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Intramolecular Hydride Shift Polymerization by Cationic Mechanism. IV. Cationic Isomerization Polymerization of Vinylcyclohexane

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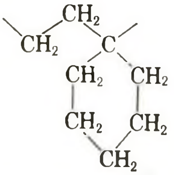
Synopsis

The cationic polymerization of vinylcyclohexane was investigated with the use of $AlCl_3$ catalyst at temperatures ranging from −144 to +7°C. The structure of the polymer was elucidated by NMR and infrared spectroscopy. These studies indicate that cationically synthesized polyvinylcyclohexane contains predominantly repeat units of the type:

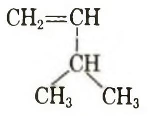


which suggests hydride shift isomerization polymerization.

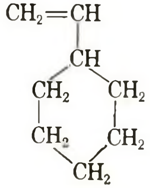
I. INTRODUCTION

The polymerization of vinylcyclohexane with a variety of catalysts has been reported, and the structure of the respective products was also investigated in some detail. Thus, Russian authors[1] mentioned the thermal, probably free radical, polymerization of vinylcyclohexane in 1939. Natta et al.[2] described the polymerization of this monomer with metal alkyl complex catalyst and investigated the structure of the product. According to the Italian group, this Ziegler-Natta type polyvinylcyclohexane is a crystalline, isotactic material having a fourfold helix with a repeat distance of 6.5 A. These workers also obtained polyvinylcyclohexane by hydrogenating polystyrene. These results imply a conventional 1,2 head-to-tail enchainment in the polymer backbone. Stereoregular polymerization of vinylcyclohexane with the use of Ziegler-Natta catalyst was studied by Campbell[3] and by Topchiev[4] who obtained crystalline polymers using metal oxide catalysts. Recent patents to the Eastman Corp. mentioned polymers obtained by three-component catalyst systems.[5] The cationic polymerization of vinylcyclohexane was carried out by Ketley and Ehrig,[6] who used aluminum halide catalysts and low temperature polymerization technique.

Vinylcyclohexane (II) can be regarded as a derivative of 3-methylbutene-1 (I) in which two methyl hydrogens of the latter are substituted by a three-membered methylene bridge:

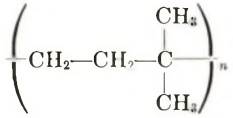


I



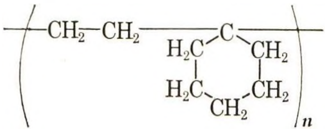
II

It was of interest to investigate the possibility of intramolecular hydride shift polymerization with vinylcyclohexane, a reaction which proceeds readily with 3-methylbutene-1. When 3-methylbutene-1 is polymerized with strong Lewis acid initiators, the initially formed secondary carbonium ion, $CH_2—CH^+—CH(CH_3)_2$, rearranges to the more stable tertiary carbonium ion, $CH_2—CH_2—{}^+C(CH_3)_2$, before propagation occurs, so that the final product consists of an α,α'-dimethylpropane repeat structure, i.e.,



$$\left(-CH_2—CH_2—\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}— \right)_n$$

Thus, it was postulated that vinylcyclohexane might undergo an identical reaction path and give a polymer having the repeat unit:



This report describes experimental work and composition research which seem to indicate that this concept is correct and that under cationic conditions, a polymer having this repeat unit is obtained.

II. EXPERIMENTAL

Materials

Vinylcyclohexane monomer was purchased from K&K Laboratories. The material was distilled before use. Gas chromatographic analysis indicated 99.9% purity and the presence of four trace impurities. The source and purity of aluminum chloride, methyl chloride, and ethyl chloride, together with general material handling technique was reported earlier.[7]

Cationic Polymerizations

These runs were carried out under nitrogen atmosphere in a stainless steel dry box.[8] Average moisture level during experimentation was 20–40 ppm. Polymerizations were carried out at −144, −133, −100, −40, and +7°C. In these experiments, the monomer was mixed with the ethyl chloride solvent, thermoequilibrated by stirring at the selected temperature level, and initiated by having the precooled catalyst solution added dropwise. The catalyst solution was $AlCl_3$ dissolved in ethyl chloride. Polymerization started soon after catalyst introduction and could be observed by haziness developing in the reactor. The reaction was terminated by introducing precooled methanol or *n*-propanol at temperatures below −100°C. The unreacted gases were evaporated, the product was filtered, washed with methanol, and dried *in vacuo* at 50°C.

Ziegler Polymerization

A glass reactor was charged with 400 ml. *n*-heptane, 25 g. vinylcyclohexane, and 1.5 mmole $AlEt_3$ at room temperature. Pretreated catalyst was added from a dropping funnel. The catalyst was prepared by mixing 2 ml. of $AlEt_3$ ($1M$) and 4 ml. $TiCl_4$ ($1M$) in 50 ml. *n*-heptane solution and aged by stirring for 30 min. at 80°C. The reaction mixture was stirred for 50 min. at 60°C. and then for an additional 90 min. at 85°C. Polymerization was terminated with methanol, the product boiled with methanol, washed with methanol and acetone, and dried *in vacuo* at 60°C.

Analytical Techniques

Infrared. Spectra were obtained with a PE 421 infrared spectrophotometer. The samples were in the form of KBr disks, as films cast upon KBr plates from carbon tetrachloride solution, or in carbon tetrachloride solution. Scale expansion was used when necessary for peaks of very low intensity. The spectrum obtained for any one polymer was the same whichever of the three sampling techniques was used, suggesting that the spectral changes between different polymers were not related to crystallinity.

NMR. Spectra were obtained of hexachlorobutadiene solutions at 150°C., with a Varian A60 instrument. Hexamethyldisiloxane was used as internal standard.

X-Ray. Diffraction patterns were obtained on powdery polymer samples with the use of a flat camera with $K\alpha$ radiation and a sample-to-specimen distance of 5 cm.

III. RESULTS AND DISCUSSION

Table 1 compiles some pertinent data and physical properties of the polymers. All the products were white powders. Polymers prepared at −100°C. and below were soluble in toluene, benzene, and carbon disulfide, whereas the higher temperature samples were partially insoluble. They were fractionated by refluxing in benzene, filtering, and reprecipitating with methanol for molecular weight determination.

Product molecular weights were very low (2000–6500) and, as expected for typical cationic systems, they increased with decreasing temperatures. Transparent films prepared by casting technique were extremely weak and brittle and the material did not exhibit fiber forming properties.

TABLE I
Experimental Data and Physical Properties of Polyvinylcyclohexanes

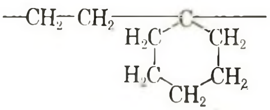
Catalyst	$AlCl_3$	$AlCl_3$	$AlCl_3$	$AlCl_3$	$AlCl_3$	Ziegler
Temp., °C.	−144	−133	−100	−40	+7	60–85
Conversion, %	5.7	1.9	8.4	82.4	77.0	13.6
Amt. of catalyst added in moles	0.00238	0.00925	0.00185	0.00094	0.00132	Complex
Amt. of monomer used, moles	0.0635	0.091	0.091	0.0635	0.0525	.227
Monomer conc., mole/l	4.50	2.27	2.27	4.50	4.45	0.473
Moles monomer/moles catalyst	26.7	9.85	49.2	67.7	39.8	—
Softening range, °C.	—	69–78	112–116	—	—	>200
Benzene insoluble fraction, %	0	0	0	2.6	3.8	—
Molecular weight (osmometry)	—	—	6548	5013	2273	(1.05[a])

[a] Inherent viscosity determined in decalin at 0.453 g./l. at 135°C.

Structure Analysis

Powdery samples prepared at −133 and −100°C. were analyzed by x-ray spectroscopy. Diffraction patterns showed only one measurable spacing at about 5.2 A., indicating a largely amorphous hydrocarbon polymer.

The nuclear magnetic resonance and infrared spectra of polyvinylcyclohexanes synthesized with Ziegler type catalyst and cationic catalyst were compared and examined. Figures 1 and 2 show the NMR spectra of these materials. The spectrum of the cationic polymer prepared at −144°C. shows two fairly well resolved peaks at 1.35 and 1.15 ppm, respectively. The spectrum of cationic polyvinylcyclohexane (Fig. 1) was compared to the NMR spectrum of 1,1-dimethylcyclohexane[9] and on the basis of this comparison, the peak at 1.35 ppm was assigned to methylene protons in the backbone. Integration of the areas under the peaks gave an area ratio of 4:10 indicating four methylene protons in the chain and 10 methylene protons in the ring:



In comparison, the NMR spectrum of Ziegler type polyvinylcyclohexane (Fig. 2). shows an unresolved complex peak at 1.70 ppm and an unsymmetrical sharper peak at 1.30 ppm. These bands are poorly resolved and

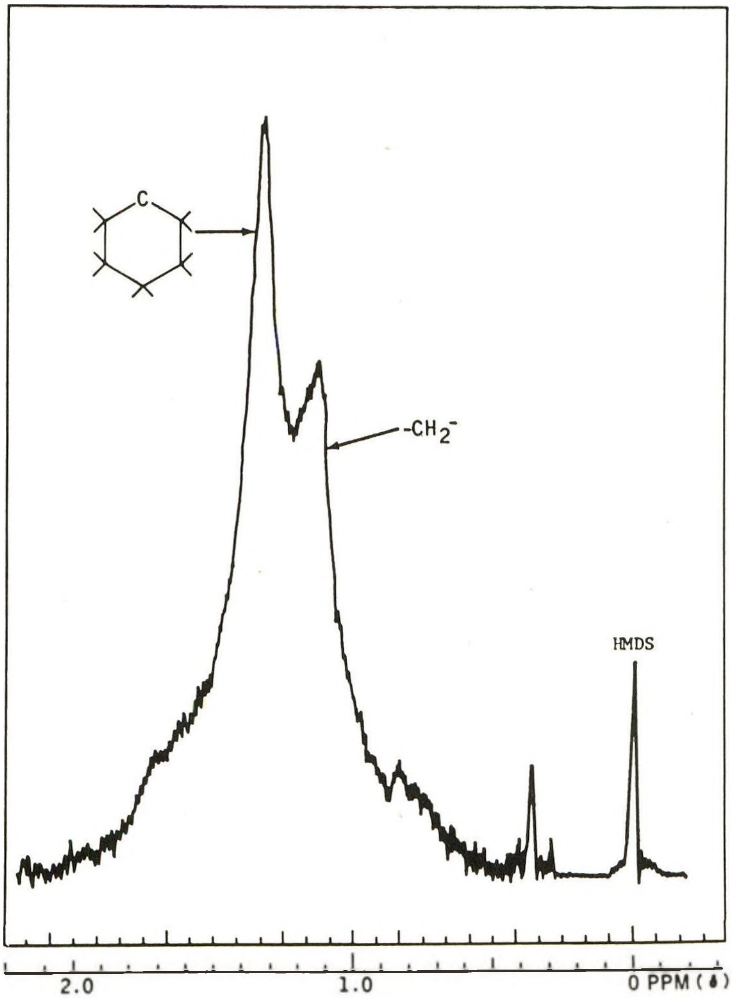
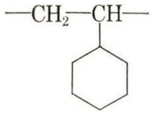


Fig. 1. NMR spectrum of cationic polyvinylcyclohexane. (HMDS at reduced amplitude setting).

area measurements could not be carried out. However, a comparison of this scan with the spectrum of isopropylcyclohexane[9] shows great similarities, indicating a conventional head-to-tail 1,2-type enchainment for the Ziegler polymer:



$$\text{—CH}_2\text{—}\underset{\text{C}_6\text{H}_{11}}{\text{CH}}\text{—}$$

A significant difference between the spectra of Ziegler and cationic polymers is the large downfield shift of the left-hand peak in the former, probably due to the equatorial ring protons.

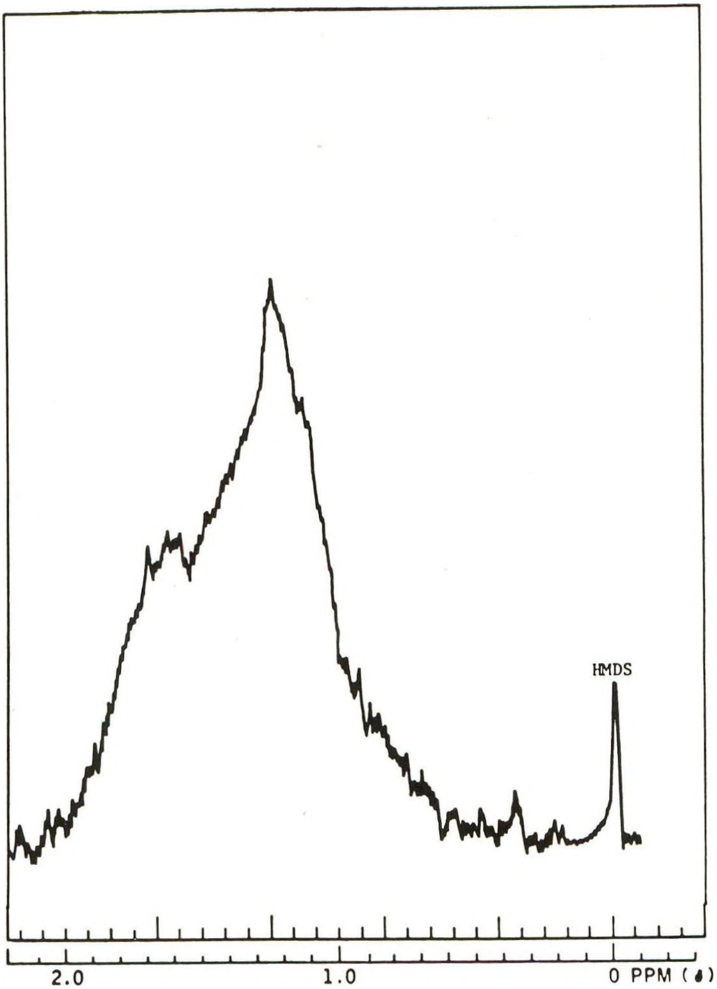


Fig. 2. NMR spectrum of Ziegler-Natta polyvinylcyclohexane. (HMDS at reduced amplitude setting).

Figures 3 and 4 show the infrared spectra of cationic and Ziegler-type polyvinylcyclohexanes, respectively. The spectrum of the Ziegler-catalyzed polymer resembles closely that of isopropylcyclohexane, again suggesting a conventional 1,2-type enchainment. The medium intensity band at 890 cm.$^{-1}$ in isopropylcyclohexane appears as a doublet at 883 and 891 cm.$^{-1}$ in the polymer. This doublet is present whether the sample is in the form of KBr disk or as a solution, which makes it unlikely that it is due to crystallinity.

The spectrum of a cationic polymer prepared at −130°C. is very different from that of the Ziegler polymer, and indicates 1,3-type enchainment. Two new bands of medium intensity of particular importance are those at 740 and 848 cm.$^{-1}$. Absorption bands appearing between 720 and 750

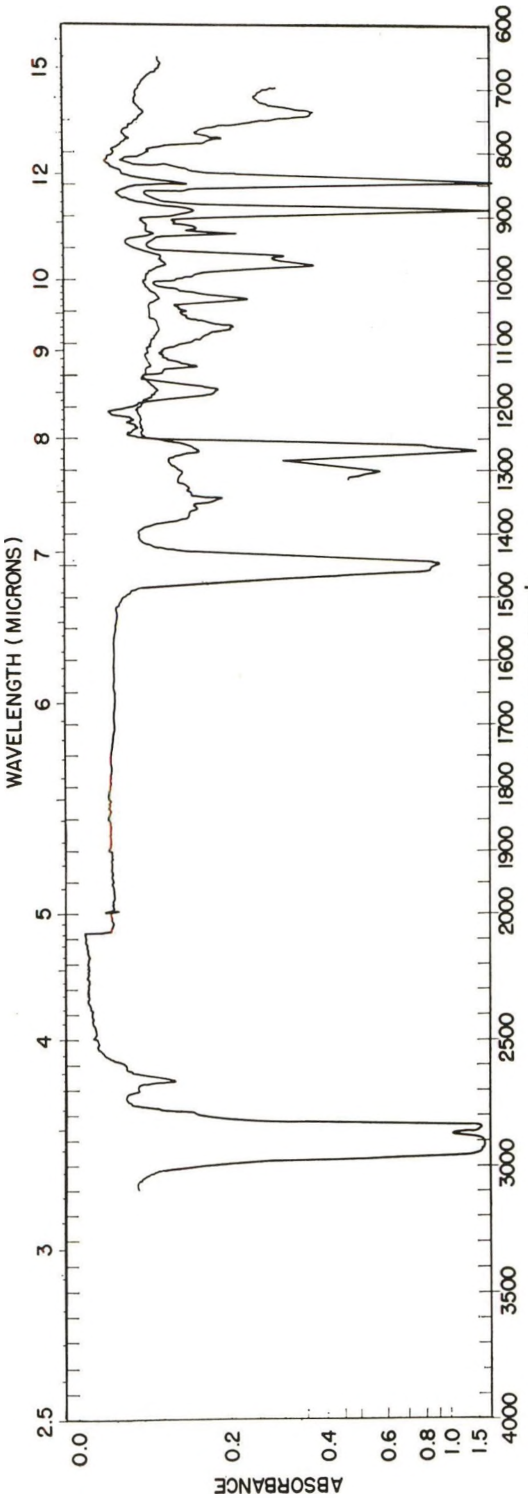


Fig. 3. Infrared spectrum of cationic polyvinylcyclohexane.

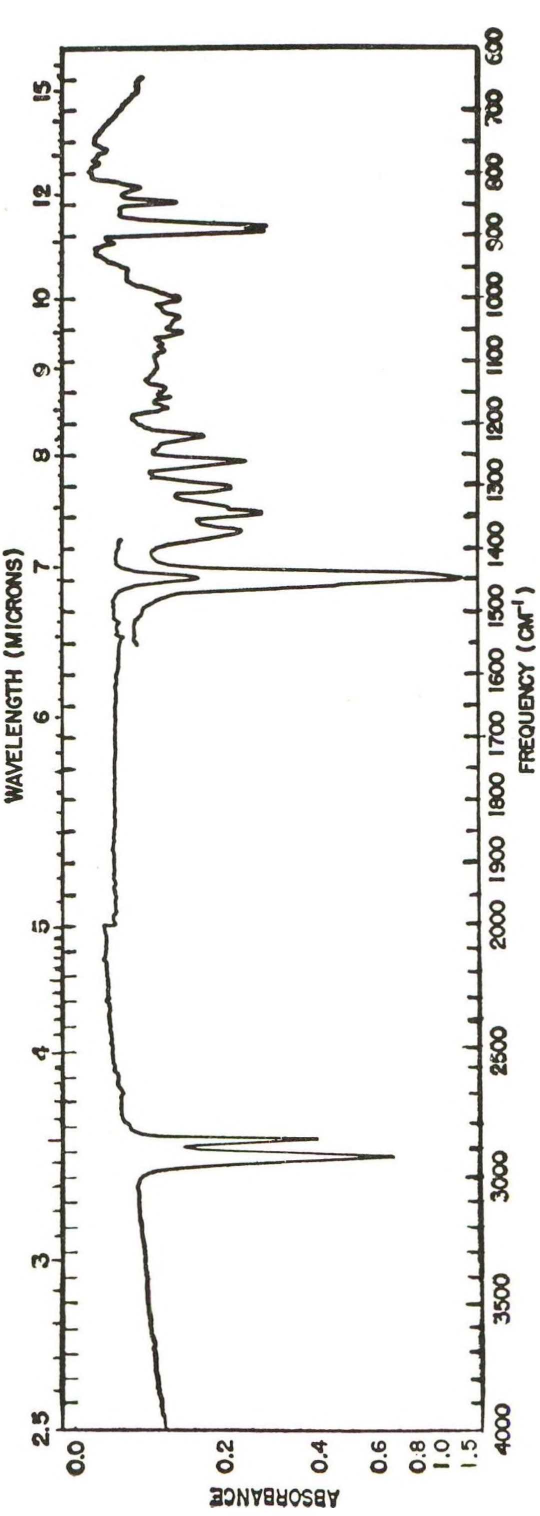


Fig. 4. Infrared spectrum of Ziegler-Natta polyvinylcyclohexane.

cm.$^{-1}$ are usually to be associated with a number of adjacent methylene units. A peak at 752 cm.$^{-1}$ is present in the spectrum of cationically polymerized 3-methylbutene-1,[10] and near 750 cm.$^{-1}$ in poly-1,1-dimethylcyclopropane[11] and in hydrogenated poly-2,3-dimethylbutadiene-1,3.[12,13] In each case, the band is assigned to the CH_2—CH_2 unit that is present in each of these polymers. Although this band in polyvinylcyclohexane is at a slightly lower frequency (740 cm.$^{-1}$), it is certainly still to be associated with this same unit. It is not present in the Ziegler polymer, nor in various substituted cyclohexanes, and its presence in the cationic polymer can only lead to the conclusion that the —CH_2—CH_2— unit is present in the backbone chain.

