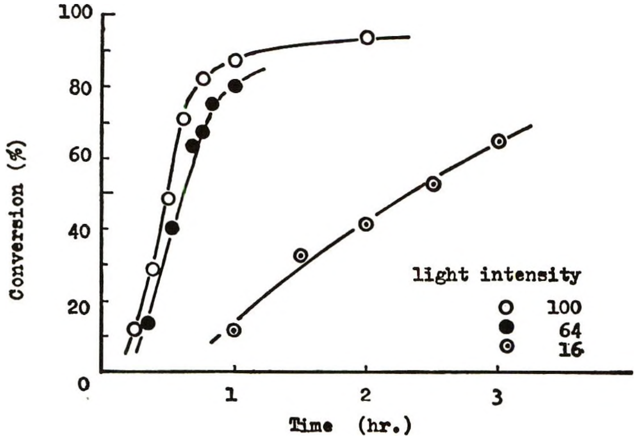


Fig. 5. Effect of light intensity on polymer yield. Polymerization conditions: 30°C; 0.125 g DSP/50 ml cyclohexane.

Here A and B necessarily behave in a different manner because of the pronounced difference in the resonance stabilization of the olefinic double bonds.

The stepwise mechanism also indirectly rules out the possibility of forming a ladder polymer which would inevitably result from a chain mechanism.

The large difference in the reduced viscosity at the same conversion (Figs. 3 and 4) is attributed chiefly to the dehydrating agent employed in the preparation of the monomer and to the polymerization temperature.

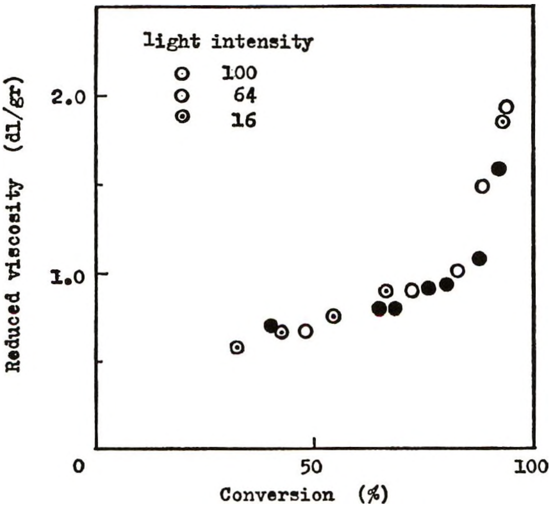


Fig. 6. Effect of light intensity on reduced viscosity. Polymerization conditions: 30°C; 0.125 g DSP/50 ml cyclohexane.

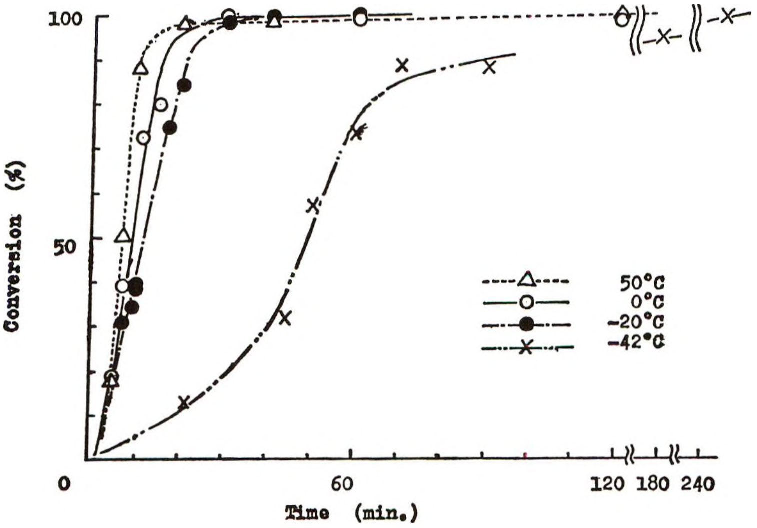


Fig 7. Effect of temperature on polymer yield. Polymerization conditions: 100 W high-pressure Hg lamp; 0.25ϕ g DSP/200 ml n-hexane.

Effect of the Light Intensity

The effect of the light intensity on the reaction rate and on the dependence of the reduced viscosity of the polymer on conversion was investigated; the results are shown in Figures 5 and 6.

As would be expected, the rate increases with the light intensity. That the reduced viscosity at a given conversion is independent of the light intensity within the range investigated might be further evidence for the stepwise mechanism.

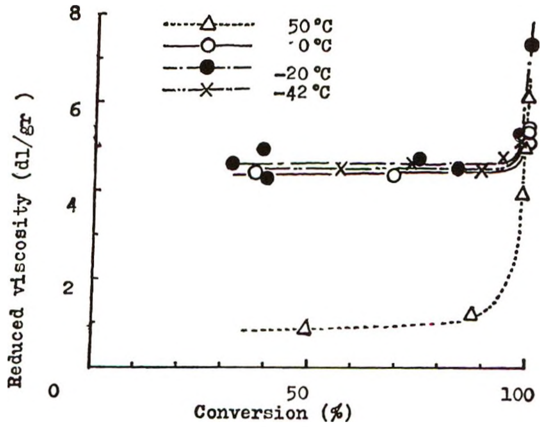


Fig 8. Effect of temperature on reduced viscosity. Polymerization conditions: 100-W high-pressure Hg lamp; 0.25 g/200 ml n-hexane.

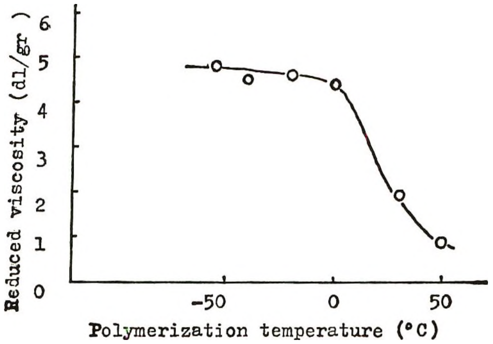


Fig. 9. Effect of temperature on reduced viscosity at 50% conversion. Polymerization conditions: 100-W high-pressure Hg lamp; 0.25 g/200 ml *n*-hexane.

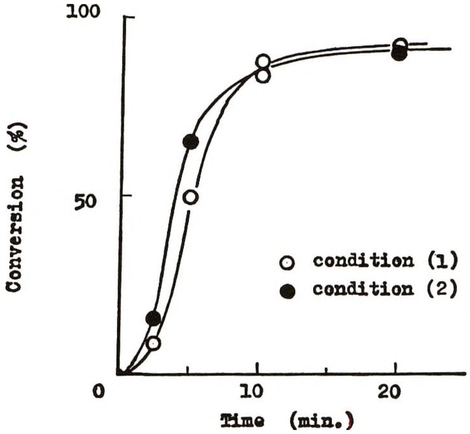


Fig. 10. Effect of the crystal on polymer yield. Polymerization conditions: 30°C; 0.25 g DSP/200 ml *n*-hexane.

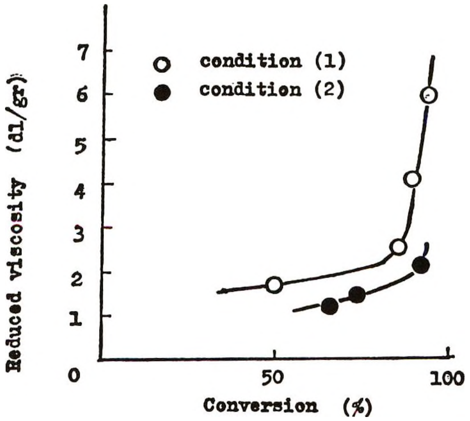


Fig. 11. Effect of the crystal on reduced viscosity. Polymerization conditions: 30°C; 0.25 g DSP/200 ml *n*-hexane.

Effect of the Polymerization Temperature

The effect of the temperature of polymerization has been investigated in *n*-hexane, in place of cyclohexane, at 50 to −42°C (Figs. 7 and 8).

The activation energy for the polymerization to 50% conversion is roughly estimated as 3 kcal/mole.

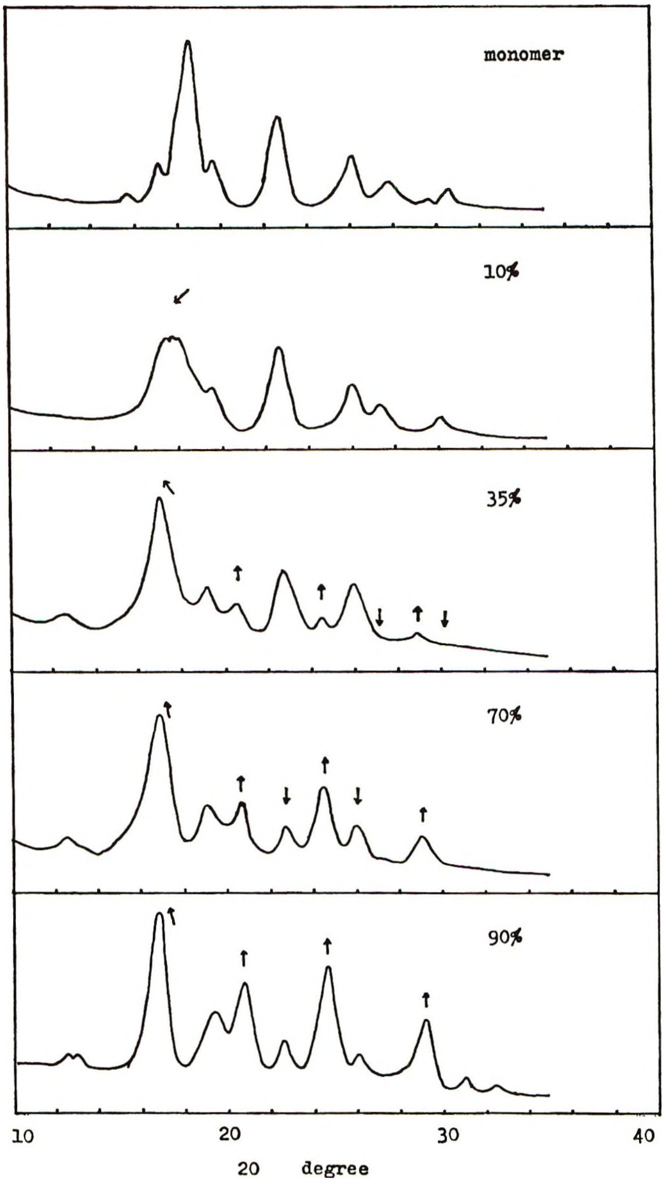


Fig. 12. Change in x-ray diffraction diagram during the polymerization.

The reduced viscosity of the polymer at 50% conversion is plotted as a function of the polymerization temperatures in Figure 9. As is seen, the reduced viscosity decreases with rising polymerization temperature slowly below 0°C but sharply between 0 and 50°C.

Crystal State of the Monomer and the Polymer

As already reported,[2] scale- or swordlike crystals of DSP, obtained by recrystallization from benzene solution photopolymerize, whereas needlelike crystals of DSP, obtained by sublimation at the elevated temperature, do not. Furthermore, the reduced viscosity of the polymer is strikingly dependent on the method of preparation of the monomer and the polymerization temperature. This suggests that the crystalline state of the monomer is significantly related to the polymerization behavior.

Two kinds of polymerizable DSP crystals were prepared by (1) crystallization by slow cooling from benzene solution (standard crystal); (2) rapid precipitation by pouring a hot benzene solution into petroleum ether (fine crystal). These two crystals are the same in crystal structure when examined by x-ray diffraction.

Rate (Fig. 10) and viscosity data (Fig. 11) indicate that fine crystalline DSP polymerizes faster but leads to a polymer with a lower molecular weight at the same conversion. Presumably the fine crystals have a corper surface and more lattice defects per a unit weight compared with the standard crystal.

Some x-ray crystallographic studies have been carried out during the polymerization (Fig. 12).

Diffraction peaks of the polymer are recognized even at 35% conversion of the crystal, which strongly suggests that the polymerization proceeds at the crystal surface in the early stage.