The second new medium intensity band appears at 848 cm.$^{-1}$. Although a weak band appears at 845 cm.$^{-1}$ in the Ziegler polymer, the 848 cm.$^{-1}$ peak is the strongest in this region of the cationic spectrum and is probably associated with the presence of a quaternary carbon atom. Fairly intense bands are found between 845 and 848 cm.$^{-1}$ in the spectrum of 3,5-spirononane and also in 1,1-dimethylcyclohexane and in 1-methyl-1-ethylcyclohexane, all of which contain a quaternary carbon atom that is also part of a cyclic system. Other new bands present in the cationic polymer that also suggest the presence of a quaternary carbon atom are those at 927 and 1175 cm.$^{-1}$.[14] The absorption band at 890 cm.$^{-1}$ confirms the retention of the cyclohexane ring, for, besides being present in the spectrum of the Ziegler polymer, though as a doublet, it is also present in the spectrum of a large number of substituted cyclohexanes, and appears characteristic of such systems. New peaks with no specific assignment appear at 962, 977, 1030 and 1270 cm.$^{-1}$, the latter also appearing in the spectrum of 3,5-spirononane. The presence of these bands, coupled with the absence of the 1000 and 1220 cm.$^{-1}$ bands that are shown by the Ziegler polymer suggests that the cationic polymer is predominantly if not entirely 1,3 in structure.

Thus, infrared spectroscopic analysis fully corroborates our conclusions derived on the basis of NMR spectra, i.e., the cationic polymerization of vinylcyclohexane at −130°C. proceeds predominantly by a hydride shift isomerization polymerization.

The spectra of cationic polymers prepared at −100, −40, and +7°C. resemble generally those of the polymers prepared at −130°C., though there are two important differences. The first is that the relative intensity of the shoulder at 1470 cm.$^{-1}$ and the bands at 1270 and 848 cm.$^{-1}$ are reduced by 10–20% in the higher temperature samples. This is probably a molecular weight effect, though it could be due to the presence of a second component appearing at these higher temperatures.

The second difference is the appearance of a new band at 908 cm.$^{-1}$ which, in the −40°C. polymer, is of equal intensity to the peak at 890 cm.$^{-1}$. At the same time, weaker absorption bands also appear at 992 and 1636 cm.$^{-1}$, again showing maximum intensity in the polymer prepared at −40°C. The assignment for these bands is not immediately obvious, though they are usually assigned to the vinyl group.

The authors are grateful to Dr. A. W. Langer for the preparation of Ziegler-type polyvinylcyclohexane.

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Résumé

On a étudié la polymérisation cationique du vinylcyclohexane avec $AlCl_3$ comme catalyseur à une température de −144 à +7°C. On a déterminé la structure de ce polymère par R.M.N. et spectroscopie infrarouge. Ces études indiquent que le polyvinylcyclohexane synthétisé cationiquement contient surtout des unités ce qui suggère une polymérisation isomérisante avec glissement d'hydrogène.

Zusammenfassung

Die kationische Polymerisation von Vinylcyclohexan wurde mit $AlCl_3$ als Katalysator im Temperaturbereich von −144 bis +7°C untersucht. Zur Klärung der Struktur des Polymeren wurden NMR- und infrarotspektroskopische Messungen ausgeführt. Diese Untersuchungen zeigen, dass kationisch gebildetes Polyvinylcyclohexan vorwiegend Bausteine enthält, was für eine Polymerisation unter Hydridverschiebungsisomerisierung spricht.

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Rubber Elasticity: Thermodynamic Properties of Deformed Networks*

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Synopsis

Some recent measurements on internal pressure P_i of two elastomers, a silicone rubber and an ethylene–propylene copolymer, at various elongation ratios λ are reported. Results so far obtained show that P_i varies with λ; this behavior is discussed in the light of recent theories of rubber elasticity.

INTRODUCTION

Recent theoretical work[1,2] on rubber elasticity has renewed special interest on thermoelasticity measurements, that is, on quantities like $(\partial f/\partial T)_{p,l}$ and $(\partial f/\partial T)_{v,l}$, where f is the stress of an elongated network, T is the temperature, p the pressure, v the volume, and l the actual length of the sample.

Whereas $(\partial f/\partial T)_{p,l}$ is easily derived from rather simple experiments, the derivative at constant volume is very difficult to measure; a new method by which it is possible to measure $(\partial f/\partial T)_{v,l}$ directly has been proposed only very recently.[3,4]

This method is based essentially on the use of an increasing hydrostatic pressure to compensate the thermal expansion of the rubber during the stress–temperature measurements.

To be able to keep constant the volume of the rubber along the range of temperatures studied, it is necessary to know the quantity:

$$\gamma = (\partial p/\partial T)_{v,l} \tag{1}$$

in the appropriate range of temperatures and elongation ratios.

Simple thermodynamics shows that:

$$\gamma = (\partial p/\partial T)_{v,l} = \alpha/\beta = (P_i - p)/T \cong P_i/T \tag{2}$$

where α is the thermal expansion coefficient, β is the isothermal compressibility, and P_i is internal pressure.

The effect of the last approximation in eq. (2) is negligible, as p is of the order of 1 atm. while P_i is around 3000 atm. for most of the rubbers.

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* Measurements here reported were presented at the International Symposium on elastomers, Turin, Italy September 1963.

From eq. (2), we see that γ can be readily obtained from internal pressure measurements, as already described in detail in previous papers.[5,6]

In the course of a study of stress–temperature coefficients for two rubbers, a polydimethylsiloxane elastomer and an ethylene–propylene copolymer, we have begun with the measurement of P_i for these rubbers at different elongations and over a range of temperatures.

Apart from the interest of these data in obtaining $(\partial p/\partial T)_{v,l}$, the values can be discussed in term of recent theories[7] on rubber elasticity.

EXPERIMENTAL

Materials

Internal pressures P_i were measured for two elastomers, a polydimethylsiloxane rubber (PDS) and a random copolymer (50–50 in composition) of ethylene and propylene (C_2–C_3). Both samples were kindly supplied by Pirelli SpA. in form of rods, 15 mm. in diameter and 150 mm. in length.

The recipe of the compounds and vulcanization conditions were as follows. For PDS, silicon rubber, 100 parts; SiO_2, 35 parts; vulcanization agents, 4 parts; vulcanization was for 15 min. at 130°C. For C_2–C_3, ethylene–propylene copolymer, 100 parts; PTCl B 4 parts; sulfur, 0.45 part; vulcanization was for 45 min. at 160°C.

Table I summarizes some physical properties of the two vulcanized rubbers; specific weights were measured by standard pycnometric technique. Thermal expansion coefficients for unstretched rubbers were measured on the sample ready for P_i measurement by attaching a precision-bore glass capillary to the cell; after measuring α, this capillary was taken off and the cell was used then for determination of P_i.

TABLE I
Physical Properties of the Vulcanized Elastomers

Elastomer	Specific gravity at 25°C., g./cc.	α, °C.$^{-1}$	M_c
Silicone rubber	1.216	0.752×10^{-3}	2,250
Ethylene–propylene copolymer	0.846	0.678×10^{-3}	12,200

Values of M_c, the average molecular weight of network chains, have been evaluated from results of swelling measurements, by using the well known equation of Flory.[8]

Swelling agents were toluene for PDS and benzene for C_2–C_3; equilibrium swelling was obtained after at least 5 days and it was extrapolated to zero time to avoid small errors deriving from breakdown of networks due to swelling itself.

Values of the interaction parameter χ used were 0.465[9] and 0.555[10] for PDS and C_2–C_3, respectively

Internal Pressure Measurements

P_i has been measured on PDS and C_2–C_3 rubbers at different elongation ratios λ, ranging from $\lambda = 1$ to $\lambda = 1.5$. To keep the sample stretched at the prefixed value of λ, the ends of each rubber rod were bonded to two steel end pieces (see Fig. 1) and the two halves of a metal cylinder (thickness 1 mm.) of appropriate length were placed between the two steel ends.

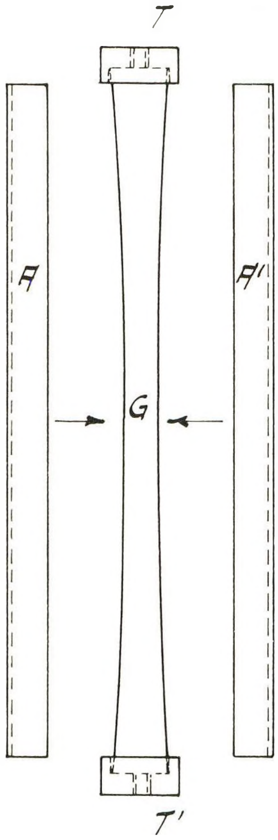

Fig. 1. Experimental device used to keep the sample stretched at the prefixed value of λ during P_i measurements: (G) elastomer, (A,A′) halves of cylinder; (T, T′) steel ends.

Eastman Kodak 910 adhesive was used to bond C_2–C_3 on steel, whereas for PDS Rhodorsil Caf 4 (Rhône-Poulenc) was found more effective.

The rubber specimen, held at various stretching ratios by the metal frame, was finally sealed into a glass cell described in Figure 2; from this point on, the procedure for P_i measurements was exactly the same as that described in earlier papers.[5,6]

The cell of Figure 2 was connected to a vacuum line and, when the pressure reached 10^{-4} mm. Hg, filled with Hg up to the line A.

It was then removed from the vacuum line and bolted into a steel pressure vessel completely filled with transformer oil and thermostatted at 25 ± 0.001°C. The pressure vessel was connected to a Budenberg dead weight pressure gauge tester capable of generating pressures from 1 to 600 atm. with a precision of ±0.01 atm.

Under a pressure of 1 atm. the temperature of the thermostat was adjusted until a pilot lamp (Fig. 3) indicated the contact between mercury and Pt wire in the cell capillary; then the temperature was raised about 0.1–0.2°C. and the new pressure required to keep mercury in the same position was recorded.

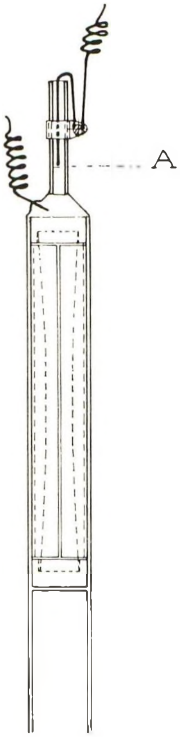

Fig. 2. Pyrex cell for P_i measurements. Cell is filled with Hg up to line A.

By repeating this procedure five or six times and by plotting p against T one obtains the thermal pressure coefficient $\gamma = (\partial p/\partial T)_{v,l}$

This quantity must be corrected for the presence of Hg and steel in the Pyrex cell and for the Pyrex dilation coefficient and compressibility.

RESULTS

It is well known[11] that relaxation precesses are more or less always present in a deformed rubber, so that it is very difficult to reach an equilibrium situation within a reasonable time.

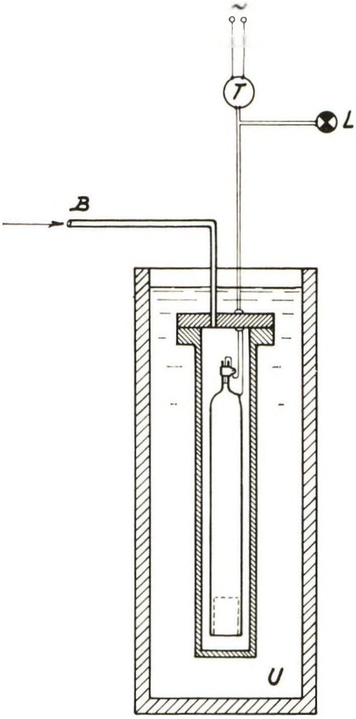

Fig. 3. Scheme of apparatus for P_i measurements: (B) connection to Budenberg pressure source; (L) electric 2.5 v. bulb; (T) transformer; (U) thermostatic bath.

However, P_i values measured at various times did not show any further measurable change after about 60 hr.; we therefore concluded that, as far as internal pressures are considered, our P_i values are indistinguishable from those pertaining to true equilibrium states.

Table II summarizes P_i values measured for PDS and C_2–C_3 at 25°C. and at various elongation ratios $\lambda = l/l_0$.

TABLE II
Internal Pressure P_i at 25°C. of Elastomers Elongated to Various Stretching Ratios λ

	P_i, cal./cc.	
λ	Silicone rubber	Ethylene–propylene copolymer
1.000	56.4	79.25
1.120	56.2	78.2
1.185	55.2	77.8
1.250	54.8	79.0
1.350	53.9	77.0
1.450	50.4	74.9
1.520	—	73.9

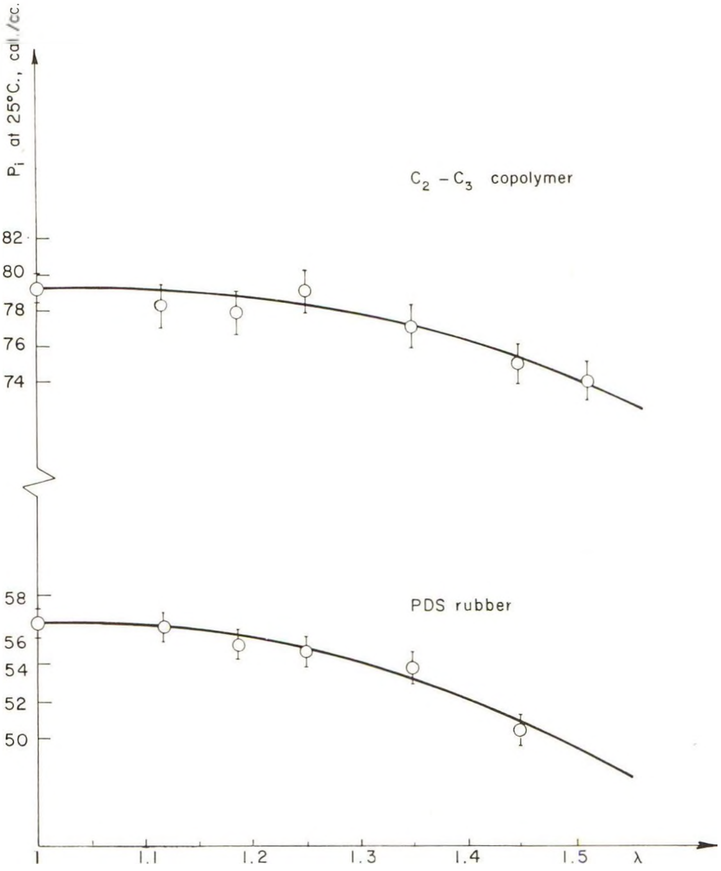

Fig. 4. Plots of P_i vs. λ at for PDS and C_2–C_3 25°C.

Values in Table II are averages of at least two independent experiments, which ordinarily agree within ±1%.

The accuracy of reported P_i values is rather difficult to estimate, because it depends on the accuracy of values of the thermal expansion coefficient and the compressibility of glass, mercury, and steel, used in the calculation of P_i from the experiments. However, as we compare a set of data all of which were obtained in the same way, this does not affect our comparison of P_i values at different elongations.

The behavior of P_i with λ at 25°C. is shown in Figure 4.

DISCUSSION

Strictly speaking, our experiments are not carried out at constant elongation or even at constant length, since the pressure and temperatures to which the system was subjected changed during the determination of P_i (change in pressure about 4 atm. for a change of 0.5°C.). Consideration of the changes involved showed that they were minute and that the change in the length of the specimen caused an uncertainty in P_i which was well within the experimental error.

Another point is the dilation of rubber on stretching, so that P_i at different elongations refer to slightly different volumes of the specimen; the dilation for our range of λ has been shown[12] to be less than one part in 10^4, so that its effect on P_i is too small to be detectable.

Inspection of Table II and Figure 4 shows that P_i decreases with increasing λ, values at $\lambda = 1.4$ being 12% and 6% lower than values at $\lambda = 1$ for PDS and C_2–C_3, respectively.

This behavior of P_i with extension is in disagreement with theoretical predictions. In fact, Flory[7] has already shown for a lightly crosslinked network

$$P_i/T \cong (\partial p/\partial T)_{v,l} = \alpha/\beta \tag{3}$$

where α and β are the ordinary bulk thermal expansion coefficient and isothermal compressibility (for uncrosslinked material), respectively.

From eq. (3) it follows that P_i should be very nearly independent on the deformation.

This independence arises from the smallness of the term ν/V which gives the number of chains per unit volume of network and occurs in all the formulations of the conformational entropy of networks.[13,14]

This is not the only example of disagreement between predictions of rubber elasticity theory and experimental values; corresponding cases have already been pointed out by Flory[8,15] in connection with the failure to obtain experimentally the theoretically suggested direct proportionality between the stress f and the "deformation factor" $(\lambda - \lambda^{-2})$.

Another example is given by the nonconstancy of the ratio f_e/f as a function of λ, where f is the total stress and f_e the part of f due to the change in internal energy; the theory suggests[7] that:

$$f_e/f = Td \ln \overline{r_0^2}/dT \tag{4}$$

where $\overline{r_0^2}$ is the unperturbed mean-square end-to-end distance of chains composing the network, so that f_e/f should be independent of λ.

Krigbaum and others have recently shown that this is not verified for natural rubber,[16] *cis*-1,4-polybutadiene,[17] and Viton.[18]

Measurements of P_i for stretched natural rubber have been for the first time reported in a recent paper[3] dealing with thermodynamic properties of rubber, but the reproducibility of these data was not sufficient to show clearly a dependence of P_i on λ.

In conclusion, we think that an understanding of the behavior of P_i with extension must obviously rest on a picture of a deformed network quite different from what it is usually assumed to be.

Work is in progress at our laboratories to investigate this problem further and to show whether the observed behavior is peculiar to the two rubbers studied or a more general phenomenon.

We would like to thank Prof. G. Gee and Dr. G. Allen of the Manchester University for having suggested this area of interest, and Prof. C. Rossi for helpful discussions. We thank also Mr. V. Morando for his collaboration during experimental work

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Résumé

On rapporte les résultats de mesures de pression interne P_i faites sur deux élastomères, gomme siliconique et copolymère éthylène-propylène, étirés à différents rapports d'allongement λ. Les résultats obtenus pouvent que P_i change avec λ; on discute celtte dépendance d'après les théories récentes sur l'élasticité de la gomme.

Zusammenfassung

Die Ergebnisse der Messung des inneren Drucks P_i an zwei elastischen Materialen, Silikongummi und Äthylen-Propylencopolymeren, bei verschiedenem Dehnungsverhältnis λ werden mitgeteilt. Es zeigt sich, dass P_i von λ abhängig ist; diese Abhängigkeit wird auf Grund der neuerern Theorien der Kautschukelastizität diskutiert.

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Polymers and Copolymers of Vinyl Pinolate and Some Reactions with Isocyanates*

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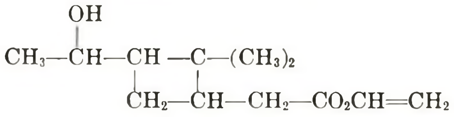
Synopsis

Vinyl pinolate has been synthesized, and its homopolymers and copolymers with vinyl chloride and vinyl acetate have been prepared. The reactions of copolymers of vinyl pinolate with vinyl acetate and vinyl chloride with some isocyanates were investigated. The emulsion copolymer of vinyl pinolate and vinyl chloride has been evaluated as a nonrigid plastic.

Vinyl pinolate (I) has an unusual cyclic structure that may contribute useful properties to polymers and copolymers



$$\begin{array}{ccccccc} & OH & & & & & \\ & | & & & & & \\ CH_3- & CH & - & CH & - & C & -(CH_3)_2 \\ & & & | & & | & \\ & & & CH_2 & - & CH & -CH_2-CO_2CH=CH_2 \end{array}$$

I

prepared from it. The hydroxyl group in vinyl pinolate may be particularly useful, because with it polymers of vinyl pinolate could possibly be extended and crosslinked with any of a number of difunctional compounds. The study described in this paper was undertaken to investigate the preparation and properties of vinyl pinolate polymers and copolymers.

PREPARATION OF VINYL PINOLATE

The preparation of vinyl pinolate[1] from pinolic acid[1,2] has been described previously. More recent work has shown that the product formed from

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* This is a partial report of work done under contract with the four Utilization Research and Development Divisions, Agriculture Research Service, U. S. Department of Agriculture and authorized by the Research and Marketing Act. The contract was supervised by Dr. J. C. Cowan of the Northern Division. The monomer synthesis and study of the reaction of the polymers with isocyanates were done at the Naval Stores Laboratory, the polymerization at the University of Arizona, and the evaluation of the vinyl chloride–vinyl pinolate copolymer at the Southern Utilization Research and Development Division.

TABLE I
Polymerization of Vinyl Pinolate

Sample	System	Weight of monomer, g.	Weight azobisiso-butyronitrile, g.	Time, hr.	Temperature, °C.	Conversion, %	Inherent viscosity[a]	Softening range, °C.
101-A	Bulk[b]	2.0	0.02	94	60	65	0.244	80–93
13-C	Solution	3.4	0.017	20	78	38	0.086	—
127-A	Solution	15.0	0.30	24	78	39	0.069	70–80
27-B	Suspension	3.0	0.03	48	60	69	0.308	80–91
31-B	Emulsion	1.5	0.019[c]	48	60	94	—	88–105

[a] Taken in tetrahydrofuran solution at 30°C. with a number 50 Cannon-Fenske viscosimeter.

[b] Prepared in a sealed tube from which the air had been evacuated. Purified by precipitation in petroleum ether from acetone solution.

[c] Catalyst $K_2S_2O_8$.

the reaction of pinolic acid, vinyl acetate, and mercuric sulfate is probably an acetoxyacetal[3] which can be hydrolyzed at room temperature with mineral acid. Infrared absorption for a hydroxyl group was completely absent in the unhydrolyzed product. Hydrolysis, however, gave the expected vinyl pinolate.

POLYMERIZATION

Polymerization of vinyl pinolate has been accomplished by free radical initiation in bulk, solution, suspension and emulsion systems. The conditions for polymerization and some properties of the samples of poly(vinyl pinolate) are summarized in Table I. Preparation of poly(vinyl pinolate) in suspension was unsuccessful until neutral buffered solution was substituted for distilled water in the polymerization recipe. In contrast, polymerization of vinyl pinolate in buffered and unbuffered emulsion systems produced the same results.

All the samples of poly(vinyl pinolate) are colorless, glasslike solids that melt between 70 and 105°C. Except for sample 31-B which is poly(vinyl pinolate) prepared in emulsion, the samples are soluble in methanol, acetone, and tetrahydrofuran, slightly soluble in benzene and insoluble in petroleum ether. Sample 31-B is soluble in acetone and tetrahydrofuran until it is dried. Then it is insoluble in acetone, tetrahydrofuran, and several other solvents.

Because poly(vinyl pinolate) contains one hydroxyl group per repeating unit, reaction with a diisocyanate would be expected to produce a high degree of crosslinking. To prepare low molecular weight polymers that contain relatively fewer hydroxyl groups than poly(vinyl pinolate) and

TABLE II
Solution Copolymerization of Vinyl Pinolate and Vinyl Acetate

Sample	Initial vinyl pinolate, mole-%	Time, hr.	Conversion, %	Inherent Viscosity[a]	Softening range, °C.	C, %	Calculated Vinyl pinolate in polymer, mole-%[b]
121-A	9.2	24	62	0.130	55–63	58.91	12
123-A	4.5	24	62	0.139	54–63	58.30	10
125-A	2.2	24	64	0.134	54–63	57.16	5
57-A	1.6	17	60	0.104	56–61	56.89	4
61-C	1.6	2[c]	21	0.115	48–64	—	—
47-A[d]	0	20	43	0.145	58–72	55.80	0

[a] Measured in tetrahydrofuran solution at 30°C. with a number 50 Cannon-Fenske viscosimeter.

[b] Calculated from carbon analysis.

[c] After 2 hr. *m*-dinitrobenzene (1% by weight of monomer) was added to the solution to inhibit further polymerization.

[d] Poly(vinyl acetate) prepared in solution for comparison with copolymers.

TABLE III
Solution Copolymerization of Vinyl Chloride and Vinyl Pinolate

Sample	Wt. vinyl ester, g.	Wt. vinyl chloride, g.	Conversion, %	Cl in polymer, %	Vinyl chloride[a] / Vinyl pinolate	Softening Range, °C.	η_{inh}[b]
VP VCl 29-1	1	9	50	51.26	31.4/1	74–85	0.136
29-2	2	8	49	48.40	20.1/1	68–75	0.135
29-3	3	8	53	45.31	13.9/1	70–81	0.148
29-4	0.5	12	61	54.13	70.8/1	73–86	0.135
44-1	1	9	63	51.82	35.3/1	80–95	0.195
44-2	2	8	65	48.12	19.0/1	72–80	0.178
44-3	3	7	50	45.19	13.6/1	76–82	0.206

[a] Molar ratio of monomers in the copolymer calculated from elemental analyses.

[b] Measured in tetrahydrofuran solution at 30°C. with a number 50 Cannon-Fenske viscosimeter.

might therefore be more suitable for extending with diisocyanates, vinyl pinolate was copolymerized in solution with vinyl acetate and vinyl chloride. Table II contains information concerning the preparation and properties of several vinyl pinolate–vinyl acetate copolymers and Table III vinyl pinolate–vinyl chloride copolymers. Transparent, colorless films can be cast from both vinyl pinolate–vinyl acetate and vinyl pinolate–vinyl chloride copolymers, but the films are brittle indicating that the vinyl pinolate units do not produce any appreciable internal plasticization.

Vinyl pinolate was copolymerized with vinyl acetate and vinyl chloride in emulsion as well as in solution. The data resulting from the copolymerization experiments are compiled in Table IV.

Poly(vinyl acetate) and poly(vinyl chloride) prepared in emulsion are soluble in acetone and tetrahydrofuran and so are the copolymers of vinyl pinolate prepared in solution and listed in Tables II and III. In contrast, the copolymers of vinyl pinolate with vinyl acetate and vinyl chloride prepared in emulsion are soluble in acetone and tetrahydrofuran only until they are dried at room temperature. Attempts to dissolve the dried co-

TABLE IV
Emulsion Copolymerization of Vinyl Chloride and Vinyl Pinolate

Sample	Wt. vinyl pinolate, g.	Wt. vinyl chloride. g.	Conversion, %	Cl in polymer, %	Vinyl chloride[a] / Vinyl pinolate
VP VCl 41-1	1.0	9.0	86	51.00	29.8/1
41-2	5.0	5.0	50	39.62	7.9/1
41-3	2.0	8.0	52	44.85	13.2/1
41-4	2.5	7.5	51	43.65	11.9/1
41-5	2.0	8.0	60	46.62	16.1/1
41-6	0.5	9.5	88	55.99	234.6/1

[a] Molar ratio of monomers in the copolymer calculated from elemental analyses.

polymer in benzene, acetone, tetrahydrofuran, and dimethyl sulfoxide resulted in the slow softening and swelling of the copolymer. Apparently even small amounts of vinyl pinolate, as small as 0.5 mole-%, copolymerized in emulsion with vinyl acetate or vinyl chloride produce a marked decrease in the solution of the dried copolymer.

Vinyl pinolate fails to copolymerize with vinylidene chloride under the emulsion polymerization conditions. Under similar conditions, the relative reactivity ratios of vinylidene chloride (0.08) and the vinyl ester of a long chain fatty acid, e.g., vinyl stearate (3.80), were determined and are unfavorable for copolymerization.[4]

REACTION OF VINYL PINOLATE COPOLYMERS WITH ISOCYANATES

To learn something of the reactions of vinyl pinolate and its vinyl chloride and vinyl acetate copolymers with isocyanates, a method was used based upon spectral analyses.[5] By determining infrared absorbancies of a stretching vibration arising from the isocyanate group at 4.5 μ of solutions of vinyl pinolate and its copolymers reacted with toluene diisocyanate and phenyl isocyanate it was possible to estimate the decrease in isocyanate concentration caused by the reaction. The change in concentration as represented by change in absorbancy gave a convenient method for measuring reactivity. Poly(vinyl acetate) and poly(vinyl chloride) homopolymers exhibited little or no reaction with either isocyanate at 75°C. (Table VI). One of the isocyanate groups of toluene diisocyanate was less reactive than the other group, since almost half the isocyanate was unreacted when equivalent quantities of vinyl pinolate and the isocyanate were reacted. Phenyl isocyanate reacted completely. Similar results were obtained with the vinyl acetate–vinyl pinolate copolymer, 123-A. Copolymers, 44-2 and a mixture of 121-A–123-A, from which excess toluene diisocyanate was removed after reaction by precipitating and washing with hexane contained free isocyanate groups. With 0.1*N* solutions of the copolymers, based on vinyl pinolate content, the residual isocyanate content was 0.07*N* for the vinyl chloride copolymer and 0.064 for the vinyl acetate copolymer.

The results of a rate study involving reactions of the copolymers 44-2 and 123-A and phenyl isocyanate are tabulated in Table V. After about 6 hr., the isocyanate concentration with both polymers was about 0.07*N* (calculated 0.07*N*) and did not change much after an additional 8 hr. heating.

TABLE V
Reaction of Vinyl Pinolate Copolymers with Phenyl Isocyanate

	Isocyanate concentration, Normality of Diluted Solution at various times (hr.)					
Copolymer	0 hr.	1 hr.	2 hr.	4 hr.	6 hr.	14 hr.
44-2	0.1	.096	.086	.084	.078	.076
123-A	0.1	.092	.079	.075	.067	.070

EXPERIMENTAL

Preparation of Vinyl Pinolate

Pinolic acid,[1,2] 372 g. (2.0 moles), freshly distilled vinyl acetate, 2200 ml., copper resinate, 1.0 g., and mercuric acetate, 8.0 g., were mixed in a 3-l. flask. Concentrated sulfuric acid, 1.0 ml., was added and agitation continued at 0–5°C. until the pinolic acid was in solution. The batch was stored in a refrigerator (10°C.) for two days. The sulfuric acid was neutralized with sodium acetate and the excess vinyl acetate and acetic acid distilled below 30°C. The residue was dissolved in 1500 ml. ether and washed with vigorous agitation for 15 min. with three 500-ml. portions of 1.5*N* hydrochloric acid. The solution was washed at 10°C. with cold water, cold 0.5*N* sodium carbonate and dried. The ether was removed and the product distilled bulb to bulb; b.p. 106°C./1.0 mm.; 334 g., 81%. The crude ester was redistilled through a column packed with glass helices, b.p. 84°C./0.2 mm., n_D^{25} 1.4656.

Polymerization of Vinyl Pinolate in Solution

A 250-ml., three-necked flask equipped with a spiral condenser, thermometer, magnetic stirring bar, and nitrogen inlet tube was charged with vinyl pinolate, azobisisobutyronitrile (2% of weight of the monomer), and 150 ml. of A. R. grade benzene. The solution was stirred at reflux temperature under nitrogen for the desired number of hours. Then the benzene was removed by aspiration and the polymer was purified by repeatedly dissolving it in acetone and precipitating it in petroleum ether (35–75°C.). Finally the polymer was dissolved in benzene and freeze-dried.

Polymerization of Vinyl Pinolate in Suspension

Into a 100-ml., two-necked flask fitted with a spiral condenser, magnetic stirring bar, and nitrogen inlet tube was placed 3.0 g. of vinyl pinolate, 0.03 g. of Duponol C (du Pont's sodium lauryl sulfate), 0.3 g. of azobisisobutyronitrile, and 10 ml. of neutral buffered solution. The suspension was stirred under nitrogen at 60°C. for 48 hr. The poly(vinyl pinolate) which had coalesced into a single lump was dissolved in acetone and precipitated first in water and then in petroleum ether. Then the polymer was dried at 60°C. in a vacuum oven at 20 mm. of mercury.

Polymerization of Vinyl Pinolate in Emulsion

A 2-oz., screw-capped bottle was charged with 0.3 g. of Triton X-301 (Rohm and Haas, sodium alkylaryl polyether sulfate, 20% aqueous dispersion), 1.5 g. of vinyl pinolate, 0.75 ml. of 25% aqueous potassium persulfate, and 3 ml. of distilled water. After the air had been flushed from the bottle with a stream of nitrogen the bottle was capped and tumbled in a water bath at 60°C. for 48 hr. A sulfuric acid–salt solution (5% H_2SO_4 saturated with salt) was used to break the emulsion. The poly(vinyl pinolate) was washed with water and purified by the same procedure described for suspension polymerization. After it had been dried, the poly(vinyl pinolate) was insoluble in dimethylformamide, methanol, acetone, 2-butanone, tetrahydrofuran, dioxane, benzene, toluene, chloroform, and carbon tetrachloride.

Copolymerization of Vinyl Pinolate and Vinyl Acetate in Solution

The same procedure described for solution polymerization of vinyl pinolate was used with the exception that a calculated amount of freshly distilled vinyl acetate was added to the solution.

Copolymerization of Vinyl Pinolate and Vinyl Chloride in Solution

Polymerization bottles (110-ml., Ace Glass T 1506) were charged with calculated amounts of vinyl pinolate, 0.2 g. of azobisisobutyronitrile, 40 ml. of A. R. grade benzene and then cooled in a Dry Ice–acetone bath. Vinyl chloride was condensed in the bottles until a slight excess was present. When the excess vinyl chloride had been allowed to evaporate, the bottles were sealed with crown-type bottle caps and tumbled in a water bath at 60°C. for 48 hr. The copolymers were coagulated by pouring the benzene solutions into 400 ml. of methanol and purified by repeatedly dissolving them in tetrahydrofuran and precipitating them in rapidly agitated methanol. After the copolymers had been dried at room temperature for 48 hr. they could be dissolved easily in acetone and tetrahydrofuran but only with difficulty in benzene.

Copolymerization of Vinyl Pinolate and Vinyl Chloride in Emulsion

The calculated amounts of vinyl pinolate, 40 ml. of oxygen-free water, 3.0 g. of Triton X-301, and 4 ml. of 2.5% potassium persulfate solution were placed into 110-ml. polymerization bottles. While the bottles were being cooled in a Dry Ice–acetone bath, a slight excess of vinyl chloride was condensed into it. When the excess had been allowed to evaporate the bottles were capped and tumbled at 50°C. for 72 hr. The copolymers were coagulated with 400 ml. of saturated salt solution and collected on filter paper. After being washed with water and then with methanol, the copolymers were repeatedly dissolved in tetrahydrofuran and precipitated in methanol. Finally, the copolymers were dried at room temperature for 48 hr. If the copolymers are overheated, on drying they become insoluble in acetone, tetrahydrofuran, dimethyl sulfoxide, dimethylformamide, and benzene.

Reaction of Polymers with Isocyanates

Exploratory experiments were made to select a solvent and to determine a suitable temperature and time for running the reactions. Tetrahydrofuran was a good solvent for the polymer; however, the isocyanates, toluene diisocyanate (a mixture of 2,4- and 2,6-isomers in a 4:1 ratio) and phenyl isocyanate were not stable in this solvent at 75°C. All reactions were run in benzene at 75°C. since this solvent did not affect the isocyanate adversely.

TABLE VI
Reactions of Vinyl Pinolate and Some of Its Copolymers with Isocyanates at 75°C. for 48 Hr.

Material		Toluene diisocyanate concentration, N		Phenyl isocyanate concentration, N	
Name	Concentration, N	Initial	Final[a]	Initial	Final[a]
Vinyl pinolate	0.05	0.1	0.064	0.1	0.065
Vinyl pinolate	0.1	0.1	0.045	0.1	0.0
Vinyl pinolate	0.1	—	—	0.2	0.09
Poly(vinyl acetate)[b]	0.86 wt.-% by volume	0.1	0.092	0.1	0.095
Poly(vinyl chloride)[b]	0.625 wt.-% by volume	0.1	0.092	0.1	0.095
Vinyl acetate copolymer 123-A	0.05[c]	—	—	0.1	0.077
	0.1[c]	0.1	0.06	0.1	0.033
Vinyl chloride copolymer 44-2	0.05[c]	0.1	0.07	0.1	0.06[d]
	0.1[c]	0.1	Insoluble	0.1	0.04[d]

[a] As observed by infrared spectral analyses.

[b] Homopolymers prepared by solution polymerization.

[c] Normality with respect to vinyl pinolate (hydroxyl) concentrations.

[d] Benzene replaced by tetrahydrofuran.

In instances indicated, the benzene was replaced with tetrahydrofuran for reasons of solubility. The benzene was removed in vacuo at room temperature and the residual polymer dissolved in the tetrahydrofuran. In other instances also, as indicated, the polymers crosslinked and became insoluble in the latter solvent.

The substances investigated are tabulated in Table VI.

Benzene solutions (0.1N with respect to vinyl pinolate) of each of the copolymers 123-A and 44-2 were made up containing 0.3N phenyl isocyanate. These were heated to 75°C. for periods of 1, 2, 4, 6, and 14 hr. After each heating period 1-ml. samples were removed and diluted with 2 ml. of tetrahydrofuran. The results are tabulated in Table V. The concentration of the hydroxyl and isocyanate initially in the diluted samples were about 0.03 and 0.1N, respectively.

In another experiment, benzene solutions containing 0.93 g. (0.1N) of a mixture of copolymers 121-A and 123-A in equal amounts, and 0.87 g. (1.0N) toluene diisocyanate diluted to 10 ml. were heated to 75°C. for 2 hr. The polymers were precipitated by pouring into hexane, washed by decantation, redissolved and reprecipitated to remove excess isocyanate. The polymers were dissolved in tetrahydrofuran and diluted to 10 ml. The isocyanate concentrations after removal of excess isocyanate were 0.064N for the 121-A–123-A polymer mixture and 0.07N for the 44-2 polymer.

Evaluation of Vinyl Pinolate and Vinyl Chloride Copolymers

An evaluation sample was prepared from vinyl pinolate and vinyl chloride in an emulsion system at the ratio of 2 g. vinyl pinolate to 8 g. of vinyl chloride. A 150-g. composite sample which had an inherent viscosity of 1.5 (0.2% in tetrahydrofuran) and which contained 16.9 moles of vinyl chloride to 1 mole of vinyl pinolate was obtained. For comparison the copolymers of vinyl chloride with vinyl pinolate acetate previously described as VPAC5 and VPAC7 (Table II)[6] were also examined in the same system. The basic formulation employed in test composition is as follows: vinyl copolymer, 68.5%; plasticizer, 30.0%; stearic acid, 0.5%; stabilizer, 1.0%. Barium cadmium dilaurate was employed as the stabilizer in all of the experimental compositions.