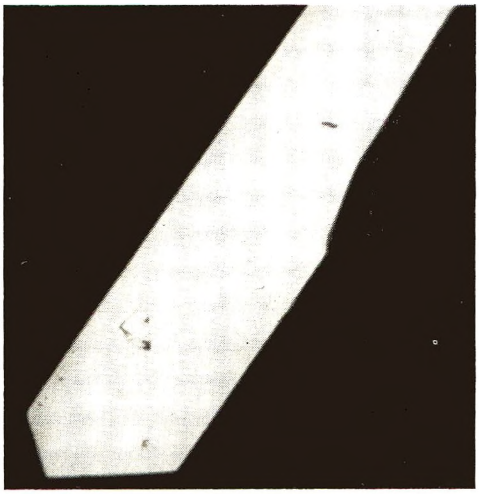
The diffraction pattern at 70% conversion is nearly the same as for pure polymer.

The crystallinity of polymer isolated at very low conversion is as high as that at high conversion. In contrast with the extremely high crystallinity of poly-DSP as polymerized, poly-DSP once dissolved is entirely amorphous and is hardly recrystallized even by appropriate heat treatment.

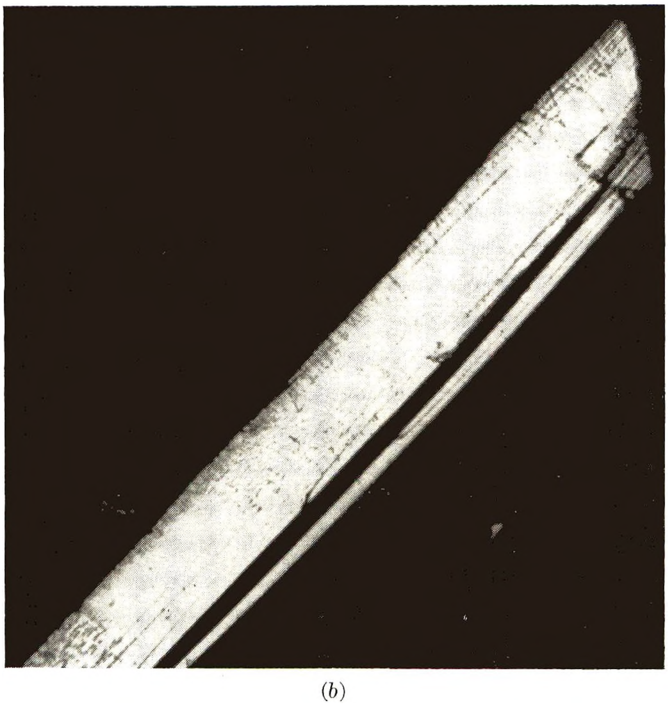
The change during the photopolymerization of a single crystal of P2VB, which has a crystal structure quite similar to that of DSP, was photographed under a polarizing microscope (Fig. 13). It was observed that fibridization occurs along the *c*-axis which is common with the fiber axis of the polymer and that in Figure 13(*d*) photopolymerization occurs only at the spot irradiated.

Specific gravities of DSP and poly-DSP at 25°C are 1.255 and 1.279, respectively. The difference explains fibridization during the polymerization.

Since the crystalline polymer is produced from the monomer in the crystalline state and a simple relation exists between those crystal units, it



(*a*)



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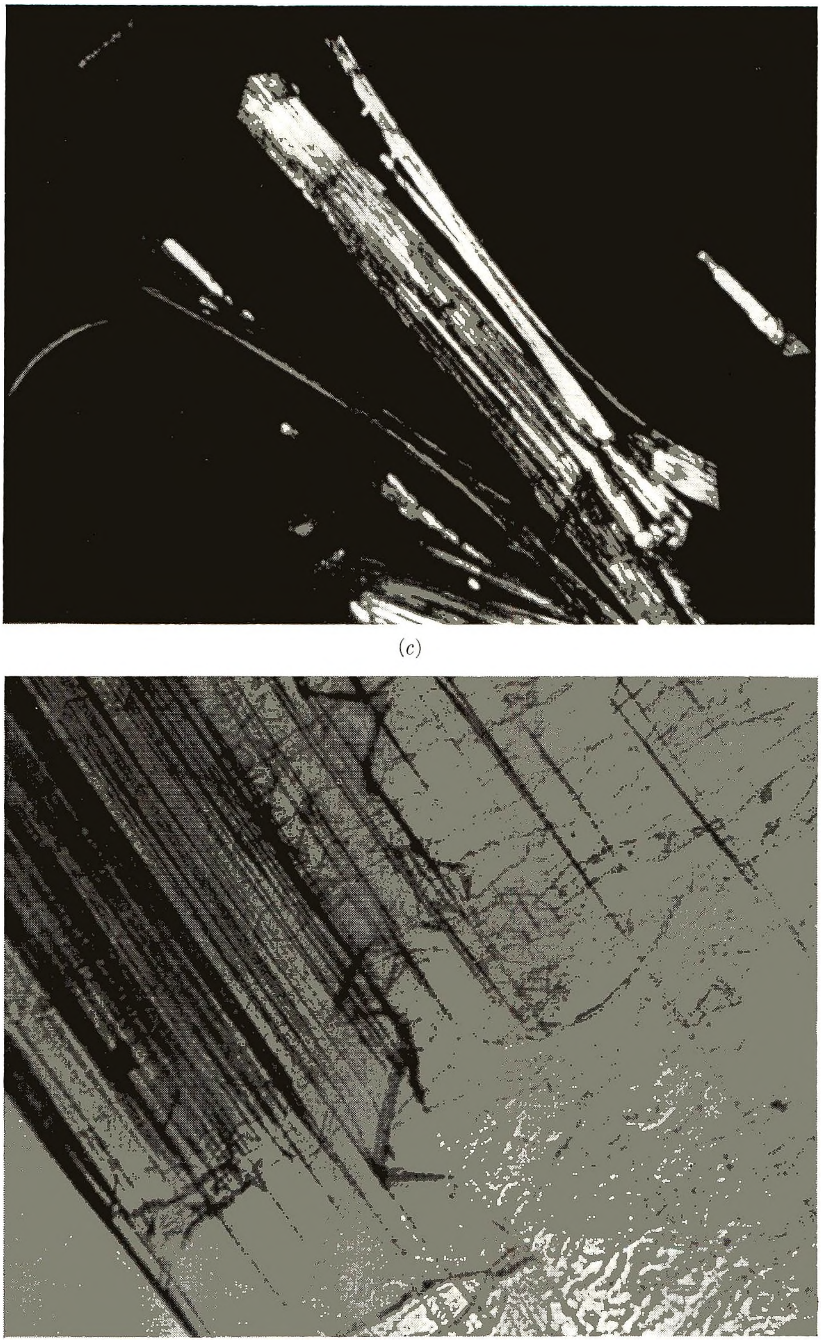

(c)

(d)

Fig. 13. Change in single crystal of P2VB accompanying photopolymerization: (a) single crystal of P2VB; (b) with a low conversion to poly-P2VB; (c) with a high conversion to poly-P2VB,; (d) irradiated only at an upper part of the crystal.

is concluded that this type of photopolymerization belongs to a topochemical reaction.

The authors wish to express their thanks to Dr. M. Iguchi for help in interpreting the x-ray patterns.

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NOTES

Spectra of Glow-Discharge Polymers from Aromatic Compounds

Introduction

It is well known that molecular vapors form polymers in electrical discharges.[1] While there has been recent interest in these glow-discharge polymers for use as surface coatings,[2,3] very little attention has been given even qualitatively to their structures. Some information is available by inference from analysis of identifiable soluble solid products from various discharges[1,4,5] and from infrared spectra of the insoluble polymers from discharges of benzene [6,7] and styrene.[2,7,8] We have surveyed the infrared spectra of glow-discharge polymers from several monosubstituted benzenes as an extension of the latter results, which at present constitute nearly the only attempts at direct determination of the structures of these insoluble, intractable materials. Our materials are collected directly on metal electrodes in contact with the conducting vapor. Other methods involve collection on surfaces adjacent to electrodeless discharges[5,9] and distillation of involatile oils onto surfaces with subsequent polymerization by exposure to an argon discharge.[2]

Experimental

The experiment has been described in detail by Schüler et al.[6] Discharges were run between electrodes of aluminized Mylar films at 200–300 V ac, 20 KHz, 1 torr pressure. Polymer collected on the electrodes. A Perkin-Elmer spectrophotometer, Model 521, with a KRS-5 crystal frustrated multiple internal reflection (FMIR) attachment was used for infrared spectra. Emission spectra were photographed from the image of the cathode and negative glow focussed on the slit of a Spex 0.75-m Czerny-Turner spectrograph with 1200 L/mm grating.

Results and Discussion

As an example the FMIR spectrum of glow-discharge polymer (GDP)-chlorobenzene is shown in Figure 1. Many similar spectra were obtained for the other materials examined and were found to be highly reproducible. Prominent common features were abstracted from these spectra and are listed as infrared group frequencies in Table I. While the features in the "Aromatic" part of Table I always appeared in GDP's from aromatic vapors, they were always absent in products from aliphatics.

Since aromatization does not occur in these discharges, all the aromatic structures observed most likely persist from molecules of starting vapor. The way in which aromatic rings are incorporated into the polymer from our discharges differs from that in the polyphenylenes from Stille's RF electrodeless discharge.[5] Our GDP-benzene spectrum,[7] like Figure 1 for GDP-chlorobenzene, shows features which most prominently indicate that the benzene rings are monosubstituted and so are pendent from the aliphatic (or alicyclic) polymer chains. This structure is similar to that reported by Schüler for GDP-benzene prepared in the positive column of a dc discharge.[6] Stille, on the other hand, reports the band at 860–800 cm^{-1}, corresponding to *para*-substitution, to be strong. We find only a weak shoulder at this wavelength and intense bands at 690 and 745 cm^{-1}, which we attribute to monosubstitution. Support for this assignment is delineated below. In fact, from Table I and Figure 2 we generalize this observation to all the GDP's from the monosubstituted aromatics investigated.

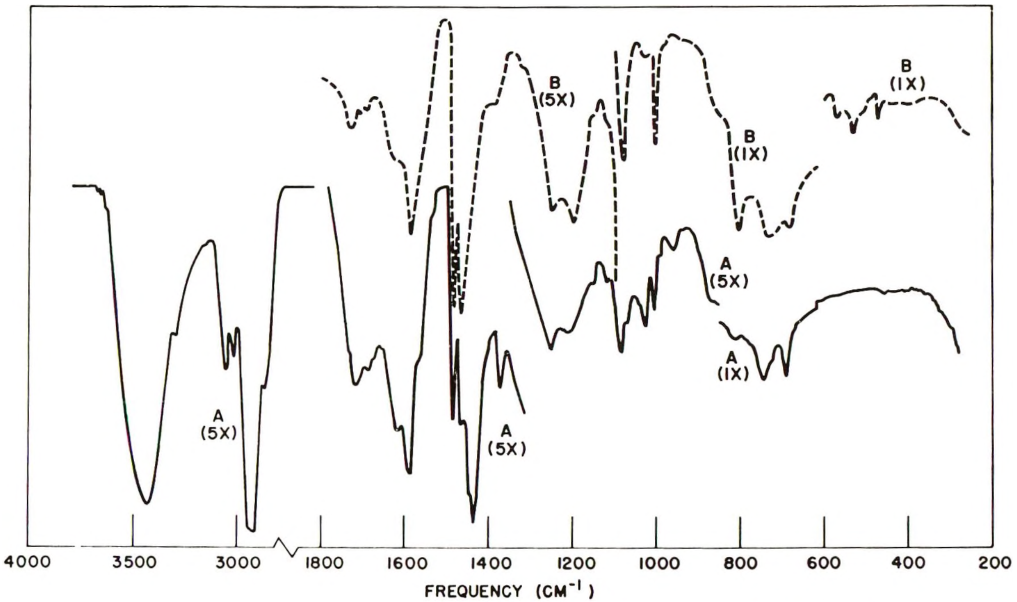

Fig. 1. Infrared spectra of polymers produced in chlorobenzene and 1,4-dichlorobenzene glow discharges: (*A*) GDP-chlorobenzene; (*B*) GDP-dichlorobenzene.

TABLE I
Group Frequencies Found in GDP

	Frequency, cm^{-1}						
	Chlorobenzene	Fluorobenzene	Benzonitrile	Acetophenone	Phenyl-acetylene	Nitrobenzene	Toluene
			Aromatic				
$\nu(=CH)$	3050		3050	3050	3050	3050	3050
	3020	3020		3015	3015		3020
$\nu(C=C)$	1590	1600	1590	1595	1595		1595
		1580		1575	1575	1585	
		1500					
	1490	1480	1480	1490	1490	1480	1490
$\beta(=CH)$	1150		1150	1150	1150	1150	1150
	1070		1060	1065	1065	1060	1070
	1025		1010	1020	1020	1010	1030
$\gamma(=CH)$	820		780				
	755		750	750	750	740	740
δ' (ring)	690		680	690	690	690	690
			Aliphatic				
$\gamma(CH)$	960		950	950	960	950	960
	840		830	835	835		840
$\nu_{as}(CH_2)$	2915	2915	2915	2915	2915	2915	2915
$\nu_s(CH_2)$	2850	2850	2850	2850	2850	2850	2850
$\nu_{as}(CH_3)$	Absent	Absent	Absent	2950	2950		2950
$\nu_s(CH_3)$	Absent	Absent	Absent	2880	2880		2880
$\delta_s(CH_3)$	Absent	Absent	Absent	1370	1370		1370

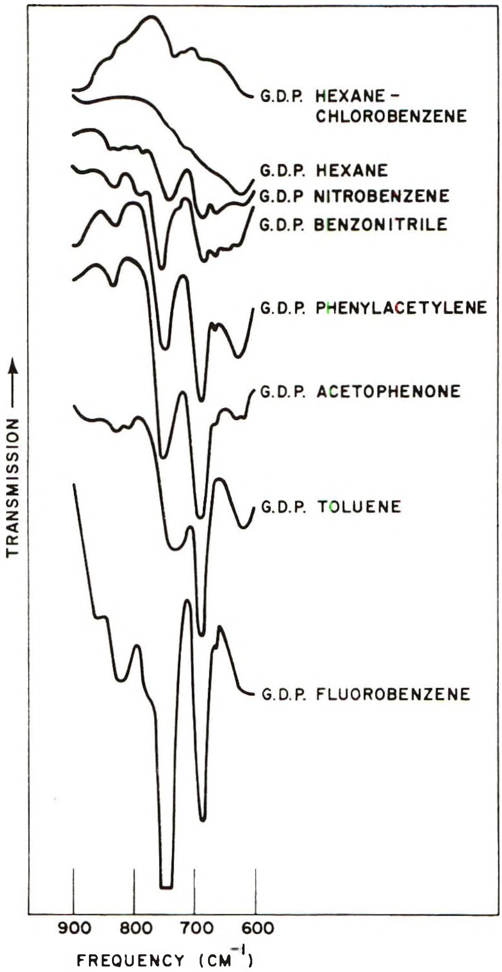

Fig. 2. Infrared spectra of polymers produced in glow discharges.

Details of the aromatic substitution are difficult to ascertain from the infrared spectra alone, the region between 1650 and 2000 cm^{-1} being obscured by an intense band attributed to a CO bond. Careful observations of the bands in the spectrum of GDP-chlorobenzene between 600 and 900 cm^{-1} show resolved bands at 820, 755, 725, and 695 cm^{-1}. Only the 725 cm^{-1} band vanishes when the polymer is heated to 250° in an inert atmosphere for 1 hr. This band is then due to a feature which is less thermally stable than the rest of the aromatic structure and may represent a four or five-carbon aliphatic fragment. The other bands are consistent with various combinations of substituted rings. Thus *meta*-substitution could give bands near 820 and 690 cm^{-1}; *para*-substitution, near 820 cm^{-1}; and monosubstitution, near 690 and 755 cm^{-1}. There seems to be no way to explain the 755 cm^{-1} band, without reference to monosubstituted rings. All our spectra, moreover, show this band with the same intensity relative to that at 690 cm^{-1}, these being the two most intense bands of the spectra of glow-discharge polymers from all the monosubstituted benzenes examined. (This is the only region in Figure 1 which is not expanded fivefold.) The relative intensities in the 690–900 cm^{-1} structure of these polymers are different from those (Fig. 1) for GDP-1,4-dichlorobenzene, in which monosubstitution would be less likely than for the materials investigated. Here the band at 820 cm^{-1} is as intense as that at 690 cm^{-1}. Thus the spectra of Figure 2 can be interpreted in greatest detail in terms of an unexpected content of monosubstituted component which does not distill off at 250°C.

Our product was collected from the region of the discharge where the ions have the greatest energy, the cathode fall nearest to the cathode surface. The infrared spectrum of polymer collected from the wall of the discharge vessel near the negative glow, another energetic reaction region, was similar. That the chemical processes which occur in the negative glow or cathode fall of a low-frequency glow discharge are different from those in an RF electrodeless discharge is not surprising. In fact we find differences in chemical intermediates between the negative glow and positive column of the same discharge. Schüler and Reinebeck present evidence that what they call the "T-spectrum" in the emissions from the positive columns of helium discharges with admixtures of benzene, toluene, or chlorobenzene is due to a small aliphatic fragment, probably C_2H or C_4H_x.[10] This spectrum is not observed in the positive column with carrier gases of lower ionization energy than helium, e.g., argon or neon, nor in aromatic vapor alone. Yet by focussing the luminous image of the negative glow and cathode glow on the slit of a spectrograph, we observe the T-spectrum from discharges of pure toluene or phenylacetylene (Table II). Consistent with this, the polymers from these vapors have acetylenic infrared bands at 2100, 2200, and 3300 cm^{-1}. Thus the conditions under which our GDP films are prepared meet the 16 to 20 eV energy requirement specified by Schüler's results. Actually, because of the quadratic field distribution in the cathode fall, a few ions impinge on the cathode with kinetic energies up to 200 eV, the applied field. Since the GDP films produced in the negative glow, where the maximum ion energies are less, have chemical features similar to those on the cathode, but greater solubility, ions with great kinetic energy do not play an important role in determining detailed chemical structure, except for the crosslinking.

TABLE II
Wavelengths of the T-Spectrum in the Emission Spectra of Glow Discharges

Band designation	Toluene		Phenylacetylene		Diacetylene[a]	
	λ, Å	ν, cm^{-1}	λ, Å	ν, cm^{-1}	λ, Å	ν, cm^{-1}
Z	4846	20635			4856	20585
A	5057	19774	5057	19774	5068.5	19725
B_1	5299	18871	5296	18882	5302.7	18853
B_2	5325	18779	5325	18779	5329.5	18757
C_1			5590	17889	5591.0	17881

[a] Data of Schüler and Reinebeck.[10]

It is difficult to formulate a mechanism by which much of the aromatic component of these GDP's could become monosubstituted. One hypothesis, unlikely at first consideration, might be that most of the GDP film is formed from nonaromatic fragments which react, not only with each other during polymerization, but subsequently with starting vapor to displace the substituent group from the benzene ring. The hypothesis implies that monosubstituted aromatics can react in that way with a fresh GDP film, an idea easily tested experimentally. Immediately after formation of a GDP-hexane film about 3 × 10^{-5} cm thick, chlorobenzene vapor was introduced into the cell at its vapor pressure and allowed to remain for 24 hr. The cell was then carefully pumped out to a pressure below 10^{-3} torr, and the procedure was repeated three times to build up a film about 10^{-4} cm thick. The spectrum of the resulting GDP film is shown in Figure 2, with bands centered at 690 and 735 cm^{-1}. Clearly the chlorobenzene was incorporated to give a polymer with features of the GDP-chlorobenzene structure (although 735 cm^{-1} is somewhat to the red of the 755 cm^{-1} GDP-chlorobenzene band). Further, this material contains no chlorine (C, 76.49%; H, 6.24%; Cl, 0.00%; O, 17.27% by difference). For chlorobenzene, then, the proposed reaction is at least a possible one. It might proceed more rapidly during the actual discharge, when the most reactive sites in the polymer would have much less than the second or so to decay which they were permitted during the opening of the stopcock in this experiment. Quantitative kinetic studies would be required to confirm this point definitely.

The GDP-chlorobenzene films prepared directly from a chlorobenzene discharge contain chlorine to give the empirical formula $C_{31}H_{22}Cl_5O$, close to that of chlorobenzene itself.

The process of GD-polymerization which can be derived from these results is one largely of fragmentation of aromatic rings to form branched polymer chains at a collecting surface, with possible subsequent addition of starting molecules with elimination of a substituent. Some aromatic material does react directly, as seen by weaker bands in the infrared spectrum of the GDP films at 820 cm^{-1} (*para*-substitution) and at 775 cm^{-1} (1,3-substitution). The contributions of these processes depend on the discharge conditions, which must be known locally for any meaningful comparison between experiments with different kinds of discharges.

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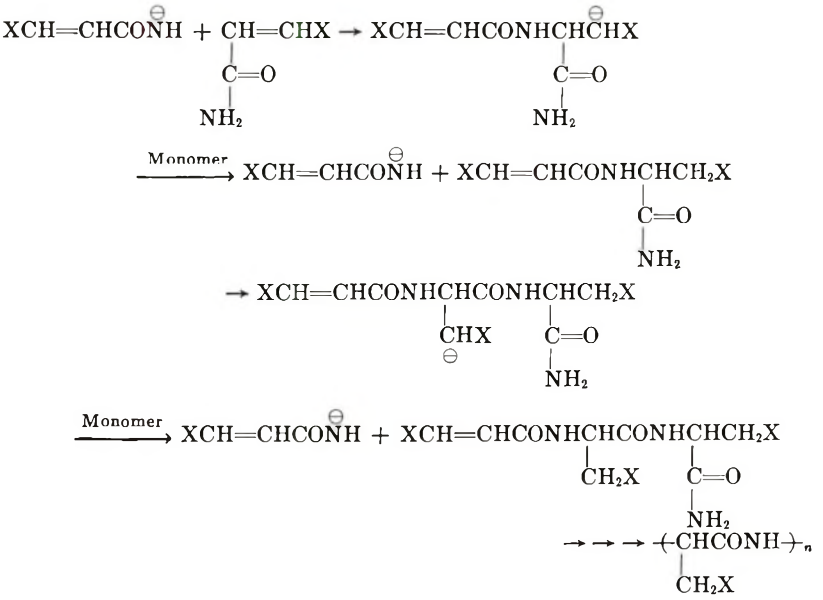
α-Polypeptide Synthesis by the Hydrogen-Migration Polymerization of trans-p-*Nitrocinnamide*

In 1957 Breslow, et al.[1] reported that acrylamide underwent polymerization coupled with a proton migration to form poly-β-alanine when treated with basic initiators. This type of reaction, known as hydrogen-migration polymerization, has subsequently been studied by a number of workers. In particular, it has been a controversial subject whether the propagation reaction occurs via an inter- or an intramolecular hydrogen migration. Recently, Nakayama, et al.[2] reported that both mechanisms were operative in anionic polymerizations of acrylamide, their relative importance being dependent on polymerization solvents used. On the other hand, Breslow, et al.[3] proposed that an intermolecular hydrogen migration is predominant.

Recently, Bamford, et al.[4] suggested the possibility of synthesizing an α-polypeptide by the hydrogen-migration polymerization of β-substituted acrylamides. In their method, as shown in scheme (1), initial addition of a monomer anion to the carbon atom carrying an amide group of the double bond in a monomer or a higher oligomer, which is facilitated by a strongly electron-withdrawing substituent (X), and a subsequent proton transfer reaction are essential to obtain an α-polypeptide.



$$\mathrm{XCH{=}CHCO\overset{\ominus}{N}H} + \underset{\substack{|\\ \mathrm{C{=}O}\\ |\\ \mathrm{NH_2}}}{\mathrm{CH}}\mathrm{{=}CHX} \rightarrow \mathrm{XCH{=}CHCONH}\underset{\substack{|\\ \mathrm{C{=}O}\\ |\\ \mathrm{NH_2}}}{\mathrm{C}}\mathrm{H\overset{\ominus}{C}HX}$$

$$\xrightarrow{\text{Monomer}} \mathrm{XCH{=}CHCO\overset{\ominus}{N}H} + \mathrm{XCH{=}CHCONH}\underset{\substack{|\\ \mathrm{C{=}O}\\ |\\ \mathrm{NH_2}}}{\mathrm{C}}\mathrm{HCH_2X}$$

$$\rightarrow \mathrm{XCH{=}CHCONH}\underset{\substack{|\\ \mathrm{CHX}\\ \ominus}}{\mathrm{C}}\mathrm{HCONH}\underset{\substack{|\\ \mathrm{C{=}O}\\ |\\ \mathrm{NH_2}}}{\mathrm{C}}\mathrm{HCH_2X}$$

$$\xrightarrow{\text{Monomer}} \mathrm{XCH{=}CHCO\overset{\ominus}{N}H} + \mathrm{XCH{=}CHCONH}\underset{\substack{|\\ \mathrm{CH_2X}}}{\mathrm{C}}\mathrm{HCONH}\underset{\substack{|\\ \mathrm{C{=}O}\\ |\\ \mathrm{NH_2}}}{\mathrm{C}}\mathrm{HCH_2X}$$

$$\rightarrow \rightarrow \rightarrow \left(\underset{\substack{|\\ \mathrm{CH_2X}}}{\mathrm{C}}\mathrm{HCONH}\right)_n \qquad (1)$$

The synthesis of an α-polypeptide as a model for a protein is of particular significance. If α-polypeptides can be synthesized from materials other than amino acid, such as acrylamide derivatives, it would be very useful. In this connection, we extended the work on the polymerization of β-substituted acrylamides to *trans-p*-nitrocinnamide, which has a strongly electron withdrawing substituent.

trans-p-Nitrocinnamide was synthesized from ethyl cinnamate as a starting material. It was recrystallized from ethanol three times. It was obtained as yellow needles and melted at 222°C.