These copolymer compositions were milled and molded at the temperatures specified in Table VII. The processibility of these copolymers was comparable to that of the commercial vinyl chloride–vinyl acetate copolymer. Some of the earlier vinyl pinolate copolymer samples which developed purple discoloration during processing were subsequently found to be contaminated with emulsifier, the removal of which by repeated solution of this polymer in THF and reprecipitation with water not only eliminated the color problem but also improved their processibility and physical characteristics.

TABLE VII
Physical Properties of Di-2-ethylhexyl Phthalate Plasticized Copolymers

	Vinyl pinolate copolymer (16.9% VP)	Vinyl pinolate acetate copolymer		
		16.0% VPA (VPAC5)	25% VPA (VPAC7)	PVCA
Plasticizer, %	30	30	30	30
Tensile strength, psi	2890	2220	1140	3390
100% Modulus, psi	1920	1760	940	2290
Elongation, %	170	130	140	300
Brittle point, °C.[a]	−11	−12	−2	−27
Milling and molding temperature, °F.	260	240	200	300

[a] Five consecutive no-break observations.

These compositions were evaluated by the standard ASTM procedures for such materials, D 412-61T for tensile strength and D 746-57T for low temperature performance, except for the use of an inclined plane tester at a loading rate of 200 lb./min. instead of the pendulum-type specified in D 412-61T.

The test data for these experimental polymers are given in Table VII. Also included for comparative purposes are the corresponding data for a commercial vinyl chloride–vinyl acetate copolymer 95/5.

The results show that none of the experimental copolymers exhibit an overall balance of tensile, low temperature, and elastic properties comparable to the model commercial copolymer plasticized by the same amount of di-2-ethylhexyl phthalate. However, the vinyl pinolate copolymer does compare quite favorably with the model copolymers in both tensile strength and modulus and all the experimental copolymers can be processed at lower temperatures.

The results of the evaluations do not establish any decided advantage of one experimental copolymer over the other at the same level of comonomer. Vinyl pinolate acetate is more favorable from the point of view of processing temperature and modulus while vinyl pinolate gives better tensile strength. It would appear from the data on the two vinyl pinolate acetate copolymers that overincorporation of comonomer can exert a regressive effect on some of the physical characteristics and that the optimum level might easily be somewhat below 16%. Similar supporting evidence is not available for the vinyl pinolate copolymer. However, considering the closeness of the relationship between these two monomers, it would not be unreasonable to assume that the optimum degree of incorporation for the vinyl pinolate comonomer closer parallels that of vinyl pinolate acetate.

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Résumé

On a synthétisé le pinolate de vinyle et on a préparé ses homopolymères et copolymères avec le chlorure de vinyle et l'acétate de vinyle. On a étudié les réactions de copolymères de pinolate de vinyle avec l'acétate de vinyle et le chlorure de vinyle avec quelques isocyanates. On a trouvé que le copolymère en émulsion du pinolate de vinyle et du chlorure de vinyle était un plastique non rigide.

Zusammenfassung

Vinylpinolat wurde synthetisiert und seine Homo- und Copolymeren mit Vinylchlorid und Vinylacetate dargestellt. Die Reaktionen der Copolymeren von Vinylpinolat mit Vinylacetat und Vinylchlorid mit einigen Ioscyanaten wurde untersucht. Die Brauchbarkeit des Emulsionscopolymeren von Vinylpinolat und Vinylchlorid als nicht-starre plastische Masse wurde ermittelt.

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Investigations on the Continuous Copolymerization of Acrylonitrile with Methyl Methacrylate in a Heterogeneous System

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Synopsis

Investigations were carried out on continuous copolymerization of acrylonitrile with methyl methacrylate in a tank type reactor and in a heterogeneous system. It was found that the reaction rate of copolymerization is directly proportional to the concentration of comonomers in the reactor and proportional to the residence time to the −0.65 power. Investigations on the influence of the concentration of initiator upon the reaction rate gave evidence of a change in the mechanism of termination reaction at higher concentrations of initiator in the system. The molecular weights of the copolymers, at sufficiently long residence times, were constant. The composition of the copolymers obtained was in accordance with theoretical anticipations. Some discrepancies between the equations derived and the experimental results were tentatively explained on the basis of the influence of the heterogeneous nature of the system.

1. INTRODUCTION

Copolymers of acrylonitrile (>90%) with methyl methacrylate represent a good fiber-forming material, and the methods of production of such copolymers on an industrial scale have already been introduced. Continuous production methods are also being proposed.[1,2] In addition, there exist some patents defining methods for molecular weight regulation and control in the continuous polymerization of acrylonitrile.[3,4] Investigations on a process of continuous acrylonitrile polymerization were carried out by Mintzer and Coman,[5] who used tubular type reactors. Thomas and Mallison[6] determined the fundamental conditions for a process of continuous polymerization of acrylonitrile in a tank-type reactor, with special consideration of the influence of the catalyst and residence time. Horikx and Hermans[7] investigated the continuous polymerization of styrene in toluene; Wall, Delbecq, and Florin[8] studied emulsion polymerization. While theoretical considerations on the solution polymerization of vinyl compounds initiated by azobisisobutyronitrile was pursued by Jenkins,[9] Denbigh[10] and Zeman and Amundson[11] carried out some theoretical considera-

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tions on the polydispersion of vinyl polymers obtained by continuous method in the tank type flow reactor.

The purpose of our work was to investigate copolymerization of acrylonitrile (about 96% molar) with methyl methacrylate in a tank flow reactor. The copolymerization was conducted in an aqueous medium; consequently, copolymer precipitation was taking place, and the reaction proceeded in a heterogeneous system. As far as we know, there have been no investigations to date conducted on the copolymerization of acrylonitrile under these conditions.

2. THEORETICAL

Carrying out a chemical reaction by the flow method involves continuous introduction of substrates into the reactor as well as continuous removal of the reaction products. Such a process can be carried out in a tank type reactor with walls approaching each other three-dimensionally, and equipped with an adequate stirring unit. The intensity of mixing and the shape of the reactor allow for a complete intermixing of the contents, which results in equalization of the concentrations and temperatures throughout the whole effective volume of the reactor. Therefore, the process may be a quasi-stationary one, no property in the reacting system being dependent on time.

The general equation of the quantitative balance for a continuous process in stationary state in a flow reactor with complete intermixing is as follows.[12] The rate of introducing the substrate to the reactor is equal to the rate of removal of the product plus the rate of removal of the unreacted substrate. This may be represented in the form:

$$N = pN + (1 - p)N \tag{1}$$

where N is the amount of substrate (moles) introduced into the reactor per unit time and p is the degree of conversion. As a consequence of the rule of stationary state, the reacting system does not undergo changes, and thus the rate of removal of the reaction product is equal to the rate of formation of the reaction product, i.e.,

$$pN = Rv_r \tag{2}$$

where R is the rate of reaction and v_r is the effective volume of the reactor. If the reaction is carried out in any chosen inert liquid medium, then:

$$N = c_0V_d \tag{3}$$

where c_0 is the concentration of substrate (molar) in the feed introduced into the reactor and V_d is the volume of the feed (in liters) introduced into the reactor per unit time. On substituting eq. (3) into eq. (2), there results:

$$c_0p = (v_r/V_d)\ R = \tau R \tag{4}$$

The quantity $\tau = v_r/V_d$ is called residence time. It is a parameter typical for processes carried out in a tank flow reactor.

If, in the reactor, a solid substance (in our case, the copolymer) is formed as a result of reaction, this may be considered a passive volume, and it must then be taken into account that the volume of the liquid phase in the reactor is smaller than the effective volume. Equation (2) must therefore be written as follows:

$$pN = Rv_r\zeta \tag{5}$$

where ζ is defined as

$$\zeta = V_c/V_u$$

and V_c is the volume of liquid (in liters) being removed from the reactor per unit time, and V_u is the volume of feed (in liters) being removed from the reactor, together with solid phase, per unit time.
On that basis:

$$c_0p = \tau\zeta R \tag{6}$$

There then is an evident dependence between the concentration of substrates c_0 in the feed and their concentration c in the reaction medium:

$$c = c_0V_d(1 - p)/V_c \tag{7}$$

The quantity c_0 calculated on the basis of eq. (7) is substituted in eq. (6), and after rearrangement, the result is:

$$R/c = [p/(1 - p)\tau](V_u/V_d) \tag{8}$$

In the case we are studying herein, the copolymer formed has a specific weight approaching that of water, and according to our experimentally obtained proofs, $V_u \simeq V_d$. We may therefore write the approximation:

$$R/c \simeq p/(1 - p)\tau \tag{8'}$$

Equations (6) and (8′) may be used to calculate the rate of the polymerization reaction in a flow type reactor with complete intermixing, on the basis of experimental data, in a similar manner as the equation $R = -dc/dt$ is used to calculate the reaction rate for periodical processes.

Let us now consider the dependence of copolymerization rate on parameters of the continuous process, while taking into account the mechanism of reaction.

If it is assumed that the termination of macroradicals occurs through mutual recombination or disproportionation, the equation for copolymerization rate in homogeneous system is as follows:

$$\begin{aligned} R_p &= -d([\mathrm{M}_1] + [\mathrm{M}_2])/dt \\ &= \frac{(r_1[\mathrm{M}_1]^2 + 2[\mathrm{M}_1][\mathrm{M}_2] + r_2[\mathrm{M}_2]^2)R_i^{0.5}}{(r_1^2\delta_1^2[\mathrm{M}_1]^2 + 2\phi\delta_1\delta_2\, r_1r_2[\mathrm{M}_1][\mathrm{M}_2] + r_2^2\delta_2^2[\mathrm{M}_2]^2)^{0.5}} \end{aligned} \tag{9}$$

where $[M_1]$, $[M_2]$ are the concentration of the comonomers in the reaction medium, R_i is the rate of initiation, r_1, r_2 are relative reactivity ratios of the comonomers, and ϕ, δ_1, δ_2 are constants. Equation (9) may be written as follows:

$$R_p = \frac{(r_1 + 2\gamma + r_2\gamma^2)R_i^{0.5}}{(r_1^2\delta_1^2 + 2\phi\delta_1\delta_2r_1r_2\gamma + r_2^2\delta_2^2\gamma^2)^{0.5}(1 + \gamma)} [M] \tag{10}$$

where

$$[M] = [M_1] + [M_2]$$

$$\gamma = [M_2]/[M_1]$$

Thus, eq. (10) can be written as follows:

$$R_p = A_\gamma R_i^{0.5}[M] \tag{10'}$$

where A_γ is the first term of the righ-hand side of eq. (10). This equation may be applied to a continuous process if it is supposed that macroradicals are not removed from the system with the feed issuing from the reactor. This supposition is permissible in the case when the rate of termination reaction is much greater than the rate of removal of macroradicals.

The rate of initiation R_i from eq. (10′) may be expressed as a function of concentration of the initiator in the feed. When the initiator is potassium peroxide, $K_2S_2O_8$, and $K_2S_2O_5$ and Fe^{2+} are used as activators, then free radicals initiating the polymerization process chiefly arise as a result of the reaction:

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{1-\cdot} + SO_4^{2-} + Fe^{3+}$$

The rate constant for this reaction has been determined by Fordham and Williams[13] as $10^{11}\, e^{-12,100/RT}$ 1. mole^{-1} sec.$^{-1}$ The $Fe^3 +$ ions formed are reduced back again to Fe^{2+} by $K_2S_2O_5$.

On the basis of eqs. (1) and (5) of the quantitative balance of continuous process, we may write:

$$(I)V_w = k[I]\,[Fe^{2+}]v_r\zeta + [I]V_c \tag{11}$$

where (I) is the concentration of initiator in water in the feed, [I] is the concentration of initiator in the reaction medium, $[Fe^{2+}]$ is the concentration of Fe^{2+} ions in the reaction medium, k is the rate constant of the reaction between $S_2O_8^{2-}$ and Fe^{2+}, V_w is the volume of water introduced into the reactor per unit time, and V_c, v_r, ζ, are as defined in eqs. (4) and (5). Hence:

$$[I] = \frac{(I)V_w}{k[Fe^{2+}]v_r\zeta + V_c}$$

$$= \frac{(I)V_w/V_c}{k[Fe^{2+}]\tau + 1} \tag{11'}$$

where $\zeta = V_c/V_u$, and $V_u \simeq V_d$. Thus we have for the rate of initiation:

$$R_i = fk[\mathrm{I}][\mathrm{Fe}^{2+}]$$
$$= \frac{fk(\mathrm{I})[\mathrm{Fe}^{2+}]V_w/V_c}{k[\mathrm{Fe}^{2+}]\tau + 1} \tag{12}$$

where f is a coefficient of efficiency of the initiation reaction. For sufficiently long residence times, $k[\mathrm{Fe}^{2+}]\tau >> 1$. For instance, for $[\mathrm{Fe}^{2+}] = 0.3 \times 10^{-3}$ mole/l., $\tau = 30$ min., and temperature 40°C., $k[\mathrm{Fe}^{2+}]\tau = 145$. Also, $V_c \simeq V_w$ for sufficiently great conversion degrees, hence:

$$R_i \simeq f(\mathrm{I})/\tau \tag{12'}$$

Substitution of eq. (12′) in (10′) yields:

$$R_p = A\gamma f^{0.5}[(\mathrm{I})^{0.5}/\tau^{0.5}][\mathrm{M}] \tag{13}$$

In the derivation of eq. (13), the mechanism of copolymerization reaction in homogeneous system and also several complementary suppositions were taken into consideration. In the experimental section of this work, we checked on the adequancy of the above equation for the heterogeneous system we were studying.

In the case of a strong occlusion of macroradicals through polymer, the termination of the growth of macroradicals may occur equally through reaction with microradicals and primary radicals derived from the decomposition of the initiator.[14] In our opinion, that mechanism is likely to manifest itself especially at a strong concentration of the initiator in the system.

Let us suppose the existence of the stationary state in the continuous process; we then assume that the rate of initiation equals the rate of reaction of termination of the kinetic chain. Then:

$$k_{i1}[\mathrm{R}\cdot][\mathrm{M}_1] + k_{i2}[\mathrm{R}\cdot][\mathrm{M}_2] = k_{t1}[\mathrm{P}_1\cdot][\mathrm{R}\cdot] + k_{t2}[\mathrm{P}_2\cdot][\mathrm{R}\cdot] \tag{14}$$

where $[\mathrm{R}\cdot]$ is the concentration of primary radicals and microradicals, $[\mathrm{P}_1\cdot]$, $[\mathrm{P}_2\cdot]$ are concentration of the corresponding macroradicals, k_{i1}, k_{i2} are constants of the initiation reaction, and k_{t1}, k_{t2} are constants of the termination reaction.

Also:

$$k_{12}[\mathrm{P}_1\cdot][\mathrm{M}_2] = k_{21}[\mathrm{P}_2\cdot][\mathrm{M}_1] \tag{15}$$

The system of eqs. (14) and (15) allows for designation of the values $[\mathrm{P}_1\cdot]$ and $[\mathrm{P}_2\cdot]$ as functions of the concentration of monomers. After substitution of these values into the general equation for copolymerization rate:

$$R_p = k_{11}[\mathrm{P}_1\cdot][\mathrm{M}_1] + k_{12}[\mathrm{P}_1\cdot][\mathrm{M}_2] + k_{22}[\mathrm{P}_2\cdot][\mathrm{M}_2] + k_{21}[\mathrm{P}_2\cdot][\mathrm{M}_1] \tag{16}$$

where k_{11}, k_{12}, k_{21}, and k_{22} are constants of rate of growth of the correspondent macroradicals, and after some rearrangement, an equation is obtained for copolymerization rate having the form:

$$R_p = \frac{(k_{i1} + k_{i2}\gamma)\ (r_1 + 2\gamma + r_2\gamma^2)}{(r_1 k_{t1}/k_{11} + r_2 k_{t2}/k_{22}\gamma)(1 + \gamma)^2}\ [\mathrm{M}]^2 \tag{17}$$

where the designations are as above mentioned. Equation (17) may be written as follows:

$$R_p = B\gamma[\mathrm{M}]^2 \tag{17'}$$

where $B\gamma$ is the first term on the right-hand side of eq. (17). As follows from the eq. (17′) in the case of such conditions where the termination of macroradicals occurs through reaction with primary radicals, the rate of copolymerization would be independent of the concentration of the initiator. The testing of the suitability of eq. (17′), as well as of eq. (13), was achieved by the authors in the experimental part of the present work.

Let us consider the dependence of molecular weight of the copolymers on the particular parameters of the continuous process. Into the general equation for the number-average degree of polymerization:

$$\bar{P}_n = R_p/R_t = R_p/R_i$$

we introduce the values R_p and R_i from eqs. (12′) and (13); we then obtain:

$$\bar{P}_n = A\gamma f^{-0.5}(\mathrm{I})^{-0.5}\tau^{0.5}[\mathrm{M}] \tag{18}$$

In eliminating from eq. (18) the value [M] with the help of eq. (6), we obtain:

$$\bar{P}_n = \frac{A\gamma\ [\mathrm{M}]}{f^{0.5}(\mathrm{I})^{0.5}\tau^{-0.5} + fA\gamma\ (\mathrm{I})} \tag{19}$$

where [M] is the concentration of the monomer in the feed. The dependence of $\bar{P}_n$ on the degree of conversion p, can be evaluated by substituting into the general equation the value R_p obtained from eq. (6); then:

$$\bar{P}_n = p[\mathrm{M}]/\zeta f(\mathrm{I}) \tag{20}$$

For two different substrates creating one reaction product according to the scheme

$$\mathrm{A}_1 + \mathrm{A}_2 \rightarrow \mathrm{B}$$

the equation for the quantitative balance discussed above may be written as follows:

$$X_1 = pF_1 + (1 - p)f_1 \tag{21}$$

$$X_2 = pF_2 + (1 - p)f_2$$

where X_1, X_2 are mole fractions of substrates in the mixture introduced into the reactor, F_1, F_2 are mole fractions of substrates within the reaction product, f_1, f_2 are mole fractions of substrates in the mixture issuing from reactor, and p is the overall degree of conversion, i.e. the ratio of the molar quantity of both reacted substrates to the molar quantity of these substrates introduced into the reactor per unit time. In the case of copolymerization:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{22}$$

Equation (22) permits evaluation of f_1 as a function of F_1:

$$f_1 = \frac{2 r_2 F_1}{1 + 2\,F_1(r_2 - 1) + [1 - 4\,(1\text{-}r_1 r_2) F_1 F_2]^{0.5}} \tag{23}$$

After substitution of this value into eq. (21), the result is:

$$X_1 = F_1 \left\{ p + \frac{2\,(1 - p) r_2}{1 + 2\,F_2(r_2 - 1) + [1 - 4(1 - r_1 r_2) F_1 F_2]^{0.5}} \right\} \tag{24}$$

Equation (24) permits direct calculation of X_1 for the assumed F_1 and p, i.e., calculation of that composition of the mixture of comonomers introduced to the reactor which is necessary to obtain a copolymer of the required chemical structure in a continuous copolymerization process, of course at a given degree of conversion. Equation (24) was tested in the experimental part of our work.

3. EXPERIMENTAL

Raw Materials

For our investigations, we used purified acrylonitrile with $n_D^{20} = 1.3911 \pm 0.0005$; purified methyl methacrylate with $n_D^{20} = 1.4130 \pm 0.0010$; potassium persulfate (over 99% $K_2S_2O_8$); potassium pyrosulfite (about 96% $K_2S_2O_5$); Mohr salt, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$) of 99% purity; sulfuric acid, and doubly distilled, deaerated water.

Method

We carried out the continuous copolymerization in a glass reactor (Fig. 1) having an effective volume of 600 ml. and equipped with reflux condenser, thermometer, mixer, and overflow for the removal of reaction products.

The reactor was placed in a thermostat maintaining a temperature of 40 ± 0.5°C. We introduced the mixture of comonomers, (0.9645 mole of acrylonitrile and 0.0355 mole of methacrylate) directly at the mixer blades, through tube passing through the shaft of the mixer. At the surface of the mixture in the reactor, we simultaneously introduced: (*a*) an aqueous solution of potassium persulfate, (*b*) an aqueous solution of potassium pyrosulfite, and (*c*) an aqueous solution of Mohr salt, acidified with sulfuric acid sufficiently to maintain of the mixture in the reactor at pH 2.5. The weight ratio of potassium persulfate, potassium pyrosulfite, and Mohr salt was in all experiments 1:1.5:0.2.

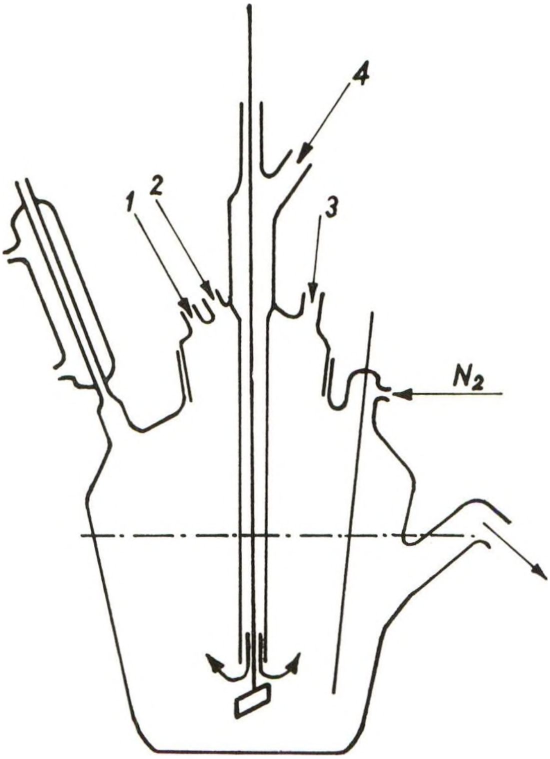

Fig. 1. Laboratory tank type reactor used for copolymerization of acrylonitrile.

The copolymerization reaction, carried out under an atmosphere of nitrogen purified of oxygen by conventional means, was started by introducing at a constant rate (regulated with an accuracy up to ±0.5%) substrates and solutions of initiators into the reactor previously filled with 400 ml. of water acidified with sulfuric acid to pH 2.5. Under given conditions, in about 5 hr. quasi-stationary state of the process was obtained. We continued separate tests for 7–9 hr. following the attainment of the above state, and then carried out measurements and analyses. Our graphs give the average values of at least three separate measurements. We applied, for different experiments, a concentration of monomers in the reactor within the limits of about 2–6 mole-%/l.; also the concentration of the initiator in the aqueous phase of the feed was controlled over a range of about 0.3–1.3 × 10^{-2} mole/l.

RESULTS

The preliminary experiments consisted in determining the length of time necessary to establish the stationary state for the continuous process in our apparatus and under the following reaction conditions: concentration of monomers in feed, 4.537 mole/l. of mixture; concentration of catalyst in feed: 0.37 × 10^{-2} mole/l. of water; residence time: 1 hr. For that pur-

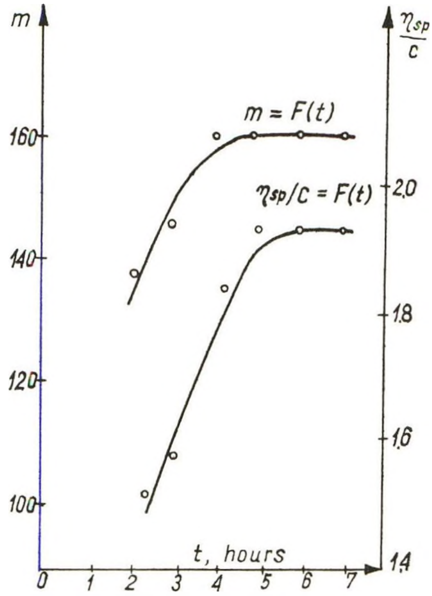

Fig. 2. Changes in weight of copolymer removed from the reactor with time and changes in η_{sp}/c of the copolymer.

pose, we studied changes of the quantity of polymer removed from the reactor as well as the viscosities of the polymer solutions in dimethylformamide. The results are given in Figure 2. We also investigated, by means of a microscope, the change in diameter of the copolymer particles removed from the reactor at different times of duration of the reaction. We found that during the first 3 hr. of reaction, small particles with a diameter of about 1×10^{-3} cm. were predominant. These small particles disappear, successively being replaced by larger ones, of a diameter from 1×10^{-3} cm. to 3×10^{-3} cm. After about 5 hr., particles of small diameter are there again appearing, and at the same time, the number of large particles rises. This distribution of dimensions of polymer particles now remains unchanged during the further course of the continuous process. This is illustrated in Figure 3. A more precise interpretation of changes as observed in dimensions of the appearing particles, will be presented in the next part of this work. According to the results obtained with regard to changes of the weight of formed copolymer, its viscosity and dimensions of its particles, it may be stated that the quasi-stationary state is attained 5 hr. after the beginning of the reaction under those conditions of the present experiments. As these conditions do not differ considerably from those used to the remaining tests, we began all measurements only after 6 hr.; of course, reproducibility of the measurements was checked.

In the first series of experiments we investigated the dependence of the degree of conversion and the rate of copolymerization on the concentration of monomers in the reactor, at different residence times. The initiator concentration in the aqueous phase of the feed and the ratio of comonomers

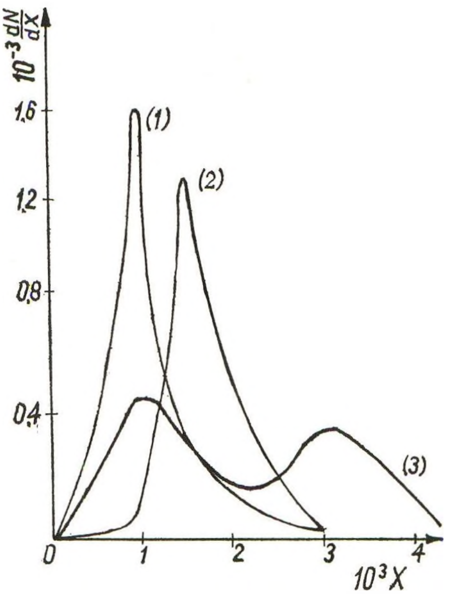

Fig. 3. Changes in diameter X (centimeters) of the copolymer particles during the first 6 hr. of the continuous process as a function of the distribution of diameters, dN/dX: (*1*) after 1 hr.; (*2*) after 4 hr.; (*3*) after 6 hr.

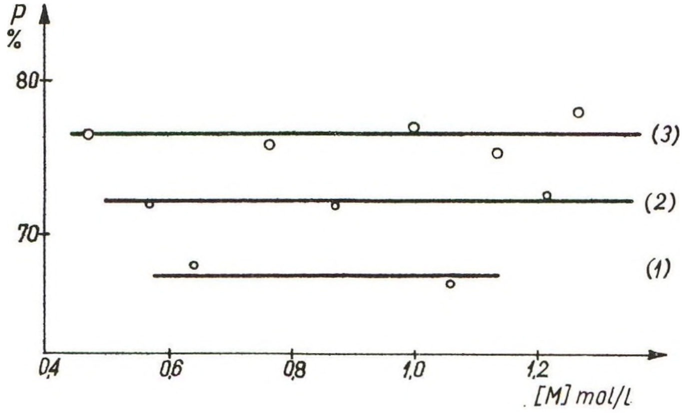

Fig. 4. Dependence of the degree of conversion p on concentration of comonomers in the reactor: (*1*) τ = 15 min.; (*2*) τ = 30 min.; (*3*) τ = 60 min.

in the feed were kept constant, i.e., (I) = 0.37×10^{-2} mole/l., acrylonitrile/methyl methacrylate = 0.9645/0.0355 mole. The rate of reaction was calculated on the basis of eq. (6), with help of data determined experimentally: degree of conversion (by weight) and the composition of copolymer obtained (established on the basis of analyses for nitrogen contents). Thereby it was possible to calculate the overall molar degree of conversion. The results are given in Figures 4 and 5.

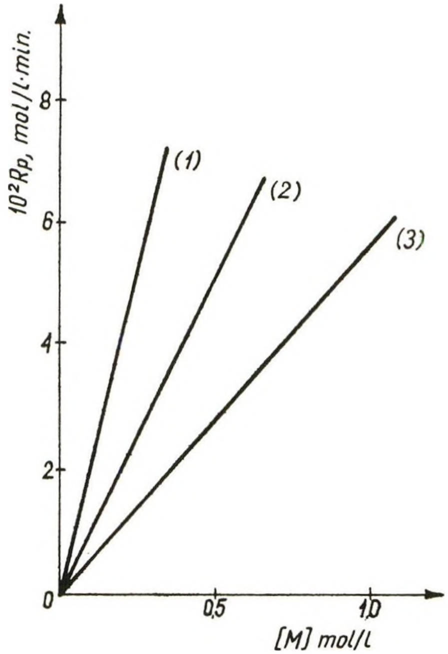

Fig. 5. Dependence of the rate of continuous copolymerization on concentration of comonomers: (*1*) τ = 15 min.; (*2*) τ = 30 min.; (*3*) τ = 60 min.

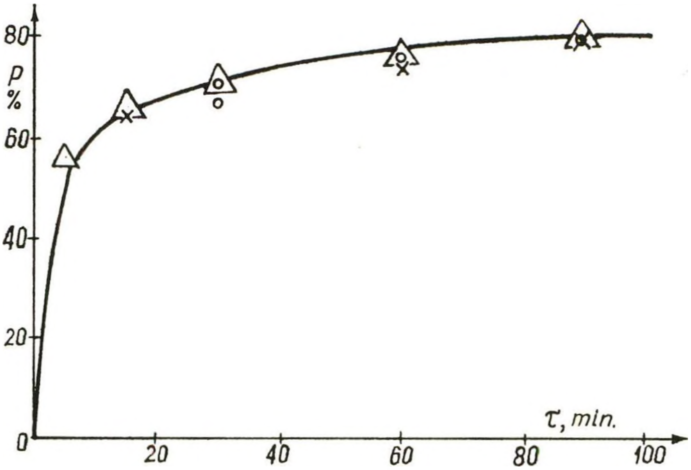

Fig. 6. Dependence of the degree of conversion p on for continuous acrylonitrile copolymerization: (△) 2.033 mole comonomers/l.; (×) 3.305 mole of comonomers/l.; (○) 4.575 mole comonomers/l.

The influence of residence time on the degree of conversion of copolymerization reaction for different concentrations of comonomers in the feed is shown in Figure 6. For a degree of conversion varying within the limits 60–80%, the molar fraction of acrylonitrile in the copolymer obtained changed only within the range of 0.948–0.958.

The data as shown in Figure 4 indicate that the copolymerization rate is proportional to concentration of comonomers in the medium, i.e., $R_p \propto [\mathrm{M}]$. Taking into account also the experimental data shown in Figure 6, it is possible to calculate the dependence of the ratio $R_p/[\mathrm{M}]$ on τ. A plot of this dependence expressed on a logarithmic scale is given in Figure 7. Calculating the slope of the plotted straight line in Figure 7, we obtained the dependence:

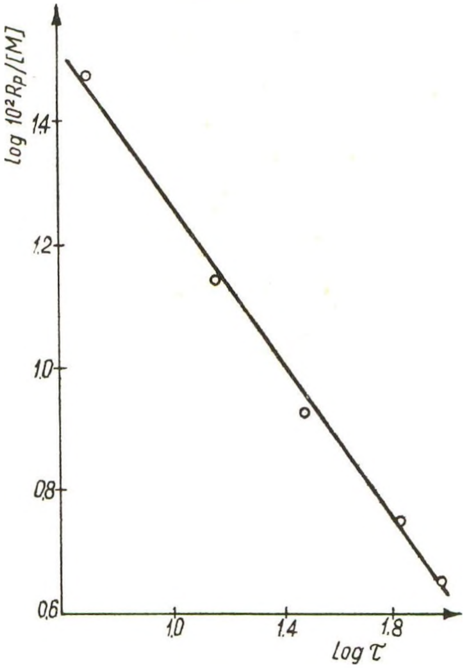

Fig. 7. Dependence of log $R_p/[\mathrm{M}]$ on log τ at T = 40°C., (I) = 0.37×10^{-2} mole/l. mixture.

$$R_p/[\mathrm{M}] \simeq \tau^{-0.65}$$

The straightness of the plot in Figure 7 indicates that the influence of moderate changes in the composition of the reacting system on the magnitude of the function $A\gamma$ is rather small.

In another series of experiments we studied the dependence of the degree of conversion and the rate of copolymerization on the concentration of initiators in the aqueous phase of the feed. The results are shown in Figure 8. As previously, the molar fraction of acrylonitrile in the copolymer changed slightly within the range 0.955–0.962. We were not able to use concentrations of initiators in the feed under 0.36×10^{-2} mole/l., owing to thickening of the polymer slurry and thus stopping of the flow.

The experimental data shown in Figure 8 indicate that the degree of conversion and the rate of reaction increase with increasing concentration of the

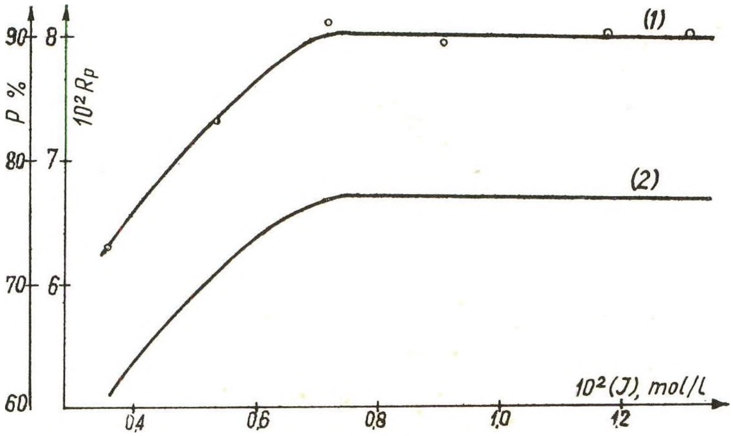

Fig. 8. Dependence of *(1)* degree of conversion on (I), $p = F(I)$, and *(2)* rate of polymerization on (I), $R_p = F(\mathrm{I})$, at $T = 40°\mathrm{C.}$, $\tau = 60$ min., and [M] = 4.575 mole/l. mixture.

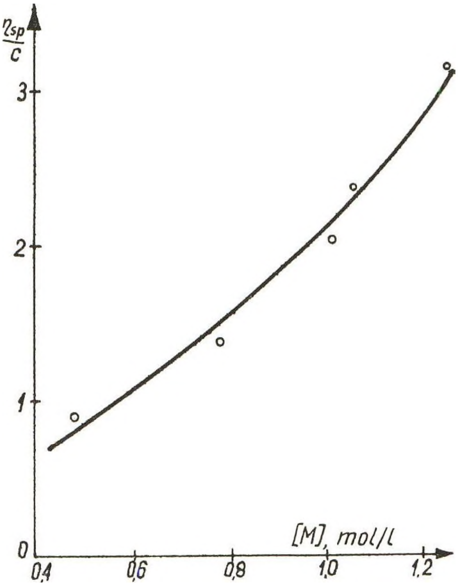

Fig. 9. Dependence of η_{sp}/c of copolymers on [M] at $T = 40°\mathrm{C.}$, $\tau = 60$ min., and (I) $= 0.37 \times 10^{-2}$ mole/l. water.

initiator in the feed up to a certain limit, and are thereafter independent of the concentration of the initiator.

We also determined the dependence of the molecular weight of copolymers (as η_{sp}/c in dimethylformamide) on the concentration of comonomers in the reactor and on the concentration of initiator in the feed (Figs. 9 and 10).

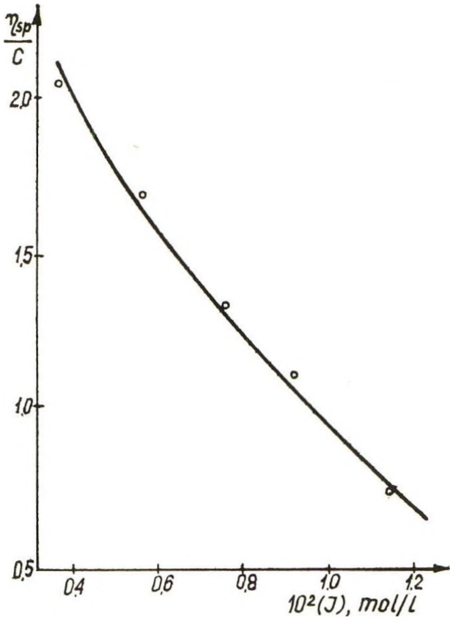

Fig. 10. Dependence of η_{sp}/c of copolymers on (I) at T = 40°C., τ = 60 min., and [M] = 4.575 mole/l. mixture.

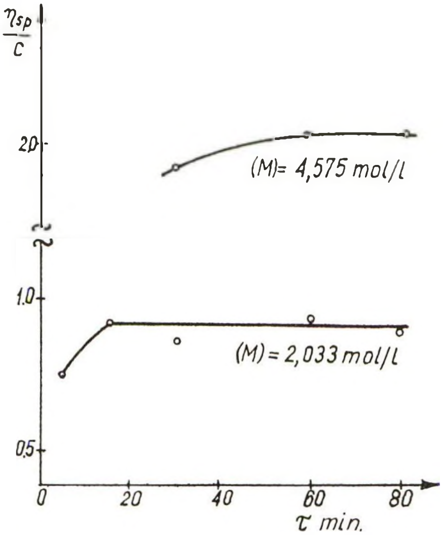

Fig. 11. Dependence of η_{sp}/c of copolymers on τ at T = 40°C., (I) = 0.37 × 10^{-2} mole/l water.

Further we studied the changes of η_{sp}/c at various τ and at constant concentrations of monomers and of initiator in the feed. The results are shown in Figure 11.

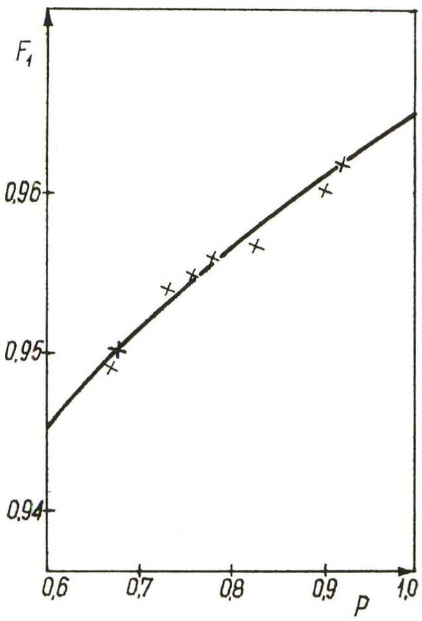

Fig. 12. Dependence of F_1 on p for the same compositions of the comonomer mixture in the feed ($X_1 = 0.9645$).

In all our previous experiments we determined the composition of copolymers obtained. It was hence possible to establish the experimental dependence of the composition of copolymers (expressed as F_1) on the degree of conversion. The results are given in Figure 12.

The points in Figure 12 are obtained experimentally, whereas the continuous curve is drawn as based upon the derived eq. (24) for the values $r_1 = 0.10$, $r_2 = 1.35$ as determined by Joshi.[15]

DISCUSSION

On the basis of determinations of the quantity of polymer formed within a given time interval, also of its molecular weight changes, we concluded that the quasi-stationary phase of the continuous process, under conditions used, begins after 5 hr.