ANAL. Calcd: C, 56.25%; H, 4.17%; N, 14.58%. Found: C, 56.24%; H, 4.25%; N, 14.59%.

n-Butyllithium was commercially available as a *n*-hexane solution (concentration

4 mole/l.). *n*-Butylmagnesium bromide was synthesized from *n*-butyl bromide and magnesium in ether (concentration 1.0 mole/l. ether). Sodium *tert*-butoxide was synthesized from *tert*-butanol and sodium.

Dimethylformamide (DMF) and dioxane (DO) were purified as usual and used as polymerization solvents.

Known amounts of *trans*-*p*-nitrocinnamide and a solvent were charged into a flask which was fixed in a thermostatted bath and flushed with nitrogen. After thermal equilibrium of the mixture was reached, the catalyst solution was added with a syringe through a self-sealing rubber cap. In the case of sodium *tert*-butoxide-catalyzed polymerization, the stopper of the reaction flask was removed and a weighed amount of catalyst was added quickly. The reaction was carried out under a nitrogen atmosphere with occasional stirring. After 24 hr the reaction solution was poured into a large amount of ether. The precipitate was collected, washed with ether, and dried. To remove unreacted monomer the product was extracted by ethanol or benzene in a Soxhlet apparatus for 3–5 days.

The reaction conditions and the product yields are shown in Table I. The ethanol-soluble parts of runs 3 and 4 were found to contain unreacted monomer as well as the reaction product. Dimethylformamide was, therefore, more suitable solvent for the reaction than dioxane. The reaction proceeded homogeneously, except when a large amount of sodium *tert*-butoxide was used.

TABLE I

Polymerization of *trans*-*p*-Nitrocinnamide[a]

	Catalyst			Product		
Run no.	Type	Concn., mmole/l.	Solvent	Extract, g	Residue, g	Yield, %
1	n-C_4H_9Li	80	DMF	0.588[b]	Little[b]	
2	t-C_4H_9ONa	104	DMF	0.884[b]	Trace[b]	
3	n-C_4H_9Li	80	DO	0.772[b]	Little[b]	
4	t-C_4H_9ONa	104	DO	0.983[b]	Trace[b]	
5	n-C_4H_9Li	80	DMF	—[c,d]	0.432[c]	43.2
6	n-C_4H_9MgBr	100	DMF	—[c,d]	0.465[c]	46.5

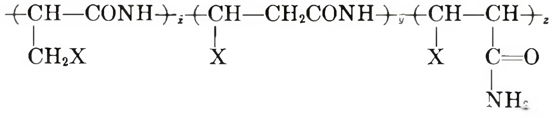
[a] Conditions: $[M]_0$: 0.52 mole/l. (1 g/solvent 10 ml.), polymerization time: 24 hr, polymerization temperature: 90°C.

[b] Extraction by ethanol.

[c] Extraction by benzene.

[d] The reaction product was only slightly extracted by benzene.

If under the present reaction conditions a polymer is formed, it would consist of three kinds of repeating units. The repeating unit A results from the combination of a first



$$\left(\underset{\substack{|\\ CH_2X}}{CH}-CONH\right)_x\left(\underset{\substack{|\\ X}}{CH}-CH_2CONH\right)_y\left(\underset{\substack{|\\ X}}{CH}-\underset{\substack{|\\ C=O\\ |\\ NH_2}}{CH}\right)_z$$

A B C

addition to a carbon atom carrying an amide group of a double bond and a subsequent hydrogen migration. This is what we aimed at. The repeating unit B results from the combination of a first addition to a carbon atom carrying a substituent X of a double bond and a subsequent hydrogen migration. The repeating unit C results from a vinyl

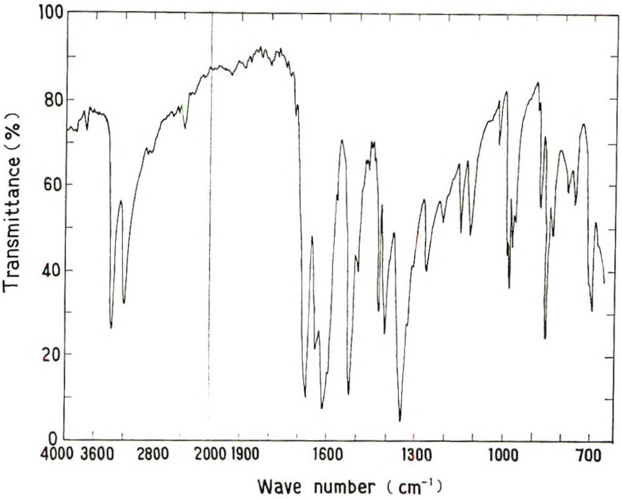


Fig. 1. Infrared spectrum of *trans-p*-nitrocinnamide.

polymerization. Concurrent hydrogen-migration and vinyl polymerizations have been observed.[5]

A comparison of the infrared spectra between *trans-p*-nitrocinnamide and the reaction product was made (Figs. 1–3).

An absorption band at 970 cm^{-1} was present in the monomer, which is due to a *trans* double bond. However, this absorption was very weak in the reaction product. Instead, some new broad absorptions appeared in the 1500–1600 cm^{-1} region in the reaction product, which may be ascribed to a substituted amide group. By analogy with acrylamide polymerization,[6] these experimental facts point to the formation of a polypeptide by the hydrogen-migration mechanism. The polymer formation was also supported by viscosity measurements. Reduced viscosities of dichloroacetic acid solution at 30°C were 0.093 for sample 5 (c = 1.00 g/dl) and 0.097 for sample 6 (c = 1.03 g/dl).

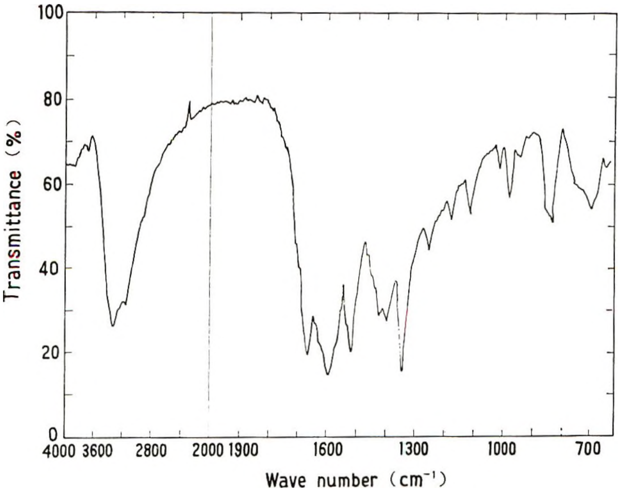


Fig. 2. Infrared spectrum of poly-*trans-p*-nitrocinnamide.

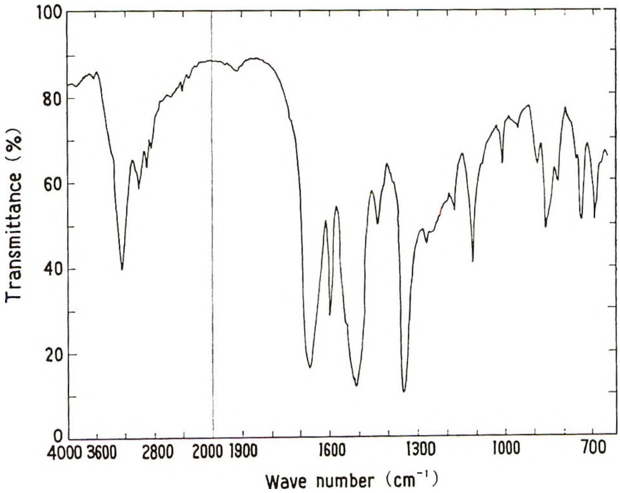


Fig. 3. Infrared spectrum of poly-*p*-nitrophenylalanine.

The polymer was hydrolyzed with 10*N* hydrochloric acid in a sealed tube at 110°C for 24 hr (concentration 10 mg/cc). The hydrolyzate was subjected to paper chromatography on Toyo filter paper No. 51, either phenol–water (4:1 v/v) or *n*-butanol–acetic acid–water (18:2:5:v/v) being used as an eluent. The chromatogram was developed by spraying with a ninhydrin solution and heating. R_f values were determined and compared in Table II.

As is seen in Table II all hydrolyzates were ninhydrin-positive. This confirms that the original reaction product was a polypeptide. If two successive hydrogen-migration polymerizations occur and the repeating unit A is formed, the hydrolyzate should contain *p*-nitrophenylalanine. In this connection, a genuine sample of *p*-nitrophenylalanine was synthesized, and poly-*p*-nitrophenylalanine was prepared by an amine-initiated polymerization of *p*-nitrophenylalanine NCA. In Table II it is seen that with *n*-butanol–acetic acid–water as an eluent, the R_f value of *p*-nitrophenylalanine is 0.53, and that all hydrolyzates give R_f values ranging from 0.52 to 0.57 except for sample 4. These findings indicate that *p*-nitrophenylalanine is present in the hydrolyzates; that is, the original polypeptide contained the α-peptide linkage A. Paper chromatography with phenol–water also confirmed this conclusion. However, the polypeptide obtained here was not a pure poly-*p*-nitrophenylalanine. This is apparent from Figure 1 which is different from the infrared spectrum of poly-*p*-nitrophenylalanine (Fig 3). In addition to *p*-nitrophenylalanine, the hydrolyzates contained several amino acids which are still unidentified. They result partly because of an incomplete hydrolysis of the reaction product and partly because of the presence of the repeating units B and C. The former was evidenced by the fact that a prolonged hydrolysis of sample 5 increased the amount of *p*-nitrophenylalanine (R_f = 0.52) and decreased the others. For the latter to be true the amide nitrogen content in the polymer (structure C) was determined and compared with the total nitrogen content. The experimental results for sample 5 are shown in Table III. Polymerization of *trans*-*p*-nitrocinnamide without hydrogen migration would give a ratio of 0.5, while complete migration (i.e., one migration for each addition) would yield a value zero for long chains. Each act of initiation must lead to the presence of a terminal amide group in the polymer; since we are probably dealing with short chains in the present system, the amide nitrogen/total nitrogen ratio 4.03/11.85 = 0.34 shows that less than two thirds of the repeating units have the structure C.

The presence of the β-peptide unit (B) was observed in polymers of other unsaturated

TABLE II

R_f Values of Amino Acids in the Hydrolyzate of Poly-*trans*-*p*-nitrocinnamide

No.	Original sample	R_f								
		Phenol–water			*n*-Butanol–acetic acid–water					
1	Ethanol-insoluble	0.70(m)	0.26(w)					0.27(w)	0.19(w)	
	part	0.77(w)	0.29(w)					0.28(w)	0.20(w)	
	Ethanol-soluble	0.78(s)	0.16(m)			0.54(m)			0.19(m)	
	part					0.53(s)		0.24(m)		0.15(m)
2	Ethanol-soluble	0.82(w)				0.57(w)			0.18(w)	
	part					0.52(w)		0.29(w)	0.18(w)	
3	Ethanol-insoluble	0.84(s)	0.26(m)				0.40(w)		0.17(w)	0.13(w)
	part								0.17(w)	0.13(w)
	Ethanol-soluble	0.64(m)					0.44(w)		0.18(w)	
	part					0.53(w)		0.28(w)	0.18(m)	
4	Ethanol-soluble		0.26(m)						0.19(m)	
	part								0.19(m)	
5	Benzene-insoluble	0.73(s)	0.53(w)	0.25(m)		0.53(w)		0.27(m)	0.17(s)	
	part	0.75(s)	0.62(w)	0.24(m)		0.52(s)		0.28(w)	0.16(m)[a]	
6	Benzene-insoluble	0.78(s)	0.22(m)			0.59(w)[b]		0.28(m)	0.22(m)	
	part									
	Poly-*p*-nitrophenyl-	0.77(s)	0.28(w)		0.75(s)	0.53(s)			0.18(w)	0.12(w)
	alanine	0.79(s)	0.27(w)		0.78(s)	0.55(s)		0.30(w)	0.20(w)	0.12(w)
	p-Nitrophenylalanine	0.78(s)				0.53(s)				

[a] Hydrolysis was carried out for 48 hr.

[b] This value is slightly larger than others. It may have been caused by the rise of room temperature. *p*-Nitrophenylalanine, which was chromatographed at the same time, gave $R_f = 0.59$.

TABLE III
Nitrogen Analysis of Poly-*trans*-*p*-nitrocinnamide Sample 5

Total nitrogen, %		
Theoretical	Observed	Amide nitrogen, %
14.58[a]	11.85[b]	4.03[c]

[a] Value for the monomer.
[b] Mean value of the data in duplicate.
[c] Mean value of six experimental values.

amides.[4] In the present investigation, however, the presence of B was not strictly confirmed.

To conclude, with basic initiators *trans*-*p*-nitrocinnamide is converted to an oligomer whose reduced viscosity is about 0.09. About one third of the polymer repeating units are linked by a peptide bond, and the rest by carbon-carbon bonding. An α-peptide linkage does exist in the polymer. As *trans*-cinnamide has been reported to give only β-polypeptide,[7] which was confirmed by the present authors as well, an electron-withdrawing *p*-nitro group is necessary to achieve an α-polypeptide formation.

We are very grateful to Mr. K. Suzuoki for the synthesis and supply of *p*-nitrophenylalanine and its polymer, and also to Dr. T. Higashimura for encouragement and discussions.

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Thermal Stability of the Polyesters of Poly(4-vinylphthalic Acid)

It is known that very few polyesters are stable above 380°C.[1] Thermal stability in esters is generally attributed to dipole interaction, molecular symmetry, close packing of linear chains, and strong intermolecular forces. When poly(4-vinylphthalic acid) was crosslinked with certain diamines, the thermal stability was greatly enhanced.[2] This fact gave reason to believe that crosslinking through ester groups might also increase thermal stability. The linear polyesters which were initially formed were soluble in conventional solvents, and it was hoped that they could be used to form fibers and films that could be crosslinked by copolymerization with another vinyl function. The polyesters were prepared and their thermal properties determined by both thermogravimetric (TGA) and differential thermal analysis (DTA).[3]

Although the polyesters could be prepared by several routes to give apparently similar products (infrared and thermal stability analysis), the melt polymerization of the acid or its anhydride with suitable diols was found to be the most satisfactory.

In the general procedure used, equimolar amounts of 4-vinylphthalic acid (prepared by the procedure of LaFerriere[4], and the diol were placed in a reaction vessel with a catalytic amount of hydrochloric acid and enough water to give a solution at 100°C. Then the solution was heated at 130–140°C for approximately 1 hr to give the linear polyester which when heated further at temperatures above 200°C formed an infusible cross-linked polymer. These polymers gave infrared spectra with absorptions attributable to the ester groups at 1730 (s), 1125 (m), 1065 (m) cm^{-1}. No absorption was present at 3000–2800 cm^{-1} due to the acid group. The amount of ester formation was estimated by the determination of the saponification equivalents of the polyesters which are recorded in Table I. The close agreement of the saponification equivalent with the theoretical values and the infrared analysis data indicate that esterification must be extensive.

TABLE I

	Saponification Equivalent		Temp. of degradation, °C
	Calculated	Found	
Poly(vinylphthalic acid)	—	—	340
Ethylene glycol polyester	109.11	108.88	370
Glycerol polyester	123.60	123.65	350 (gradual)
1,4-Butanediol polyester	123.13	120.91	340
1,5-Pentanediol polyester	130.15	130.17	300
Oxydiethanol polyester	131.13	130.93	295
1,10-Decanediol polyester	165.22	165.47	301
Xylylene glycol polyester	147.16	143.61	280

The thermal stabilities of the polyesters were determined both by TGA at a heating rate of 2.5°C/min and DTA to give results which were found to be in close agreement in all cases. As can be seen from Table I, there is some improvement in thermal stability above that shown by poly(vinylphthalic acid). Thus, in some cases the crosslinking does give slightly increased stability, and the lower stability of the polymers obtained from the longer-chain alcohols can be attributed to a breakdown of the chain which usually occurs between 325 and 350°C. The thermal stability data further indicates a trend toward lower stability with increasing chain length of the aliphatic diols.

The decomposition of these compounds as determined by DTA is a typical two-step ester decomposition, the first step occurring between 150 and 225°C and the second at a faster rate above 280°C. While the cause of the lower temperature endotherm is presently open to question, the second is attributed to a cleavage of bonds in the ester group.

Attempts to prepare the corresponding aromatic polyesters by the same methods which were used to prepare their vinyl unsubstituted analogs were, unfortunately, unsuccessful.[5,6] It would be expected that such polymers would have high thermal stability, good solubility,[1] and in addition, the ability to undergo copolymerization.

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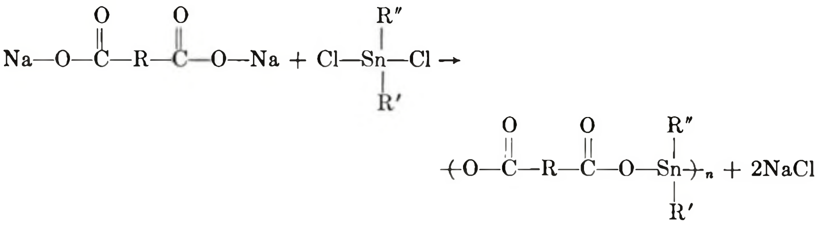
Pyrolysis **in Vacuo** *of Poly(di-***n***-butyltin Terephthalate)*

INTRODUCTION

In two previous publications[1,2] the nonisothermal stability, glass transition, and volatile degradation products of organotin polyesters were discussed. These polymers were prepared by a low-temperature polycondensation reaction reported by Frankel et al.[3] in which the dicarboxylic acid is first neutralized with an inorganic base to phenolphthalein endpoint and then reacted with a solution of dialkyltin dihalide according to eq. (1):



$$\mathrm{Na{-}O{-}\overset{O}{\overset{\|}{C}}{-}R{-}\overset{O}{\overset{\|}{C}}{-}O{-}Na + Cl{-}\underset{R'}{\overset{R''}{Sn}}{-}Cl \rightarrow \left(O{-}\overset{O}{\overset{\|}{C}}{-}R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{R'}{\overset{R''}{Sn}} \right)_n + 2NaCl} \qquad (1)$$

Since organotin esters are sensitive to acids and bases, the neutralization step permitted the preparation of polymers in contrast to an earlier procedure of Andrews, et al.,[4] in which only cyclic or open-chain oligomers with low melting points were obtained.

The object of this paper is to report the results of isothermal pyrolysis studies *in vacuo* of poly(di-*n*-butyltin terephthalate) and to correlate the data with the previous findings.

Experimental

Poly(di-*n*-butyltin terephthalate) was prepared by the method of Frankel, et al.,[3] as already reported in a previous paper.[1] The lack of solubility of this polymer prevented the determination of its intrinsic viscosity, in contrast to the previously reported poly-(di-*n*-butyltin adipate). The polymer has a melting point of 368°C and exhibits a glass transition at 285°C, as determined by a Perkin-Elmer differential scanning calorimeter, Model DSC-1B. Isothermal degradation studies were carried out with a Cahn RG electrobalance in a vacuum of approximately 1×10^{-4} mm of mercury by continuous pumping, with 5–7 mg dried, powdered samples by a method described elsewhere.[5,6]

Results and Discussion

Previous studies[1,2] with poly(di-*n*-butyltin adipate), poly(di-*n*-butyltin fumarate), and poly(di-*n*-butyltin terephthalate) showed that under programmed thermogravimetric conditions these polymers leave residues when thermally degraded in either air or *in vacuo*. On the basis of these weight loss measurements alone, all three organotin polyesters seem to exhibit greater stability in air than *in vacuo*. This difference is especially pronounced in the case of poly(di-*n*-butyltin terephthalate). It was shown by infrared absorption evidence that when poly(di-*n*-butyltin terephthalate) is degraded in air at 350°C, a major initial step in the degradation reaction appears to be the cleavage of the butyl side groups of the tin atoms. In a vacuum, on the other hand, no such preferential cleavage of the butyl groups is observed, and the polyester loses approximately 50% of its original weight between 270 and 350°C.

To study the nature of the degradation process in greater detail in the region of greatest weight loss, isothermal rate studies were carried out in a vacuum between 280 and 340°C. Figures 1–3 illustrate the per cent volatilization as a function of time for poly(di-*n*-butyltin terephthalate). Zero times signify the start of the isothermal heating period which was usually reached within 15 min from the time the preheated furnace was raised around

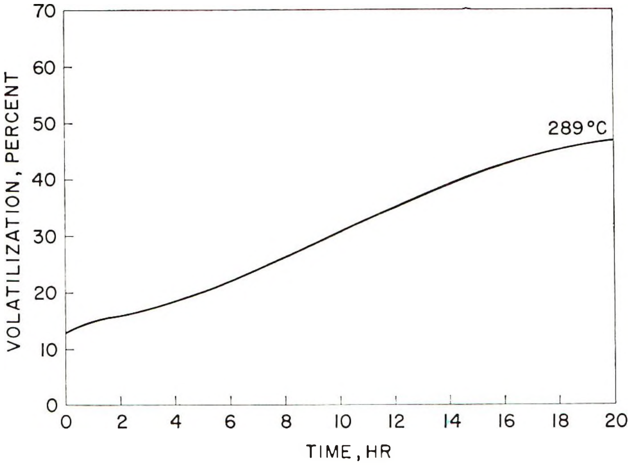


Fig. 1. Isothermal degradation of poly(di-*n*-butyltin terephthalate) *in vacuo* at 289°C.

the sample tube. It is apparent that under isothermal conditions, 12.5–17.4% weight loss occurred during this heating-up period, and hence this initial degradation can not be included in the calculated rate curves. The data also show that the polymer is sensitive to relatively small changes in temperature, inasmuch as at 336°C about 52% of the sample volatilized after only 13 min of isothermal heating, whereas at 289°C approximately 20 hr of isothermal heating was required to volatilize 47% of the material.

The rates of degradation were calculated from the isothermal weight loss curves with an electronic computer. The results are shown on Figures 4–6, in which the rates are plotted against percent volatilization (conversion). The data indicate the appearance of maxima, although these occur at somewhat higher conversions than predicted for purely random scission.[7]

It has been shown in the case of many polymer decompositions that the isothermal rate curves exhibit maxima.[8,9] In the case of purely random decompositions these maxima occur at 26% conversions, whereas decompositions in which the initiation is a

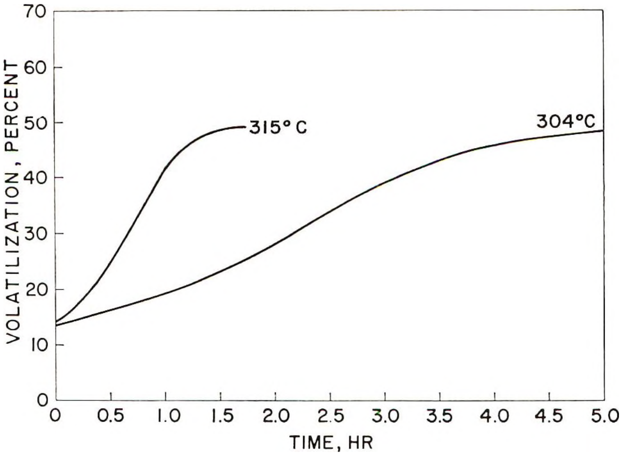


Fig. 2. Isothermal degradation of poly(di-*n*-butyltin terephthalate) *in vacuo* at 304° and 315°C.