The course of the process in the prestationary period features a change in dimensions of the precipitated polymer particles (Fig. 3). The disappearance of small particles during the first part of the prestationary process, as well as the increase in the average size of particles, shows that there are practically no new particles arising in the reacting system. New polymer molecules appearing in the water phase are thus entirely adsorbed on the surface of previously formed particles. As process continues, the number of particles in the reactor diminishes as a result of their elimination in the stream of the feed leaving the reactor. Thus the surface of the solid phase diminishes gradually, which deteriorates the conditions of adsorption. The concentration of comonomers in the water phase is simultaneously increasing, and this increases the rate of the formation of macromolecules. After some time (about 4–5 hr.), the rate of polymer formation in the water phase exceeds the possibility of completed adsorption, and yields a spontaneous start in the growth of new small polymer particles. This must lead to a state of balance, where the rate of formation of the particles equals the rate of their elimination from the reactor. Hence, at the quasi-stationary state, the quantity of particles in the reactor is practically constant. Thomas and Mallison[6] in certain cases observed sudden appearance of new small particles in the system. They considered this process to be cyclic. In our opinion, the cyclic appearance of an increased number of new particles and their disappearance, could result from oscillations around the state of balance we described. This phenomenon is probably related to the method of mixing. Also in the case of the periodical polymerization of acrylonitrile, maintenance of a constant quantity of precipitated particles of the polymer in reacting system has been observed.[16] However, this was evidently connected with a lack of formation of new particles, and differs from the phenomenon taking place in the continuous process. Taking into account the reaction conditions applied, the dimensions of particles we studied were considerably larger than those observed by Thomas.[16]

The completed experiments on the influence of the concentration of comonomers in the reactor upon copolymerization reaction rate basically confirm the suitability of our eq. (13).

We demonstrated experimentally that the reaction rate was proportional to the concentration of monomers:

$$R_p \propto [\mathrm{M}]\tau^{-0.65}$$

The exponent for τ experimentally found, however, differs from the theoretical one, this being equal to -0.5. This difference, in our opinion cannot be attributed to the simplifying assumptions involved in our derivation, i.e., that macroradicals are not eliminated from the reaction system. That assumption must not necessarily be entirely exact. However, the possibility of partial elimination of macroradicals occluded in polymer particles when leaving the reactor should contribute to increasing the exponent at τ, instead of diminishing it. That difference we may meanwhile ascribe to the influence of the heterogenity of the system, particularly to changes in structure of the particles of polymer with τ.

The independence of the degree of conversion from the comonomer concentration in the reactor (Fig. 4) at constant monomer ratio is due to the proportionality of the reaction rate to the concentration of comonomers. This may be easily demonstrated by substituting the reaction rate value from eq. (13) in eq. (8′).

The dependence of the copolymerization reaction rate on the concentration of initiator in the feed is, for initiator concentrations not above 0.7×10^{-2} mole/l. of water, qualitatively in accord with eq. (13). With a further increase of the concentration of initiator we noticed the reaction rate to be independent of (I), which is qualitatively consistent with eq. (17′). This indicates that, at high concentration of initiator, a change of the mechanism of the chain termination occurs. Such termination, under our experimental conditions, consists mostly in binding of macroradicals with primary radicals.

From investigations on changes of the molecular weight of copolymer with τ (Fig. 11), it follows that, at sufficiently long residence time (over 20 min.), the value of molecular weight is practically independent of residence time. From the derived equation, eq. (20), it follows on the other hand that the molecular weight should increase with the degree of conversion, which, in turn, increases imperceptibly together with increasing τ (Fig. 6.). This slight discrepancy may be, in our opinion, ascribed to the leveling influence of the transfer reaction of the kinetic chain to HSO_3^- ions[16] or to monomer.[17]

The experimental results show (Fig. 12) that the composition of copolymers obtained is consistent with the derived eq. (24). Usually, the presence of solid phase exerts an influence upon copolymer composition. It may result from selective adsorption of monomers. With the experimental conditions and comonomers used, this phenomenon can occur to only a very slight degree.

To obtain further confirmation of the accuracy of the derived equations and theoretical considerations we intend to carry out copolymerizations of acrylonitrile with other comonomers.

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Résumé

On a accompli des recherches sur la copolymérisation continue d'acrylonitrile avec le méthacrylate de méthyle en réacteur-citerne et en milieu hétéerogène. Il a été établi que la vitesse de réaction de la copolymérisation est en proportion directe avec la concentration de comonomères dans le réacteur ainsi qu'avec le temps de fluage $\tau^{-0.65}$. On fournit, à partir de recherches sur l'influence de la concentration d'initiateur sur la vitesse de réaction, la preuve du changement de mécanisme de la réaction de terminaison pour des concentrations supérieures d'initiateur dans le système. Il a été établi que le poids moléculaire des copolymères reste constant, aux temps de fluage suffisamment élevés. La composition des copolymères obtenus a été conforme aux prévisions théoriques. On a cherché à attribuer certaines divergences entre les équations déduites d'une part, et les résultats expérimentaux d'autre part, à l'influence de la nature hétérogène du système.

Zusammenfassung

Die kontinuierliche Copolymerisation von Acrylnitril mit Methylmethacrylat in einem tankförmigen Reaktor unter heterogenen Bedingungen wurde untersucht. Die Reaktionsgeschwindigkeit der Copolymerisation ist der Comonomerkonzentration im Reaktor und der Durchflusszeit zur Potenz $-0{,}65$ direkt proportional. Der Einfluss der Starterkonzentration auf die Reaktionsgeschwindigkeit lässt erkennen, dass bei höheren Starterkonzentrationen eine Änderung im Mechanismus der Abbruchreaktion stattfindet. Es wurde festgestellt, dass das Molekulargewicht der Copolymeren bei genügend hoher Durchflusszeit konstant ist. Die Zusammensetzung der gewonnen Copolymeren entsprach den theoretischen Voraussagen. Gewisse Abweichungen zwirschen den theoretischen Beziehungen und den Versuchsergebnissen werden auf den Einfluss der Heterogenität des Systems zurückgeführt.

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Dynamic Mechanical Behavior of Some High Polymers at Temperatures from 6°K.: Polyethylene, Nylon 66, Polypropylene, Poly(vinyl Chloride), Poly(*d,l*-propylene Oxide), Polybutene-1, Poly(4-methyl-Pentene-1), Poly(methyl Methacrylate), Poly(ethyl Methacrylate), Poly-4-methylpentene-1 and Poly(isobutyl Methacrylate)

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Synopsis

Measurements of the dynamic mechanical properties of various polymers have been made in the 6–300°K. temperature range at resonant frequencies of about 10^4 cycles/sec. by using a longitudinal vibration apparatus. The polymers studied include polyethylene, nylon 66, three poly(methacrylate esters), and five poly-α-olefins and related polymers. Results for poly(methyl methacrylate) and poly(ethyl methacrylate) indicate the occurrence of low temperature relaxation processes (6°K. and 52°K., respectively) involving configurational rearrangements in the hydrocarbon portion of the ester side groups. The data provide no evidence for mechanical loss processes associated with hindered rotation of the main-chain methyl groups in the poly(methacrylate esters) or polypropylene. Very weak relaxation processes or loss plateaus are observed in the 20°K. region for polypropylene, poly(vinyl chloride), poly(*d,l*-propylene oxide), poly(isobutyl methacrylate) and possibly nylon 66, while for poly-4-methylpentene-1 a sizeable loss peak is observed at 25°K. The mechanisms responsible for these loss peaks are not yet understood. No relaxation phenomenon is observed below 77°K. for either polyethylene or polybutene-1. For poly(*d,l*-propylene oxide) a loss maximum or shoulder appears at 70–120°K. which is possibly associated with chain motions accompanying the methyl reorientation process.

INTRODUCTION

At the present time a considerable amount of information[1] is available concerning the dynamic mechanical behavior of high polymers, over several decades of frequency, in the temperature range from 77°K. to their melting

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point. In addition, nuclear magnetic resonance (NMR)[2,3] and dielectric studies[4] have provided much additional information over comparable frequencies and temperatures. However, the dynamic mechanical properties of only a few polymers at temperatures below 77°K. have been reported,[5–9] with most of these measurements confined to frequencies of 1–10 cycles/sec.[5–7]

Mechanical loss maxima of low strength, attributed to methyl group reorientation, have been found[7] for polypropylene at 19°K. (6 cycles/sec.) and 53°K. (7 cycles/sec.), while a more noticeable maximum at 41°K. (9 cycles/sec.) has been reported[6] for poly(ethyl methacrylate), PEMA, presumably due to ethyl group reorientation. For poly(methyl methacrylate), PMMA, a minimum in the mechanical loss at 26°K. (1–10 cycles/sec.),[6] a maximum at 110°K. (6–40 kcycles/sec.),[8] and another maximum at ~100°K. (1 cycles/sec.)[10] have been reported. In order to obtain further information about low temperature relaxation processes for these polymers, internal friction and resonant frequency (f_0) measurements were obtained from 6°K. at frequencies of about 10^4 cycles/sec. using longitudinal vibrations. As a result of this study it is believed that some modifications in the interpretations of past results are necessary. Data have also been obtained for high density polyethylene, poly(hexamethylene adipamide); nylon 66; poly(*d,l*-propylene oxide), PdlPO; poly(vinyl chloride), PVC; polybutene-1, PB1; poly-4-methyl-pentene-1, P4MP1; and poly(isobutyl methacrylate), PiBMA; these are presented and discussed herein.

EXPERIMENTAL

The apparatus and procedures for measuring the dynamic mechanical properties have been described previously.[9] The band-width method of measuring Q^{-1} was used to obtain all data except for polyethylene, PB1, and PMMA at low temperatures, for which the free-decay method was employed.

Some characteristics of the samples used are given in Table I. The PVC, P4MP1, and nylon 66 specimens were received as rods which were subsequently machined to the dimensions given. The other specimens were formed in these laboratories by the molding technique indicated in Table I and then machined to the dimensions given. In attempts to improve the resonance curves for PEMA, polypropylene, PdlPO and PB1 obtained in initial runs, the specimens were shortened from length 1 (l_1) to length 2 (l_2) given in Table I.

The PMMA was prepared at the Rohm and Haas research laboratories and was found to have a number-average molecular weight of 8×10^4; the PEMA and PiBMA were reported as plasticizer-free. Prior to molding, the PdlPO was dissolved in benzene and washed repeatedly with a dilute solution of HCl in distilled water. When no trace of catalyst remained, as determined by using KSCN, the solvents were removed by freeze-drying the polymer. The PB1 was mixed with isopropyl alcohol and repeated

TABLE I
Sample Characteristics

Sample	Supplier	Length, cm.	Diameter, cm.	Density, g./cc.	Molding history	Approximate crystallinity, %
PMMA	Rohm and Haas	13.7	0.635	1.179 (23°C.)	500–1000 psi compress. at 160°C.	0
PEMA	du Pont	15.2(l_1) 12.7(l_2)	0.635	1.121 (20°C.)	500–1000 psi compress. at 150°C.	0
PiBMA	du Pont	15.0	0.762	1.044 (25°C.)	500–1000 psi compress. at 150°C.	0
Polyethylene (Marlex 50)	Phillips Petroleum	15.2	0.762	0.968 (25°C.)	Zone-cooled from 140°C.	90[a]
Polypropylene (unannealed)	Hercules Powder	13.7	0.762	0.903 (25°C.)	Zone-cooled from 180°C.	
Polypropylene (annealed)	Hercules Powder	13.7(l_1) 13.4(l_2) 13.25(l_3)	0.762	0.914 (25°C.)	Annealed at 160°C.	74[b]
PVC	Goodrich	15.2	0.762	1.386 (26°C.)	Extruded	10–30
PdlPO	Dow	13.3(l_1) 12.7(l_2)	0.762	1.048 (25°C.)	Zone-cooled from 80°C.	Low
PB1	Union Carbide	14.6(l_1) 14.3(l_2)	0.748	0.922 (20°C.)	Zone-cooled from 135°C.	45[b]
P4MP1	Union Carbide	11.0	0.762	0.829 (23°C.)	Compression	∼50[c]
Nylon 6-6	du Pont	15.2	0.762	1.148 (25°C.)	Compression	50[d]

[a] From x-ray measurements.[11]

[b] From density by use of equation of Danusso et al.[12]

[c] Value found for a similar sample by an NMR technique.[13]

[d] From density by use of the equation of Starkweather and Moynihan.[14]

washing made with a dilute solution of HCl in distilled water until no detectable trace of catalyst remained. The solvents were then removed by heating under vacuum. Extraction of the polypropylene powder was carried out with boiling n-heptane.

The zone-cooling was carried out at about 1 μ pressure at a heater removal rate of about 5 cm./hr.

Densities were determined by the displacement technique with the use of either absolute alcohol or distilled water as the liquid at room temperature. The estimated error in the values shown in Table I is ±0.001 g./cc.

The annealed polypropylene sample was obtained by taking the unannealed one following dynamic mechanical determinations and heating it under vacuum at 140°C. for 7 days then at 160°C. for 8 hr., followed by slow cooling to room temperature.

RESULTS

The results obtained for two linear polymers, high density polyethylene and nylon 66, are given in Figures 1 and 2, respectively. For these materials, as well as all other polymers tested, the elastic storage modulus E' was calculated from the resonant frequency f_0 ($E' = 4l^2\rho f_0^2$, where l and ρ are the sample length and density, respectively), with the use of room, temperature values of the length and density. No loss maxima below 75°K. are apparent for either polyethylene or nylon 66, but both polymers show an upswing starting at about 45°K. which is a manifestation of the so-called γ peak found at 165–170°K. (10^3 cycles/sec.).[11,15] It should be noted that the damping in the temperature range below 75°K. is 3–4 times larger for nylon 66 than for linear polyethylene.

The data for polyethylene shown in Figure 1 from 6 to 45°K. were obtained by using the free-decay method and those from 45 to 80°K. by using the band-width method.[9] A discontinuity in Q^{-1} is found at 45°K. as a consequence of a change from the free-decay to the band-width type measurement. The reason for the discrepancy between the two methods is not

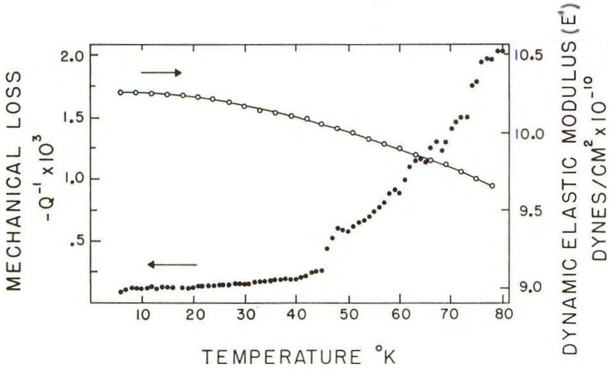

Fig. 1. Mechanical loss and dynamic elastic storage modulus vs. temperature for linear polyethylene.

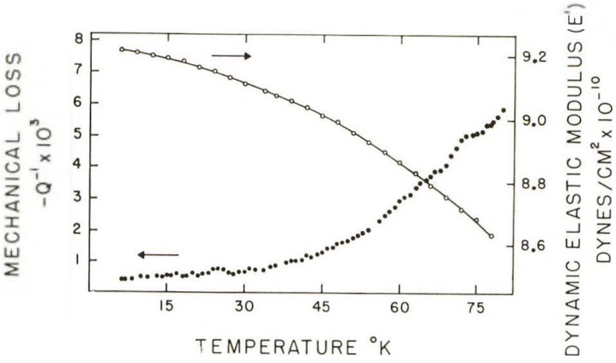

Fig. 2. Mechanical loss and dynamic elastic storage modulus vs. temperature for nylon 66.

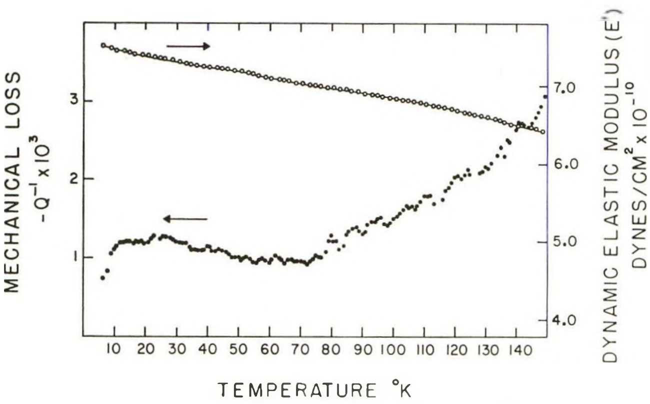

Fig. 3. Mechanical loss and dynamic elastic storage modulus vs. temperature for isotactic polypropylene (annealed).

known. A discrepancy also occurred for PB1 (see Fig. 6) and PMMA, but none was observed for a lead specimen.[9] A second run was made with the same polyethylene specimen, the free-decay method being used alone in the 10–42°K. region, both methods in the 41–50°K. region, and the band-width method alone from 50 to 60°K. at 1°K. intervals. The values in the second free-decay run are lower than those in the first by about 40% at 10°K. and 10% at 20°K., with the two sets of data agreeing within ±3% in the temperature range of 25–45°K. A Q^{-1} value for polyethylene at 10°K. of 6.7×10^{-5} was the smallest found for any of the polymers investigated.

It can be seen in Figures 1 and 2 and in some subsequent ones that at temperatures where the band-width method was used a small modulation of the Q^{-1} values may take place, an effect which was subsequently identified as due to friction in the drive shaft coupling the level recorder to the sweep oscillator. This is most pronounced when the band width corresponds to a change in oscillator frequency which is equivalent to a half revolution of the drive shaft. A similar effect was found to occur if the worm

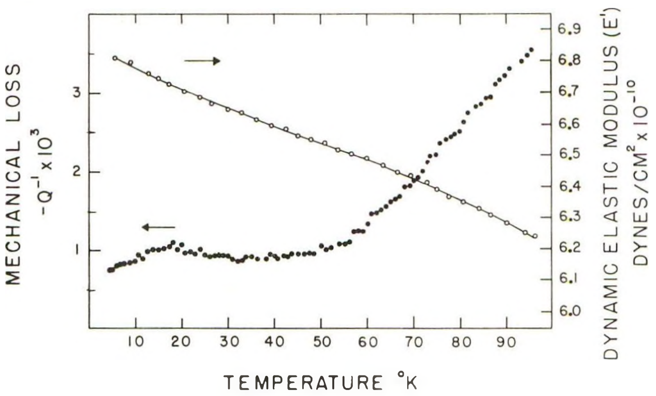

Fig. 4. Mechanical loss and dynamic elastic storage modulus vs. temperature for poly(vinyl chloride).

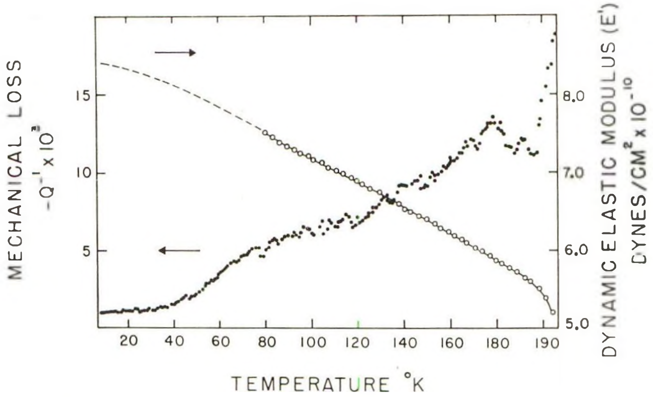

Fig. 5. Mechanical loss and dynamic elastic storage modulus vs. temperature for poly(*d,l*-propylene oxide).

gear coupling the drive shaft to the variable capacitor of the oscillator was slightly eccentric.

Results for an annealed isotactic polypropylene sample obtained in the 6–150°K. temperature range are given in Figure 3. The data given for temperatures of 7–80°K. were obtained at sample length l_1 while those at 80–150°K. were taken seven months later at length l_2. A third run at 102–150°K. was made three months after the second run at length l_3 with essentially the same results as those shown in this temperature range.