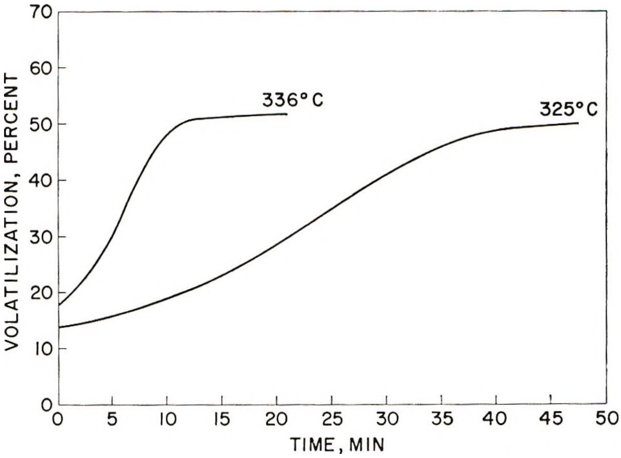


Fig. 3. Isothermal degradation of poly(di-*n*-butyltin terephthalate) *in vacuo* at 325° and 336°C.

nonrandom one show maxima that are shifted to higher conversions. Such is the case in depolymerizations in which the initiation occurs at chain ends and the zip length is moderate, and also in degradations which are influenced by competing hydrolytic processes as with some condensation polymers. The latter mechanism has been shown to be responsible for the production of large quantities of carbon dioxide in the case of polycondensation polymers, under the influence of trace amounts of acidic catalysts and tightly held hydrogen-bonded moisture (which cannot be removed by ordinary drying procedures), since purely random scissions would be expected to yield carbon monoxide and only trace amounts of carbon dioxide.[10,11] In the case of polyesters, hydrolytic competing processes can produce the free acid which upon decarboxylation gives off carbon dioxide, according to the reactions shown in eqs. (2) and (3).

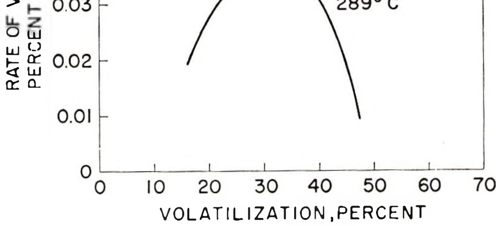


Fig. 4. Rates of isothermal degradation of poly(di-*n*-butyltin terephthalate) *in vacuo* at 289°C.

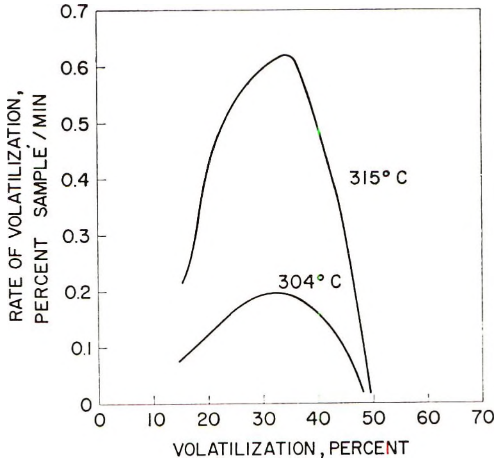
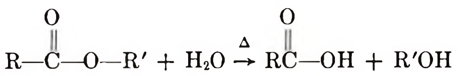
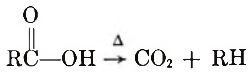


Fig. 5. Rates of isothermal degradation of poly(di-*n*-butyltin terephthalate) *in vacuo* at 304° and 315°C.



$$R{-}\overset{O}{\overset{\|}{C}}{-}O{-}R' + H_2O \xrightarrow{\Delta} R\overset{O}{\overset{\|}{C}}{-}OH + R'OH \tag{2}$$



$$R\overset{O}{\overset{\|}{C}}{-}OH \xrightarrow{\Delta} CO_2 + RH \tag{3}$$

A previous communication[2] showed that the thermal degradation in vacuum of organotin polyesters is accompanied by the evolution of large quantities of carbon dioxide but only trace amounts of carbon monoxide, as indicated by mass spectrometric analysis. This by itself would be indicative of a hydrolytic type cleavage, but the appearance of numerous other small fragments, including butane, among the volatile degradation products suggests the competing effect of random chain scission and the splitting of the

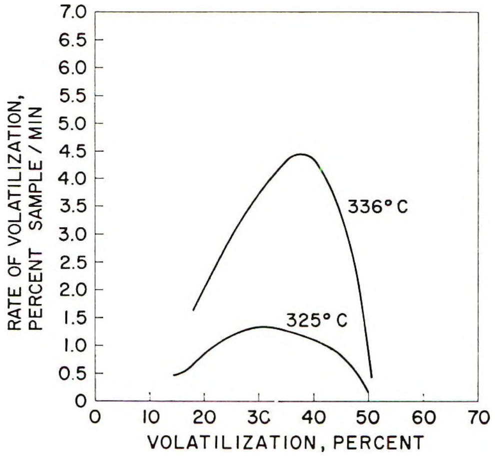


Fig. 6. Rates of isothermal degradation of poly(di-*n*-butyltin terephthalate) *in vacuo* at 325° and 336°C.

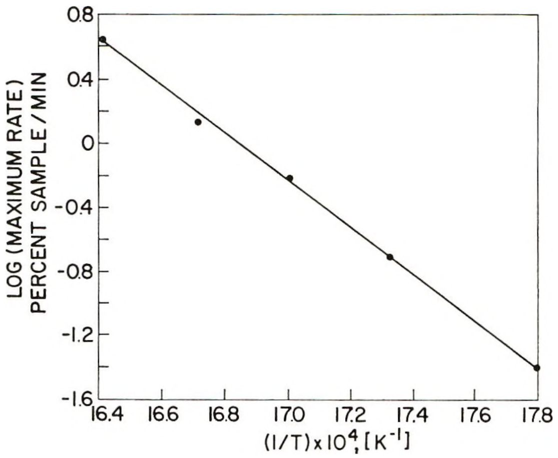
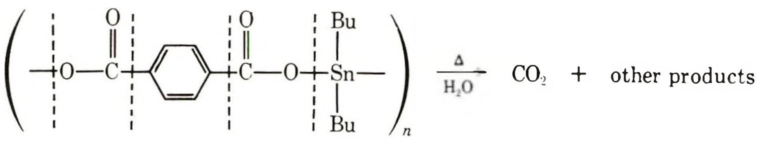


Fig. 7. Arrhenius plot for the isothermal degradation of poly (di-*n*-butyltin terephthalate) *in vacuo*.

butyl side groups. The character of the isothermal rate curves reported in this communication adds further weight to this interpretation, inasmuch as the decomposition rates show maxima that are shifted from the theoretically predicted conversion of 26% for pure random scissions, to approximately 30–35% conversion due to the influence of competing nonrandom processes.

Figures 4–6 indicate that the maximum rates vary only slightly with temperature. Hence the maximum rates were used for the calculation of the overall approximate activation energy of degradation. The Arrhenius type plot (Fig. 7) yields an activation energy of 68 kcal/mole and a frequency factor of 1.1×10^{26} sec^{-1}.

In summary, the available evidence indicates that the vacuum pyrolysis of poly(di-*n*-butyltin terephthalate) in the region of 280–340°C follows a random-type degradation mechanism which, however, is influenced by a competing nonrandom initiation process including the splitting of the butyl side groups and the hydrolytic cleavage of the ester groups. The hydrolytic reaction should occur with the initial cleavage of the Sn–O bonds of the polymer under the influence of trace quantities of acidic catalyst and moisture present in the material [eq. (4)].



$$\left(-O-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_4-\overset{\overset{\displaystyle O}{\|}}{C}-O-\underset{\underset{\displaystyle Bu}{|}}{\overset{\overset{\displaystyle Bu}{|}}{Sn}}- \right)_n \xrightarrow[H_2O]{\Delta} CO_2 + \text{other products} \qquad (4)$$

In addition, the simultaneous random scission of the chain accounts for the numerous smaller volatile fragments reported earlier.[2] The rather high overall activation energy supports this mechanism.

Part of the experimental part of this work was carried out at the IBM Thomas J. Watson Research Center, with the technical assistance of Mr. Alex Taranko.

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Reaction of Ethylaluminum Dichloride with Electron-Donor Compounds in Three-Component Catalysts for Olefin Polymerization

INTRODUCTION

Two theories have been proposed to explain the role of certain electron donors in promoting stereospecific polymerization of propylene by three-component catalysts. Zambelli et al.[1] have shown that the donor promotes a disproportionation of the monoalkylaluminum dihalide:

$$2\ \mathrm{RAlCl_2} + \mathrm{D}: \rightleftharpoons \mathrm{D}:\mathrm{AlCl_3} + \mathrm{R_2AlCl}$$

Initiation of stereospecific polymerization can then be attributed to the presence of diethylaluminum chloride (DEAC), which is known to give active stereospecific catalysts when mixed with a titanium halide.

Coover, on the other hand, postulates formation of a stable complex of the donor compound with ethylaluminum dichloride (EADC).[2] This permits formation of a carbon bridge between aluminum and titanium which is the polymerization-active site, as proposed by Patat and Sinn.[3] In the absence of a donor compound, the alkylaluminum dihalides do not give stereospecific initiators, because the aluminum and titanium are linked through a halogen bridge to the exclusion of an alkyl bridge.

To date there has been no reconciliation of these views, and both theories have been supported by subsequent publications.[4-10]

The infrared absorption spectrum of DEAC has a characteristic band at 538 $\mathrm{cm^{-1}}$ not exhibited by EADC. (Zambelli et al.[4] place this band between 544 and 549 $\mathrm{cm^{-1}}$. On our instrument it consistently appeared between 535 and 540 $\mathrm{cm^{-1}}$.) McConnell et al.[5] suggested the appearance of this band could be used as evidence that the reaction of EADC with an electron donor produces DEAC and, conversely, its absence would suggest DEAC is not a product of the reaction. McConnell and co-workers did not observe a band at 538 $\mathrm{cm^{-1}}$ in mixtures of EADC with hexamethylphosphoric triamide (HPT) and concluded no DEAC was present.

Zambelli et al.[4] criticized the work of McConnell and co-workers, first because their experimental technic did not include precautions to prevent reaction between EADC and the potassium bromide optics used in infrared studies, and second because the absorption band at 538 $\mathrm{cm^{-1}}$ is rather weak and the spectra of donor:$\mathrm{AlCl_3}$ complexes exhibit more intense broad bands in this vicinity. These criticisms seem well taken but do not invalidate the underlying idea that with proper conditions DEAC might be detected in mixtures of EADC and an electron donor by means of the absorption band at 538 $\mathrm{cm^{-1}}$.

The reaction of EADC with triethylamine and HPT was investigated. Heptane-soluble and -insoluble products of the reaction were separated and their infrared absorption spectra taken, with attention to the precautions recommended by Zambelli et al.

EXPERIMENTAL

Polymerization Procedure

Polymerizations were carried out in 200-ml heavy-walled polymer bottles. Diluent (benzene or heptane), catalyst components and a magnetic stirring bar were added to the polymer bottles inside a dry-box under a nitrogen atmosphere. The bottles were capped with a solid Buna-N gasket and a crown cap with a $^1/_8$-in. hole. The closed bottles were immersed in a constant temperature bath maintained at 70°C. Contents of the bottles were agitated by magnetic stirring. The monomer was introduced from a gas manifold by means of $^1/_{16}$-in. stainless steel tubing injected through the Buna-N gasket. Pressure was maintained at 40 psig throughout the test.

At the end of a test, the entire contents of the reactor were poured into a threefold excess of a 50% solution (by volume) of methanol in isopropanol. The polymer was filtered off and washed twice with methanol in a Waring Blendor. Finally the polymer was dried for 17 hr in a vacuum oven at 50°C.

Stereospecificity index, expressed as percentage of polymer insoluble in boiling heptane, in accordance with the convention established by Natta,[6] was determined by extracting 2 g of polymer with boiling heptane for 20 hr in a bituminous extractor.

Melting points were determined by means of a duPont No. 900 differential thermal analyzer at a heating rate of 20°C/min. Samples were heated to 180°C, cooled to room temperature at a uniform rate, then reheated as originally. The endothermal peak noted on the second heating was taken as the melting point.

Infrared Studies

A technic suggested by H. Pobiner of this laboratory, was used for infrared analysis. A polyethylene spacer 0.5 mm in thickness was sealed inside a small envelope of low-density polyethylene 0.025 mm thick. The alkylaluminum solution to be studied was injected into the envelope by means of a hypodermic needle, and the envelope, with the spacer properly positioned, was clamped between potassium bromide optics in a demountable cell. A Perkin-Elmer Model 521 infrared spectrophotometer was used to record spectra.

Analysis for Chlorine and Aluminum

Solutions of alkylaluminum compounds in benzene or heptane were added slowly to 15% aqueous KOH. The pH was adjusted and aluminum was determined gravimetrically by using 8-hydroxyquinoline. Chloride was determined by a standard silver nitrate gravimetric method.

RESULTS AND DISCUSSION

When triethylamine is mixed with ethylaluminum dichloride in heptane, a precipitate forms at once. The precipitate usually comes down as an oil, but this oil will crystallize on standing at room temperature for 8 hr or more or with gentle heating (to 70°C) followed by cooling to 0°C.

The supernatant (heptane-soluble phase) and residue (heptane-insoluble phase) from reaction of EADC with $^1/_2$ Et_3N were separated and analyzed for chlorine and aluminum. The chlorine-to-aluminum ratios were 1.4–1.5:1 for the supernatant and 2.5–2.8:1 for the residue. Zambelli et al.[1] found this ratio to depend on the particular electron donor used, although the Cl/Al ratio in the heptane-soluble phase was always below 2:1, whereas that in the insoluble phase was greater than 2:1.

Although the experimentally determined Cl/Al ratios merely approach the theoretical values of 1:1 for the supernatant and 3:1 for the residue and do not constitute a proof of the presence of DEAC, the results do indicate a constitutional difference between the heptane-soluble and insoluble phases, as predicted by the disproportionation theory of Zambelli, DiPietro and Gatti. On the other hand, if EADC and Et_3N react to form a stable complex which is partitioned between supernatant and residue because of partial solubility in the heptane reaction medium, the Cl/Al ratio in both phases should be the same (i.e., 2:1).

The heptane-soluble fraction of the Et_3N EADC reaction mixture, when combined with $(TiCl_3)_3 \cdot AlCl_3$, will initiate stereospecific polymerization of propylene. The stereospecificity index of the resulting polymer is comparable to that of polyopropylene prepared with the use of DEAC–$(TiCl_3)_3 \cdot AlCl_3$ as catalyst (see Table I). Our results

TABLE I
Comparison of Cocatalysts: DEAC vs. Heptane-Soluble Fraction of Donor–EADC Mixtures[a]

Cocatalyst	Diluent	Polymer, g	Reaction rate, g/g $TiCl_3$/hr	Heptane-insolubles, %	MP, °C (DTA)[b]	η_{inh}[c]
2.38 mmole DEAC	Benzene	23.5	54.7	88.0	154	2.3
	"	23.9	55.6	87.9	155	1.9
EADC + $^1/_2$ Et$_3$N (heptane-soluble)	"	15.9	37.0	89.7	153	2.6
	"	16.7	38.8	89.2	154	2.8
EADC + $^1/_2$ HPT (heptane-soluble)	"	20.3	47.2	87.9	155	1.8
	"	18.6	43.3	87.3	154	1.5
2.38 mmole DEAC	Heptane	21.7	50.5	93.7	156	2.3
	"	24.1	56.1	93.1	156	2.0
EADC + $^1/_2$ Et$_3$N (heptane-soluble)	"	10.8	25.1	94.4	159	2.5
	"	10.9	25.4	94.3	159	2.3
EADC + $^1/_2$ HPT (heptane-soluble)	"	16.1	37.5	95.3	156	1.3
	"	15.8	36.8	94.8	158	1.6

[a] Polymerization of propylene in 100 ml of diluent at 70°C, 40 psig for 2 hr initiated by 277 mg $(TiCl_3)_3 \cdot AlCl_3$ plus cocatalyst.

[b] Crude polymer before extraction with heptane.

[c] Heptane-insoluble fraction in tetralin at 135°C.

agree with the data of Natta and co-workers.[10] McConnell et al., on the other hand, found the heptane-soluble phase of an EADC–HPT reaction mixture gave a much lower stereospecificity index than that observed with catalysts containing DEAC.

The heptane-insoluble residue from reaction of EADC with $^1/_2$ Et$_3$N is soluble in benzene. The benzene solution, mixed with $(TiCl_3)_3 \cdot AlCl_3$, does not initiate stereospecific polymerization of propylene.

The infrared absorption spectrum of the supernatant from reaction of EADC with $^1/_2$ Et$_3$N in heptane shows a band at 538 cm^{-1} (Fig. 1*A*). It seems reasonable to attribute this to DEAC, which exhibits an absorption band in the same place (Fig. 1*E*). Neither EADC (Fig. 1*F*) nor triethylamine (Fig. 1*G*) absorb in this region. Possible interference from a triethylamine:AlCl$_3$ complex is eliminated by carrying out the reaction in heptane, in which the complex has very low solubility. The absorption spectrum of a benzene solution of the heptane-insoluble residue shows a broad absorption band around 500 cm^{-1} (Fig. 1*C*). It is possible this broad band, which Zambelli et al.[4] attribute to the Et$_3$N:AlCl$_3$ complex, would obscure the band at 538 cm^{-1}. By reacting EADC and triethylamine in heptane and separating the two phases before taking infrared spectra, this potential overlap is avoided.

In addition to the band at 538 cm^{-1}, the spectrum of the heptane-soluble phase shows a band at 480 cm^{-1}. This may be due to the complex Et$_3$N:EADC, which Zambelli et al.[4] have shown has a strong band in this region. Zambelli et al.[7] suggested mixtures of EADC with electron donors in benzene will contain donor:EADC complexes as a result of the equilibrium:

$$(\mathrm{AlRCl_2})_2 + 2\ \mathrm{AlRCl_2{:}D} \rightleftharpoons 2\ \mathrm{AlCl_3{:}D} + (\mathrm{AlR_2Cl})_2$$

Although in heptane the equilibrium will be shifted to the right due to precipitation of D:AlCl$_3$, there is still the possibility reaction is less than complete and some Et$_3$N:EADC complex is present.

The reaction of EADC with $^1/_2$ HPT gave results very similar to those observed for the EADC + $^1/_2$ Et$_3$N reaction. The infrared spectrum of the heptane-soluble phase

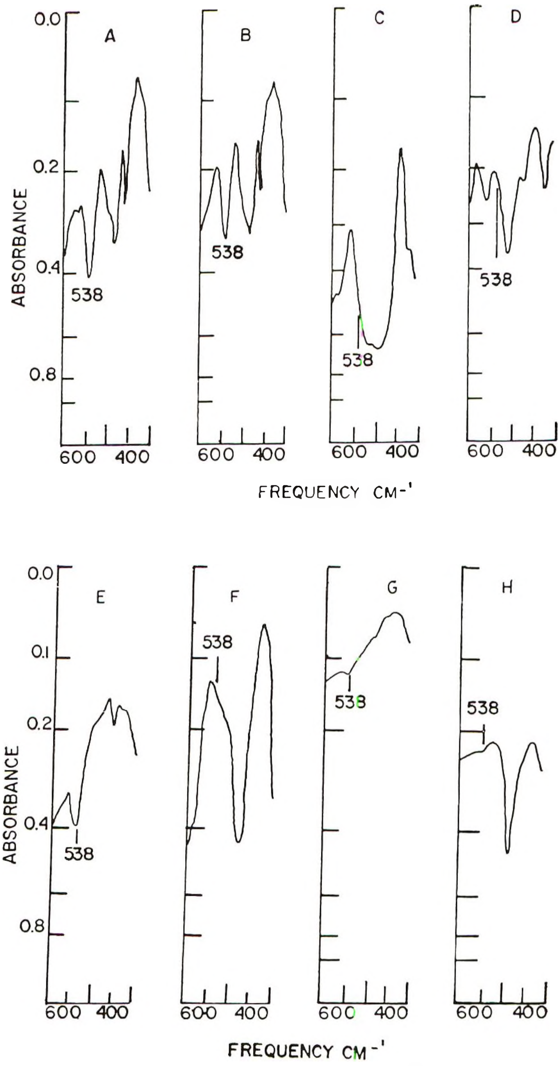

Fig. 1. Infrared absorption spectra of reactants and products of reaction of ethylaluminum dichloride with triethylaluminum and hexamethylphosphoric triamide: (*A*) heptane-soluble phase, 30.4 mmole EADC + 14.5 mmole Et_3N in 80 ml heptane; (*B*) heptane-soluble phase, 30.4 mmole EADC + 15.0 mmole HPT in 80 ml heptane; (*C*) heptane-insoluble phase, prepared from 30.4 mmole EADC + 20.2 mmole Et_3N and dissolved in 20 ml benzene; (*D*) heptane-insoluble phase, prepared from 30.4 mmole EADC + 15.0 mole HPT and dissolved in 20 ml benzene; (*E*) 0.318*M* DEAC in heptane; (*F*) 0.304*M* EADC in heptane; (*G*) 0.289*M* Et_3N in heptane; (*H*) 0.282*M* HPT in heptane.

shows an absorption band at 538 cm^{-1} (Figure 1-B). When combined with $(TiCl_3)_3 \cdot AlCl_3$, the heptane-soluble phase initiates stereospecific polymerization. The stereospecificity index of the polymer is comparable with that of polymer prepared with the use of $DEAC \cdot (TiCl_3)_3 \cdot AlCl_3$ (Table I).

These experiments show that an absorption band at 538 cm^{-1} is exhibited by the heptane-soluble phase from reaction of EADC with $^1/_2$ Et_3N and EADC with $^1/_2$ HPT, supporting the claim of Zambelli, DiPietro, and Gatti[1] that a product of the reaction is diethylalaminum chloride.

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BOOK REVIEWS

Nuclear Magnetic Resonance Spectra and Chemical Structure. By Werner Brügel, Badische Anilin-and Soda-Fabrik AG, Ludwigshafen (Rhine), Germany. Academic, New York, 1967, pp. xvii + 235, 23 × 35 cm (looseleaf). $35.00

The usefulness of nuclear magnetic resonance spectra for the analysis of organic structures is now established beyond question. As a research area, in just 20 years, nuclear magnetic resonance spectroscopy has gone from a happy initial period of pell-mell, helter-skelter discoveries to an era of encyclopedic compilations, no better illustration for which is provided by this bulky collection of chemical shift and coupling parameters (not the spectra themselves) for the compounds corresponding to some 3000 index entries and 520 literature references up to 1967. Polymer chemists should be gratified by the general emphasis given to unsaturated compounds by researchers in the area and particularly the author, himself.

Much of the data reported has been obtained by difficult computer analyses of complex spectra and it can hardly be expected that the results will be of much use in direct identification of compounds. What I mean by this can best be illustrated by an example. Suppose one had an unknown that actually contained vinylacetylene, a substance which at 60 MHz gives a quite complex and completely nonfirst-order proton spectrum. If one had the present tables of shifts and couplings, he would hardly be tempted to use it in conjunction with a digital computer to grind out theoretical spectra of all of the reasonable possibilities to compare with the unknown. The value of this compilation lies more in helping one reason by analogy and in its providing a treasure trove of data for theoretical calculations or correlations for a wide variety of compounds.

It is not certain how much of the data reported is reliable. That any given fit of parameters to a spectrum at a particular frequency is not necessarily unique is now well known. In many cases, the parameters cannot be regarded as established unless spectra are taken at two, or perhaps even more, different frequences. A useful, but often less applicable, method to achieve the same result is to employ different solvents in hope that the chemical shifts but not the couplings will change. Use of such criteria is not mentioned, nor is there any account of how spectra are analyzed. An unknown number of possibly useful coupling constants have been omitted by the ruling that coupling constants reported without the corresponding chemical shifts are not worth compilation. The solvent variabilities of chemical shifts are often so great that one could well wonder if this was a wise decision.