A weak flat maximum is apparent at 10–30°K (10 kcycles/sec.). The isotactic polypropylene sample was also run prior to the annealing treatment (length l_1) with the result that the damping maximum was about 20% larger and the dynamic storage modulus about 10% smaller. The observed Q^{-1} peak in Figure 3 has similar strength and width as the one reported by Sinnott[7] centered at 19°K. (6 cycles/sec.). However, the maximum reported by that author at 53°K. (7 cycles/sec.) for a 75% crystalline sample

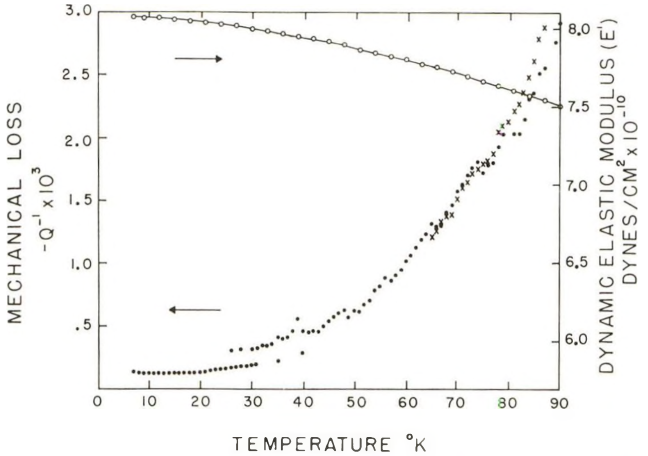

Fig. 6. Mechanical loss and dynamic elastic storage modulus vs. temperature for polybutene-1: (●) length l_1; (×) length l_2.

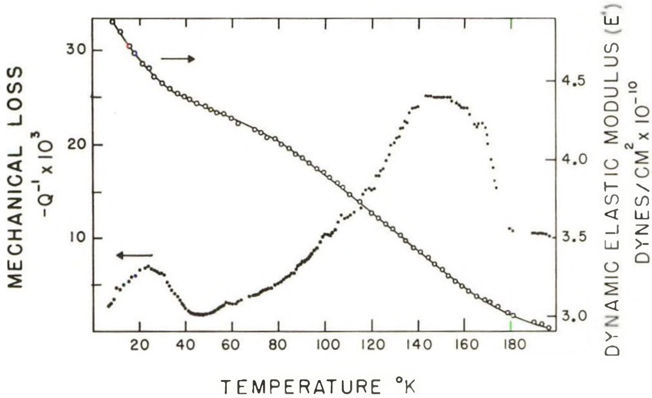

Fig. 7. Mechanical loss and dynamic elastic storage modulus vs. temperature for poly-4-methylpentene-1.

was not observed at this or higher temperatures for the present specimen in either the unannealed or annealed state. Additional measurements (not shown in Fig. 3) were made on the annealed sample at temperatures up to 270°K., with the secondary peak found previously[16] at 230°K. or greater (10^3 cycles/sec.) being apparent.

The dynamic mechanical properties of PVC are shown in Figure 4. A loss maximum is found at ~18°K. (7225 cycles/sec.) with about the same characteristics as that for polypropylene. A plateau in Q^{-1} in this temperature region with values of the order of those for the maxima in polypropylene and PVC is found for a related polymer PdIPO (see Fig. 5). In addition, PdIPO also exhibits a broad shoulder in Q^{-1} in the 70–120°K. region (10 kcycles/sec.) and a sharp peak at 180°K. (9343 cycles/sec.). From measurements with the use of a torsional pendulum a loss maximum

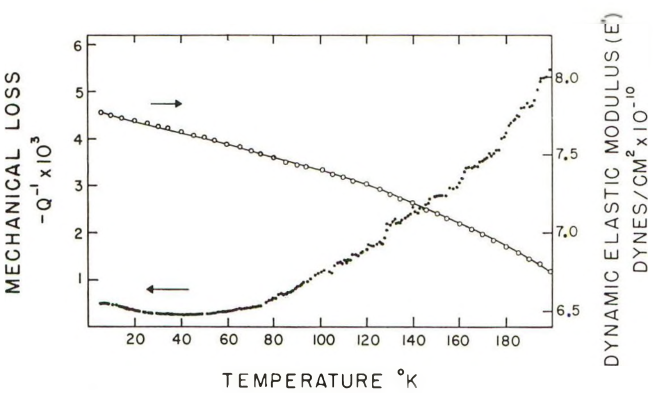

Fig. 8. Mechanical loss and dynamic elastic storage modulus vs. temperature for poly(methyl methacrylate).

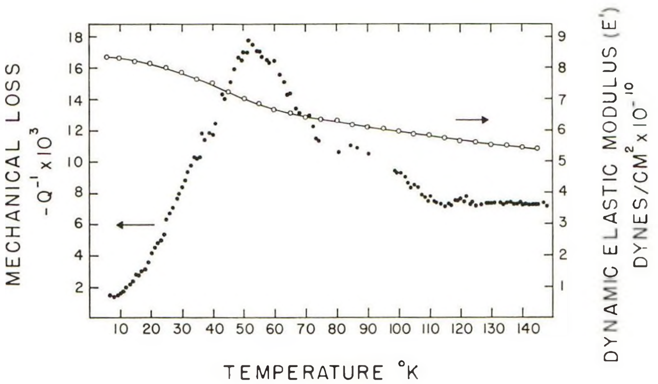

Fig. 9. Mechanical loss and dynamic elastic storage modulus vs. temperature for poly(ethyl methacrylate).

was previously reported[17] at 120°K. (0.59 cycle/sec.). When the E' values were calculated from the experimental f_0 values for PdlPO, a discontinuity was observed at about 80°K., the values at temperatures below 80°K. being calculated to be 0.50×10^{10} dynes/cm.^{2} larger at all temperatures than the dotted line given in Figure 5. The sample used for these measurements was first run at 6–80°K. (length l_1) and was shortened to length l_2 and run at 80°K. six months later. It is believed that an error was made in measuring or recording the original specimen length which could lead to such a constant error in the calculation of E' in the 6–80°K. region.

Measurements were carried out on two other poly-α-olefins, PB1 and P4MP1, the results being given in Figures 6 and 7, respectively. For PB1 a run was first made at 6–90°K. by the band-width method, followed by a second run at 7–40°K. a month later by the free-decay method, both with sample length l_1. It should be pointed out that only the data taken at 26–90°K. in the first run are shown in Figure 6. After shortening the sample a third run was made three months later at 65–135°K. by the band-width

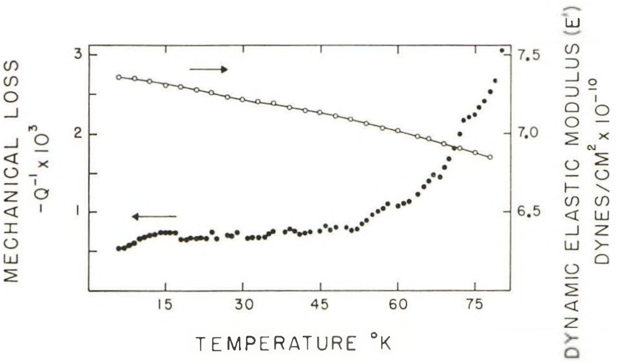

Fig. 10. Mechanical loss and dynamic elastic storage modulus vs. temperature for poly(isobutyl methacrylate).

method. The E' values given in Figure 6 from 65°K were calculated using the f_0 values for the first run.

No maxima are evident for PB1, the upswing at higher temperatures being a manifestation of the γ peak found at 150°K. (3160 cycles/sec.).[18] A small upswing at low temperatures was observed, Q^{-1} values of 1.16×10^{-4} and 1.3×10^{-4} being found at 12 and 6°K., respectively. The discontinuity at low temperatures due to the change in measuring method has already been noted above. In contrast to PB1, the data for P4MP1 shows a well defined low temperature maximum at 25°K. (10,066 cycles/sec. The γ peak[19] is also evident at 150°K. (9031 cycles/sec.); the data on the high temperature side of this latter maximum may be distorted due to apparatus resonance.

In Figures 8, 9, and 10 data are given for three poly(methacrylate esters), the methyl, ethyl and isobutyl esters, respectively. The data shown for PMMA at 6–77°K. were obtained by the free-decay method and those above 77°K. by the band-width method. The Q^{-1} values at 77°K. are 4.96×10^{-4} (free decay) and 5.65×10^{-4} (band width). After the sample had been held at 77°K. for about 24 hr., a number of Q^{-1} measurements were made at this temperature by both methods, values of $(4.41 \pm 0.06) \times 10^{-4}$ (average of five determinations) for the free-decay and $(4.58 \pm 0.09) \times 10^{-4}$ (average of nine determinations) for the band-width method being found. Although a difference in values obtained by the two methods exists, it is smaller for PMMA at 77°K. than for PB1 and polyethylene at low temperatures. Furthermore, establishment of temperature equilibrium and making simultaneous measurements to avoid thermal history effects appears to minimize the differences.

The data given in Figure 9 for PEMA were obtained as follows. Determinations were first made at 6–260°K. with length l_1. Due to poor resonance curves, it was necessary to discard the Q^{-1} data in the 42–80°K. range. Since difficulties were also encountered in the 80–110°K. region due to an apparatus resonance, the few Q^{-1} points given in that region are approxi-

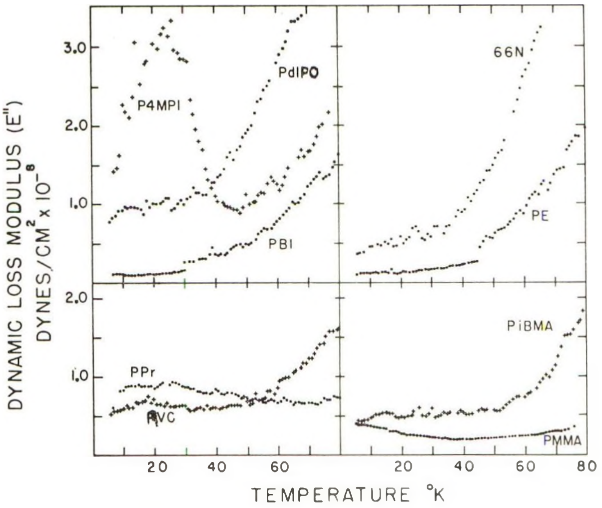

Fig. 11. Dynamic loss modulus at 6–80°K. for polyethylene (PE); nylon 66 (66N); poly-4-methylpentene-1 (P4MP1); poly(*d,l*-propylene oxide), (PdlPO); poly(butene-1) (PB1); polypropylene (PPr); poly(vinylchloride) (PVC); poly(isobutyl methacrylate) (PiBMA); and poly(methyl methacrylate) (PMMA).

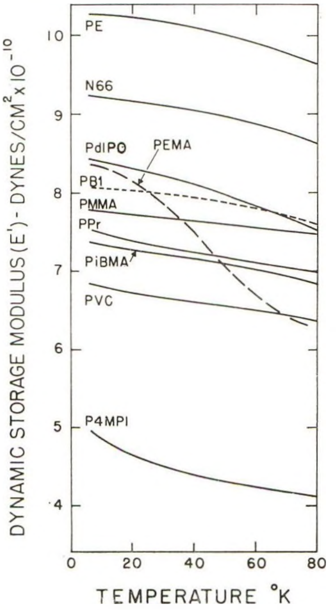

Fig. 12. Dynamic storage modulus at 6–80°K. for various polymers.

mate only. To obtain the data from 44 to 80°K. the sample was shortened and rerun.

For PMMA a weak apparent maximum is found at about 6°K. (9384 cycles/sec.), a result in agreement with previous work at lower frequencies.[6]

TABLE II

Summary of Low Temperature Relaxation Processes

Sample	Max. temp. of test, °K.	$T_{\max}$, °K.	$\nu_{\max}$, kcps	$Q^{-1}_{\max} \times 10^3$	Remarks
Polyethylene	77	No peaks	—	—	—
Polypropylene	270	$\sim$24	10.04	1–1.5	Very weak, broad
		246	9.05	18	—
Poly(vinyl chloride)	95	$\sim$18	7.23	1	Weak, broad
Poly(*d*,*l*-propylene oxide)	205	$\sim$20	10.87	$\sim$1	Weak shoulder
		$\sim$90	10.43	$\sim$6	Broad shoulder
		180	9.34	14	Sharp
Polybutene-1	135	No peaks	—	—	—
Poly-4-methylpentene-1	200	25	10.07	7	Sharp, symmetric
		$\sim$150	9.03	25	Very strong
Nylon 66	80	No peaks	—	—	—
Poly(methyl methacrylate)	200	$\sim$6	9.38	$\sim$0.5	Slight upswing below 30°K.
Poly(ethyl methacrylate)	260	52	9.84	18	Very strong
Poly(isobutyl methacrylate)	80	No peaks	—	—	—

When an unpurified commercial PMMA sample was investigated, the results were markedly different from those given in Figure 8, two maxima being found, one at 42°K. (14,280 cycles/sec.) and the other at 140–170°K. The origin of these maxima have not been systematically investigated to date, but are thought to be due to the presence of either plasticizer or higher poly(methacrylate esters). The small maxima at about 100°K. (1 cycles/sec.)[10] and 110°K. (6–40 cycles/sec.)[8] reported previously for PMMA may have a similar origin to that found at 140–170°K. in this investigation for the unpurified sample. A test was also made on a purified PMMA specimen containing 1.05 wt.-% water in the 77–180°K temperature range. Although the damping was found to rise more steeply with increasing temperature than that for dry purified PMMA, no additional maxima were evident.

For PEMA a Q^{-1} maximum at 52°K. (9836 cycles/sec.) is noticeable in Figure 9. A maximum of similar shape located at 41°K. (9.02 cycles/sec.) has been reported by Sinnott.[6] Sandiford[20] also finds a peak for PEMA but reports the $T_{\max}$ as 62°K. at a frequency of 470 cycles/sec. This apparent discrepancy with the present data may be a result of differences in specimen composition and purity. Finally an upswing in Q^{-1} was found to start at about 170°K.

The test results for PiBMA (Fig. 10) show a plateau in Q^{-1} from about 10 to 50°K. with damping values about three times those for PMMA above 30°K.

The dynamic loss modulus (E'') has been calculated from the equation, $E'' = Q^{-1}E'$, and the values in the 6–80°K. region for all the polymers studied except PEMA are given in Figure 11. E'' values obtained for PEMA at 7, 20, 30, 40, 52, 60, and 75°K. are 1.15, 3.39, 6.40, 8.79, 12.32, 11.06, and 7.28 $\times$ 10^{-8} dynes/cm.^{2}, respectively. With the exception of P4MP1 and PEMA these polymers have E'' values of 1 $\times$ 10^8 dynes/cm.^{2} or less in the 6–40°K. range; the lowest values are found for polyethylene and PB1, those for PMMA, nylon 66, PiBMA, and PVC being next, and those for polypropylene and PdlPO the largest for the eight polymers.

To facilitate comparison, lines representing the dynamic elastic storage modulus E' at 6–80°K. are given in Figure 12 for the ten polymers studied. It is seen that the two linear polymers have the highest E' values while P4MP1 has the lowest ones in this temperature region.

Finally, a summary of the relaxation phenomena found in this study is given in Table II.

DISCUSSION

Polyethylene

As might be expected, the dynamic mechanical behavior at very low temperatures for high density polyethylene—a polymer comprised of linear sequences of CH_2 units having essentially no side groups but a high degree of crystalline order—reflects little, if any, molecular activity. Indeed, the experimental values of the internal friction are extremely small, and at very low temperatures approach in magnitude values observed for some metals, for example lead, which is found to have a Q^{-1} of 6×10^{-5} at 6°K.[9] In fact the loss modulus E'' at 6°K. for this metal (0.156×10^8 dynes/cm.^{2}) is larger by a factor of about two than that for polyethylene (0.07–0.09×10^8 dynes/cm.^{2}). This molecular inactivity for polyethylene is also reflected in the storage modulus, which at 6°K. ($E' = 10.2 \times 10^{10}$ dynes/cm.^{2}) is the highest found for any polymer to date but is a factor of about $2^1/_2$ lower than that for lead (26×10^{10} dynes/cm.^{2}).

Poly-α-olefins and Related Polymers

The weak broad loss maximum in isotactic polypropylene at ~24°K. was previously assigned by Sinnott[7] as due to hindered methyl group rotation in the amorphous parts of the polymer. On the basis of nuclear magnetic resonance measurements, including measurements of line width and spin-lattice relaxation time, T_1, and in light of the present dynamic mechanical results for PVC, this assignment appears to be incorrect.

For highly amorphous atactic polypropylene a line-narrowing process occurs in the <77–120°K. range which, according to theoretical second-moment calculations, is believed to be due to methyl group reorientations.[21] Since the effective frequency of this reorientation is about 10^4–10^5 cycles/sec., any mechanical loss peak associated with such motions should also occur in the <77–120°K. range when a measuring frequency of this magnitude is employed. Spin-lattice relaxation time measurements[22,23] fail to show more than one minimum in the 77–300°K. region, the position of this minimum being essentially the same for atactic and isotactic material. Since the reorientation frequency for these measurements is of the order of 3×10^7 cycles/sec., it might be expected that this hypothetical second process, although not visible above 77°K. at 10^4–10^5 cycles/sec., would give rise to a second minimum in T_1 measurements. This is the case for ester methyl reorientation processes in PMMA[24–26] and poly(methyl acrylate).[10,25,26]

Further support for the above arguments is provided by the results for PVC. If the small mechanical loss maximum observed at 24°K. for polypropylene is in fact a manifestation of methyl group rotation, then replacement of the methyl groups by chlorine atoms should significantly alter the low temperature behavior. The presence of a similar small loss peak for PVC at ~18°K. strongly suggests that the observed loss peak in polypropylene is not associated with methyl group rotation.

Although the evidence appears fairly conclusive that the broad but small peak found in polypropylene is not related to methyl group rotation, the mechanism underlying it is not yet understood.

Annealing of the polypropylene sample, which results in a density increase, causes a decrease in the height of both the E'' and Q^{-1} maxima by about 10%, suggesting that this process may be associated with motions in disordered or defect regions of the polymer. However, a peak or plateau in E'' in the 10–40°K. temperature region is apparent for moderately crystalline polymer samples of polypropylene, P4MP1, and possibly nylon 66, for slightly crystalline samples of PVC and PdlPO, and for essentially amorphous specimens of PiBMA, poly-*o*-methylstyrene ($Q^{-1}{}_{\max} = 5.3 \times 10^{-3}$ at 37°K.),[27] a polyvinyltoluene copolymer containing 65% *m*-methylstyrene and 35% *p*-methylstyrene ($Q^{-1}{}_{\max} = 3.5 \times 10^{-3}$ at 37°K.),[27] a 76% styrene–24% acrylonitrile copolymer ($Q^{-1}{}_{\max} = 3.2 \times 10^{-3}$ at 30°K.),[27] and poly-α-methylstyrene ($Q^{-1}{}_{\text{plateau}} \sim 2 \times 10^{-3}$ at 10–50°K.).[27] The magnitude of $E''_{\max}$ appears to have no connection with crystallinity.

Bordoni[28] has reported loss peaks at about 10^4 cycles/sec. for various face-centered cubic metals, these maxima occurring at temperatures of about one third the Debye temperature. These have been interpreted in terms of oscillatory motions of crystal dislocations under the influence of an applied stress. A loss maximum at 20°K. for crystalline synthetic quartz, a process absent in amorphous samples, has been attributed to the same cause.[29] This explanation does not appear to apply to the phenomena observed in polymers, since a number of the samples which exhibit these low temperature loss processes are highly amorphous.