The tables are set up very legibly and clearly, with numbered atoms in the structural formulas for identification of the reported shifts and couplings. The pages are printed on one side only, with plenty of space for future marginal notes. The whole is delivered in an especially awkward looseleaf binder which will not be likely to fit on anyone's library shelf. Despite the physical clumsiness and high cost of the collection, it will be of great value to those interested in the detailed analysis of NMR spectra or the use of such spectra for structure determinations.

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Man-Made Fibers. Science and Technology, Vol. II. H. F. MARK, S. M. ATLAS, and E. CERNIA, Eds. Interscience, New York, 1968. 493 pp. $19.95.

The literature of man-made and synthetic fiber science and technology, particularly in this country, is sparse in relation to the complexity and economic importance of the field and to the amount of research conducted within it. Competitive factors discourage publication not only of the details of processes and equipment but of much scientific information; patents are the principal sources of information on many topics. A book such as *Man-Made Fibers: Science and Technology*, in which a group of authors, chosen worldwide, survey many areas of fiber science and technology, is therefore most welcome.

The book is in three volumes, of which the second is the subject of this review. Volume I deals mainly with general principles; somewhat more than half is devoted to fiber formation processes and the remainder principally to general questions of fiber structure. Volume II discusses the science and technology of individual chemical types of fibers, and Volume III continues the discussion of types and concludes with chapters on finishing, dyeing and fiber testing.

Considering the chapters of Volume II individually, we find first a very brief chapter, "Cellulosic Fibers Made from Cuprammonium," by John L. Hathaway (Beaunit Fibers); the absence of references is regrettable. Next the two chapters "Viscose Rayon Textile Fibers," by H. Peter von Bucker (Chemtex Inc., New York) and "Viscose Rayon Tire Yarn," by W. J. McGarry and M. H. Priest (I.C.I.), between them convey a great deal of information about modern viscose rayons. The latter has an extensive bibliography, while the former lists five books of which the first two are indispensable to anyone who wishes to read deeply into the science and technology of rayon. Two chapters, "Cellulose Acetate Fibers," by Z. A. Rogovin and Yu. A. Kostrov (U.S.S.R.), and "Fibers of Cellulose Triacetate," by K. C. Laughlin (University of California, Davis), deal somewhat less thoroughly with fibers from cellulose secondary acetate and triacetate. There follows a long chapter by H. Krassig (Chemiefaster Lenzing, A.G., Austria), "Characterization of Cellulose Fibers," which returns to the subject of fiber structure treated in the latter part of Volume I in a discussion of ways of characterizing regenerated cellulose fibers by x-ray diffraction supplemented by other techniques and of the relationships of structural parameters to fiber properties for the various types of rayons. This chapter has a very extensive bibliography. These chapters on the cellulosic fibers comprise roughly two-fifths of the volume.

The aliphatic polyamide fibers are discussed in three chapters: "Nylon 66," by H. Hopfe Swiss Federal Institute of Technology, Zurich), "Nylon 6," by W. Sbrolli (Bombrini Parodi-Delfino, Rome), and "Higher Nylons," by J. Chambion (Rhodiaceta, Lyon). Taken together, these chapters constitute a quite satisfactory introductory treatment of the industrial chemistry, fiber preparation technology, and fiber properties of the major and minor nylons. They are all documented with adequate bibliographies.

A final group of three chapters deals with polymers and fibers produced in relatively recent programs of systematic research and, with the exception of Du Pont's Nomex high temperature fiber, not in commercial production. "Synthetic Polypeptides," by D. G. H. Ballard (I.C.I.) summarizes interestingly the polymerization and the steric properties of polypeptides formed from naturally occurring amino acids. Very few of these polymers have been spun into fibers even experimentally, as the costs are prohibitive; the fibers which have been spun are more or less silklike. "Fiber-Forming Aromatic Polyamides," by W. B. Black and J. Preston (Chemstrand Research Center) and "Wholly Aromatic and Aliphatic-Aromatic Polyimides," by Preston and Black, discuss research directed toward synthetic fibers having good thermal stability and good mechanical properties at high temperatures, a large part of which has been funded by the U.S. Air Force with the needs of supersonic aircraft and of space technology in view. This work is very interestingly and competently described and well documented.

This book has some faults. There is the inevitable lack of unity of an edited compendium; the individual chapters differ widely among themselves in approach, depth, critical spirit and thoroughness, and a few are not well documented. Some of those written by authors to whom English is not native would have been much improved by more thorough editing for style, idiom, and choice of words. There does not appear to be, in any of the three volumes, a chapter on poly(ethylene terephthalate) fiber technology. (The reader wishing to survey this field will find a good treatment in *Polyesters*, Vol. I, by I. Goodman, American Elsevier, 1965). But despite these faults, the book has much value. As the foreword states, the last book in English to treat this subject matter comprehensively was *Fibers from Synthetic Polymers*, edited by Rowland Hill, which appeared in 1953. While the increase of knowledge of fiber science and the development of fiber technology since 1953 are not uniformly reflected in the present book, there is a great deal of information in it that is new since that time. The book certainly belongs in the libraries of colleges and universities where chemistry and chemical engineering are emphasized, and of companies having any basis for interest in man-made fiber technology. Many individual chemists will want one or more volumes for their private libraries.

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Reagents for Organic Synthesis. L. F. FIESER and M. FIESER. Wiley, New York, 1967. ix + 1457 pp. $27.50.

This book is in the nature of an encyclopedia or handbook, strongly oriented toward practical use. For each of the hundreds of reagents included, are given sources of supply, methods of preparation, and one or more examples of its use, together with critical comments and references. Methods of handling difficult substances appear throughout the book, often with detailed descriptions or illustrations of special apparatus. There is a vast amount of information in the book, at an extremely low cost per page; much of it is information difficult to find, or even unavailable, elsewhere.

The entries vary from one to two lines to several pages. They are arranged alphabetically, sometimes under the name of the reagent (e.g., silver oxide), sometimes the name of a reaction (Birch reduction), and occasionally under the name of a non-isolable intermediate (diimide). This system has some disadvantages, for it is not always obvious where to look. The reagent *N*-methyl-*N*-nitrosotoluenesulfonamide, for example, cannot be located in either the text or the index under that name, although the commercial code name "Diazald" is indexed; the substance is actually discussed under the heading "Diazomethane." The Fiesers' usual special concern with nomenclature is not as helpful as it might be, for the book contains many inconsistencies to trap the searcher. An entry under "Gold chloride" actually deals with chlorauric acid (under which it is not listed), but the analogous iridium reagent appears under "Chloroiridic acid," for example. There is also the occasional nomenclatural horror, such as "sodium 2-nitropropanenitronate" (p. 1101) for the salt of 2-nitropropane.

Much of the difficulty of finding what one is after is mitigated by the several different types of index. In addition to a subject index, there is an "apparatus" index, a "suppliers" index that includes addresses, an "author" index, and a "type of reaction" index. This last enables one to find the names of all the various reagents that might be used to bring about a given reaction; each one can then be consulted in turn for the maximum amount of information. Even so, it is not completely reliable, for the index heading "polymerization" does not include azoisobutyronitrile, although that reagent is discussed in the text.

The principal criticism that can be raised is that some of the references are dreadfully out of date, in some cases twenty years or more. This comes from a heavy reliance on *Organic Reactions* and *Organic Syntheses* as the last word, without apparent concern as to vintage. The user should definitely not expect the Fiesers' book to give the latest improvements on an old reaction, although it nevertheless covers many recently introduced reagents, such as the Simmons-Smith reagent for cyclopropanes, the various alkoxyaluminum hydrides, etc.

There are a few technical errors, such as the characterization of the removal of hydrogen sulfide from a thiourea by mercuric oxide as an oxidation (p. 231) and the confusion of the pyrazole ring with that of imidazole (p. 1215), but the number is very small for a work of this size. The book is fun to browse in, and that is an excellent way to use it. There can be hardly a chemist who would not learn a great deal from it. It is a book for personal ownership; the library copies will be greatly overworked.

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Macromolecular Reviews. Volume II. A. Peterlin, M. Goodman, S. Okamura, B. H. Zimm, and H. F. Mark, Eds., Interscience, New York, N. Y., 1967. pp. ix + 295. Price $13.50

The second volume of this series consists of four reviews, the first of which, *The Technique of Neutron Scattering and Its Application to Polymers*, by G. J. Stafford and A. W. Naumann (33 pp., 34 references) describes the relatively new spectroscopic technique of neutron inelastic scattering. The authors review the fact that neutron scattering in a sample is dependent upon molecular vibrations and that the energy of neutrons can be selected to permit characteristics of lattice or chain vibrations in a polymer to be readily observed. The theory and instrumentation of the process are described as well as applications to a number of common polymers.

The second review, *Syndiotactic Polypropylene*, by E. A. Youngman and J. Boor, Jr., and the fourth review, *The Nature of the Active Site in the Ziegler-Type Catalyst*, by J. Boor, Jr., overlap and perhaps could have been made part of the same chapter. The author states in the latter review that his objective has been to be both selective and speculative. These criteria are in general very well met, although with 266 references there are possibly not a vast number of significant papers which have been overlooked. The Boor chapter (154 pages) covers the most ground, and the author is both critical and thoughtful in firmly stating his case for such ideas as chain growth at the transition metal–carbon bond and for a propagation process proceeding by a *cis*- four-center insertion rather than coordination followed by rearrangement. To some extent Boor uses a chronological approach, and although this makes a good story, it often leads to somewhat lengthy discussions of earlier ideas which have been shown to be wrong by relatively simple experiments.

The third review by Maurice Morton and L. J. Fettes is entitled, *Homogeneous Anionic Polymerization of Unsaturated Monomers* (42 pp. 347 references). The authors do not review mechanisms of anionic polymerization but instead they have sought "to assemble all available experimental data on the living type of anionic polymerization. . . ." The review contains extensive tables of homopolymers, block and graft copolymers, branched polymers, and functional endgroup polymers culled from the large number of references. The reliability of the various syntheses is not critically discussed, but the chapter is undoubtedly an extremely useful source of information concerning the syntheses of unusual polymer types only recently available by the use of anionic initiators.

Volume II is a useful addition to the library of polymer chemists.

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Environmental Effects on Polymeric Materials. Volume II: Materials. D. V. Rosato and R. T. Schwartz, Eds., Interscience, New York, 1968. pp. 1002 × xvi. $42.00.

This second volume summarizes the damaging effects of environmental conditions on the various types of important materials.

A chapter on fibers by J. H. Ross discusses in great detail and with the aid of many illustrations and tables, from simple webbings and knittings to parachutes and heavy nylon ropes, the influence of heat, radiation, and various chemicals on the strength and flex life of the most important fibers. The next chapter by M. B. Hays and C. A. Cassola contains very interesting information on flight clothing and sea survival equipment. Entirely different materials—solid lubricants—are discussed in a chapter by M. J. Devine with emphasis on the problem of high temperature-high pressure lubrication. Coatings are treated in a very carefully planned and excellently written chapter by P. A. DiMattia. It is followed by an equally attractive review of the response of elastomers to various environmental conditions. The two following chapters on *Reinforced Plastics* and on *Other Materials* are, to a certain extent, the core of the book and are a remarkable presentation of these complex subjects written by a group of particularly eminent experts, namely A. G. H. Dietz, H. S. Schwartz, D. V. Rosato, and F. J. Riel. A brief but very informative Summary Review concludes the book which is a most welcome addition to the literature and will be a fountain of information for all experts who are interested in the field.

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ERRATA

Factors Controlling Particle Surface Area and Rate of Polymerization in the Emulsion Polymerization of Vinyl Acetate

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(article in *Journal of Polymer Science A-1*, **6**, 2265–2280, 1968)

Page 2266, third line from the bottom: 12 in. should be 12 ft.
Page 2268, column 6, last line: 11.3 should read 1.13.
Page 2276, Table II, heading to column 3: 0.1 should read 0.1*N*.

Method for Computing the Specific Rate of Hydrolysis of Glucosidic Bonds in Some Trisaccharides

(article in *Journal of Polymer Science A-1*, **6**, 2415–2417, 1968)

By ALEXANDER MELLER

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Figures 1 and 2 have been transposed. The caption to Figure 2 appears under Figure 1. The caption to Figure 1 should read:

Kinetic reaction scheme of hydrolysis of isomaltotriitol.