Another possibility is that motion caused by the presence of impurities such as exchange gas atoms, monomer, metal atoms or compounds, decomposition products, etc., is responsible for the process. For example, an internal friction peak at 50°K. reported for hydrogen-charged steel[30] has been associated with stress-biased diffusion of hydrogen atoms. However, stress-biased diffusion of helium exchange gas atoms does not appear to be the proper explanation of the 25°K. loss maximum in P4MP1, since substitution of neon for helium brought about no change in this maximum. Although the effects of impurities such as monomer or catalyst fragments have not been systematically studied, the fact that a partially purified PdlPO sample showed a plateau in the 10–40°K. range would appear to make the presence of such impurities a doubtful cause of this phenomenon. It should be pointed out that after molding the PdlPO sample was discolored, but similar discoloration was also found in the PBI specimen, a material which does not show a maximum at low temperatures.

Upon examination of the P4MP1 specimen after making measurements, it was found to be composed of layers of polymer pressed together which could be easily separated from each other. It is possible therefore that stress-biased slipping of the layers accounts for the loss peak at 25°K. as well as for the low values of E' compared to the other polymers studied (see Fig. 12).

It appears that further studies are necessary before the mechanism responsible for the process or processes at about 20–30°K. can be given with any certainty.

PdlPO appears to be unique, in that it shows two additional processes in the 40–200°K. temperature region. Similar results have been obtained in recent dielectric loss studies[31] and an NMR line-narrowing process, presumably due to methyl group reorientation ($\sim 10^4$–10^5 cycles/sec.) occurs in the ≤ 77–110°K. region.[32] In light of the later result it would seem appropriate to assign the ~90°K. mechanical loss process to motion of the methyl substituent or of other units as a consequence of or in cooperation with the methyl reorientation. However, processes of this nature are not apparent above the background loss in the dynamic mechanical data for PMMA, PEMA, or isotactic polypropylene, all of which show NMR line narrowing in the 77–200°K. region attributed to α-methyl reorientations.[10,13,21,24] This discrepancy may be due to the fact that this process is affected by chain flexibility, which appears to be greater for PdlPO than for the other three polymers, as reflected in a lower glass transition temperature.

The large maximum at about 180°K. for PdlPO has been tentatively attributed[17] to cooperative torsional motions of a few chain units in the amorphous region. It is believed that this secondary maximum in PdlPO and those found for polypropylene (~230°K., 10^3 cycles/sec.)[16] and PVC (280°K., 570 cycles/sec.)[33] are caused by a similar mechanism. On the basis of the mechanical loss data obtained at 0.6 cycles/sec.[17] and 10^4 cycles/sec. (present work) and dielectric loss data obtained in the 50–10^5 cycle/sec. region,[31] a plot of $\ln f_0$ versus $1/T_{\max}$ gives a straight line yielding an activation energy of 8 kcal./mole. This is comparable with the value of 13 kcal./mole found by using numerous data for polypropylene.[34]

The strong loss maximum at 150°K. shown by P4MP1 is believed to be due mainly to side chain reorientations as discussed previously.[19]

In contrast to the other poly-α-olefins studied, PB1 has Q^{-1} values similar to those for polyethylene at temperatures below about 40°K. This is one of the facts which makes assignment of a molecular origin to the 24°K. process difficult.

Poly(methacrylate Esters)

The small mechanical loss process apparent for PMMA in this investigation around 6°K. had been tentatively assigned, on the basis of low frequency data only, to hindered ester methyl group rotation.[6] In view of the data in Figure 8, there is now little doubt that a low temperature maximum is exhibited by this polymer, and the assignment given appears plausible. The weakness of this process would be explained as a consequence of the symmetry of CH_3 rotation, and would account for the nonobservance, by dynamic mechanical methods, of α-methyl group motion in the polymethacrylates and in polypropylene above the sizeable background losses that are present at the temperatures at which these processes occur. The assignment of the low temperature process to side chain methyl group reorientation also receives support from NMR investigations,[25,26] which show a T_1 minimum attributed to such motion in the neighborhood of 77°K.

The large loss peak observed at 52°K. in PEMA has been attributed to configurational rearrangements involving the side chain ester ethyl groups.[6] In view of the absence of this peak for PMMA, such an assignment appears correct. In addition, a T_1 minimum attributed to ethyl group motion was found at 143°K. (3.5×10^7 cycles/sec.).[20] By using mechanical loss values obtained by Sinnott,[6] Sandiford,[20] and in the present work along with the T_1 minimum data,[20] an activation energy of 2 kcal./mole is obtained. Due to the ambiguities in the data, mentioned in the experimental section, this value is to be considered only an estimate.

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Résumé

Des mesures de propriétés mécaniques dynamiques de plusieurs polymères ont été effectuées dans la région de 6–300°K à des fréquences de résonance d'environ 10^4 cps en utilisant un appareil de vibration longitudinale. Les polymères étudiés sont le polyéthylène, le nylon 66, trois polyesters méthacryliques, cinq poly(alpha-oléfines) et des polymères du même genre. Les résultats pour le polyméthacrylate de méthyle et le polyméthacrylate d'éthyle indiquent des processus de relaxation à basse température (6 et 52°K respectivement), comprenant des réarrangements de configuration dans la partie hydrocarbonée des groupements esters latéraux. Les résultats ne permettent pas la mise en évidence de processus de perte mécanique associée à une rotation inhibée des groupements méthyles de la chaine principale des polyesters méthacryliques ou du polypropylène. Des phénomènes de relaxation très faibles qui se traduisent par une diminution du plateau, sont observés dans la région de 20°K pour le polypropylène, le chlorure de polyvinyle, le poly(*d,l*-propylène-oxyde), le polyméthacrylate disobutyle et probablement le nylon 66, tandis que pour le poly(4-méthyle-pentène-1) on observe une diminution du pic à 25°K. Les mécanismes responsables de ces diminutions de pics n'ont pas encore été trouvés. On n'a pas observé de phénomène de relaxation en dessous de 77°K pour le polyéthylène ou le polybutène-1. Pour le poly(*d,l*-propylène-oxyde) une diminution du maximum ou un épaulement apparaît à 70–120°K, probablement associé aux mouvements de la chaîne, accompagnant le processus de réorientation des groupements méthyles.

Zusammenfassung

Messungen der dynamisch-mechanischen Eigenschaften verschiedener Polymerer wurden im Temperaturbereich von 6 bis 300°K bei Resonanzfrequenzen von etwa 10^4 Hz mittels eines Longitudinalschwingungsapparates ausgeführt. Als Polymere wurden Polyäthylen, 6,6-Nylon, drei Poly(methacrylatester) und fünf Poly(α-olefine) sowie verwandte Polymere untersucht. Ergebnisse für Poly(methylmethacrylat) und Poly(äthylmethacrylat) weisen auf das Auftreten von Tieftemperaturrelaxationsprozessen (6 bzw. 52°K) mit Konfigurationsumwandlungen im Kohlenwasserstoffteil der Esterseitengruppen hin. Die Ergebnisse liefern keinen Hinweis auf mechanische, mit der behinderten Rotation der Hauptkettenmethylgruppen in den Poly(methacrylatestern) oder Polypropylen verknüfte Verlustprozesse. Sehr schwache Relaxationsvorgänge oder Verlustplateaus werden im 20°K-Bereich an Polypropylen, Poly(vinylchlorid), Poly(*d,l*-propylenoxid), Poly(isobutylmethacrylat) und möglicherweise Nylon 6,6 beobachtet, während an Poly(4 methylpenten-1) ein nachweisbares Verlustmaximum bei 25°K beobachtet wird. Der für die Verlustmaxima verantwortliche Mechanismus ist noch nicht klar. Keine Relaxationsphänomene werden unterhalb 77°K an Polyäthylen oder Polybuten-1 beobachtet. Bei Poly(*d,l*-propylenoxid) erscheint bei 70–120°K ein Verlustmaximum oder eine Schulter, die möglicherweise mit Kettenbewegungen in Begleitung des Methylreorientierungsprozesses verknüpft sind.

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Graft Copolymerization of Vinylpyrrolidone onto Polydimethylsiloxane

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Synopsis

Graft copolymers of polyvinylpyrrolidone (PVP) onto polydimethylsiloxane have been prepared by the mutual irradiation technique utilizing high energy electrons (3 M.e.v.) generated by Van de Graaf. Water has been shown to have an acceleration effect of polymerization of vinylpyrrolidone and a reduction in the penetration of the monomer solution in the polymer. The dependence of the molecular weight of polyvinylpyrrolidone on the dose, and the dependence of the penetration of the grafted layer in the trunk polymer on the dose and the water content in the monomer solutions have been determined. The graft copolymers are hydrophilic and their hydrophilicity is proportional to the amount of polyvinylpyrrolidone grafted onto the silicone. The location of the graft copolymer is determined by staining and sectioning technique. Grafting varied from surface grafting to apparently homogeneous grafting depending on the water content in the monomer solution and on the total dose.

Modification of the surface properties of polymers is one of the most important and practical applications of the graft copolymerization. For this application, the amount of polymers added onto the trunk polymers, including polymers *in situ* which cannot be extracted by ordinary extraction procedures, is of prime interest.

Previous works on grafting of styrene onto cellulose acetate[1,2] indicate that the heterogeneous grafting by mutual irradiation produces extremely high molecular weight side chain polymers, due to the diffusion-controlled termination process, and that the weight increase is proportional to the molecular weight of the side chains. From the viewpoint of the modification of the surface properties of polymers, the number rather than the length of the side chains grafted might be more important. Presumably a larger quantity of shorter side chains would be preferred to a fewer number of longer side chains.

Although the polymerization of aqueous solution of vinylpyrrolidone by irradiation,[3-5] the G value of free radical formation of polydimethylsiloxane,[6] graft copolymerization of olefins and organosilicones,[7] and grafting of vinylpyrrolidone onto poly(methyl methacrylate)[8,9] have been reported, the graft copolymers of vinylpyrrolidone and polydimethylsiloxane have not been found in the literature.

With specific reference to the medical application of polymers, the grafting of vinylpyrrolidone onto silicone rubber has been investigated.

Polyvinylpyrrolidone (PVP) is a hydrophilic polymer with minimal tissue toxicity.[10] Silicone rubbers are some of the most widely used synthetic polymers in medicine; their hydrophobic nature, nevertheless, makes them unsatisfactory for certain applications.

For this study, a 3-m.e.v. electron beam generated by a Van de Graaf machine was used for initiating the graft copolymerization in anticipation of obtaining a shorter but larger number of side chains.

Experimental

Polydimethylsiloxane sheets of 0.005 and 0.003 in. thickness (Medical Silastic 372 from Dow Corning Center for Aid to Medical Research) were used in this study. This polymer is in the form of silicone rubber and contains a filler, SiO_2, but no other additives.

The sheets were cut in strips of approximately 1.5 × 10 cm. and were washed by boiling in soap solution followed by boiling in distilled water. The graft copolymerization was carried out in Pyrex tubes; the films and solvent monomer mixtures were degassed by repeating freezing and thawing cycles at least three times, and then sealed under vacuum. The amount of monomer in the sealed tubes was controlled just enough to cover the silicone rubber sheets when the sealed tubes were laid down horizontally.

The monomer, 1-vinyl-2-pyrrolidone, (Monomer-Polymer Laboratories, Borden Chemical Co., Philadelphia, Pa.) was distilled under vacuum before use; $n_D^{25} = 1.5106$.

The irradiations were carried out at about 25°C. by 3 M.e.v. electrons generated by the Van de Graaf at Massachusetts Institute of Technology, Cambridge, Mass. The irradiation dose given on each pass was 1.5 Mrad. No special attempt to maintain the temperatures of the tubes was made.

After the irradiation, the grafted silicone rubber was washed thoroughly with distilled water and then extracted with water in a Soxhlet extractor for three days. The washed samples were dried by blotting papers, to eliminate the superficial water, and then weighed to determine the water absorbed by the grafted silicone. Each sample was then thoroughly dried in a vacuum desiccator with Drierite, and weighed to determine the weight increase due to the grafted polyvinylpyrrolidone.

Homopolymers polymerized in the tubes were collected for molecular weight studies by diluting with distilled water and precipitating with acetone. No quantitative determination of the amount of homopolymer was made. When acetone is added to the water solution of polyvinylpyrrolidone the low molecular weight fractions remain in solution or in suspension. Only the higher molecular weight fractions from each experiment were collected. Precipitants were redissolved in water and were freeze dried prior to viscosity measurements.

The intrinsic viscosities were determined in water at 25°C. and were converted to viscosity-average molecular weights by using the formula:[11]

$$M = 142[\eta]^{1.8}$$

The increase in thickness of the grafted silicone rubber sheets and the depth of the grafted layers were measured by a staining and sectioning technique. Polyvinylpyrrolidone-grafted silicone was found able to be stained by many dyes used for staining proteins. Small pieces of samples were placed in eosin solution (5 g. eosin in 150 ml. H_2O and 50 ml. 95% ethanol) for 15 hr., and then washed in distilled water for 2 hr. The stained samples were frozen by CO_2 gas blown on a freezing microtome and were sectioned at approximately 15 μ. Sections were mounted on microscope slide glasses from water and dried in air at room temperature for 20 hr. Then the sections were covered with balsam and cover glasses. All sections were photographed shortly after covering, and the depth of polyvinylpyrrolidone-grafted layers was measured by projecting the slides to a certain magnification. Since eosin absorbed by polyvinylpyrrolidone migrates to the balsam medium, photographs were taken shortly after sections were mounted in balsam. The depth of penetration, both from top and bottom surfaces, is converted to the per cent of penetration in total thickness of the grafted sheets.

Results and Discussion

Weight increases and nitrogen content of grafted silicone rubber are shown in Tables I and II. The accelerating effect of solvents generally found in radiation-induced heterogeneous graft copolymerization is also found in this case, but the effect of the solvent is complicated by the fact that the water participates in the polymerization mechanism of vinylpyrrolidone. This is seen in the increase of molecular weight of homopolymers with the increasing amount of water in monomer solution shown in Table III. It was suggested that hydrate formation plays a part in the aqueous polymerization of vinylpyrrolidone with H_2O_2 and NH_4OH initiator system.[10] An aqueous solution of polyvinylpyrrolidone polymerized by electron irradiation without water has a slight yellowish color, whereas polymers obtained from the monomer–water mixture give a completely color-free aqueous solution.

Unlike many reported cases of radiation-induced heterogeneous graft copolymerization, water in this system is not a swelling agent of the poly-

TABLE I

Monomer/H_2O	Thickness of silicone sheets, mils	PVP grafted to silicone, wt.-%		
		1.5 Mrad	3.0 Mrad	4.5 Mrad
100	5	10.4	54.5	64.1
90/10	5	14.5	29.6	58.0
80/20	5	13.3	24.7	44.4
100	3	6.3	29.2	33.0
90/10	3	14.4	35.0	71.8
80/20	3	13.5	32.6	—

TABLE II

Monomer/H_2O	Thickness of silicone sheets, mils	Nitrogen content in PVP-grafted silicone, % 1.5 Mrad	3.0 Mrad	4.5 Mrad
100	5	1.54 (12.2)[a]	4.50 (35.3)	4.65 (36.9)
90/10	5	2.04 (15.9)	3.28 (26.3)	5.09 (40.5)
80/20	5	1.35 (10.7)	2.86 (22.7)	3.81 (31.1)
100	3	0.79 (6.2)	3.24 (25.7)	3.10 (24.6)
90/10	3	1.78 (14.3)	3.55 (28.2)	3.99 (31.7)
80/20	3	1.83 (14.4)	3.27 (25.9)	—

[a] Numbers in parentheses are weight per cent of polyvinylpyrrolidone (based on the original silicone rubber) calculated from the nitrogen contents.

TABLE III
Molecular Weight of PVP Polymerized by 3 M.e.v. Electron Irradiation

Monomer/H_2O	Molecular weight $\times 10^{-3}$ 1.5 Mrad	3.0 Mrad	4.5 Mrad	6.0 Mrad
100	74.5	74.0	102	123
90/10	96.5	104	450	—
80/20	100	175	543	—

mer. Absorption of vinylpyrrolidone by the silicone rubber is found to be about 1.7% at equilibrium at room temperature, whereas the absorption of water by the polymer is only 0.1–0.15%. Accordingly, in this particular system, water behaves as the controlling agent of the swelling of the polymer and as an accelerator for polymerization of vinylpyrrolidone. These two effects were reflected clearly in the location of the grafting shown as the grafted layer in Table IV. The deeper penetration at higher dose might be due to the increase of temperature on the irradiation. The irradiation of 3 Mrad in one pass gave results similar to those obtained by two passes of 1.5 Mrad. This may exclude the effect of diffusion of monomer in the interval time between irradiations.

TABLE IV
Depth of Grafted Layer in Grafted Sheets (5 Mils Silicone Rubber Sheet)

Monomer/H_2O	Depth of grafted layers, % 1.5 Mrad	3.0 Mrad	4.5 Mrad
100	12.2 (100)[a]	32.0 (102)	100 (130)
90/10	22.2 (110)	82.8 (118)	100 (134)
80/20	16.0 (102)	65.4 (106)	90.5 (128)

[a] Numbers in parentheses are the thicknesses relative to the original silicone rubber.

At the very high dosage rate available by the Van de Graaf generator, the reaction will be less dependent on the diffusion of monomers or on the swelling of polymers by monomer solutions. Similar experimental conditions reported previously[2] were repeated at this high dose rate; i.e., 0.0025 mm. thick cellulose acetate films were irradiated in the presence of 90/10 styrene–pyridine solution for a total dose of 10 Mrads. At the dose rate of 0.34 Mrad/hr. by γ-rays, the molecular weight of the polystyrene produced in the solution was 72,000 and the molecular weight of the polystyrene side chains was 755,000. The corresponding weight increase was about 104.7%. On the other hand, at the dose rate of approximately 5000 Mrad/hr. by Van de Graaf, there was very little weight increase and too few side chain polymers to permit measurement of the molecular weight; the molecular weight of polystyrene produced in the solution was found to be 15,000, which is surprisingly higher than one would expect from the dependence of the molecular weight on the dose rate.

Grafted silicone rubbers were found to be more rigid in their dry state; however, the surfaces of the grafted samples were wettable to water and retained the rubbery nature in wet state. The amounts of water absorbed by grafted silicone rubber and their ratio to the amount polyvinylpyrrolidone grafted are shown in Tables V and VI respectively.

The properties of vinylpyrrolidone-grafted silicone rubber, especially with respect to tissue tolerence, will be reported shortly elsewhere.

TABLE V

Monomer/H_2O	Thickness of silicone sheets, mils	Water absorbed by grafted silicone, wt.-% 1.5 Mrad	3.0 Mrad	4.5 Mrad
100	5	9.4	87.2	96.3
90/10	5	15.9	36.7	37.8
80/20	5	14.0	29.8	82.5
100	3	6.3	31.4	50.8
90/10	3	21.6	52.3	111.0
80/02	3	16.3	47.1	—

TABLE VI

Monomer/H_2O	Thickness of silicone sheets, mils	Water absorbed per PVP grafted 1.5 Mrad	3.0 Mrad	4.5 Mrad
100	5	1.0	2.4	2.5
90/10	5	1.2	1.6	1.3
80/20	5	1.2	1.5	2.6
100	3	1.0	2.7	1.5
90/10	3	1.5	1.5	1.5
80/20	3	1.2	1.4	—

Special thanks are due to Mr. K. A. Wright, Department of Engineering, Massachusetts Institute of Technology, for the use of the Van de Graaf generator.

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Résumé

Des copolymères greffés de la poly(vinyl-pyrrolidone) (PVP) sur des poly(diméthylsiloxane) ont été préparés par la technique d'irradiation mutuelle en utilisant des électrons de haute énergie (3 M.e.v.) engendrés par un appareil de Van de Graaf. On a montré que la présence d'eau accélérait la polymérisation de la vinyl-pyrrolidone et réduisait la pénétration de la solution de monomère dans le polymère. On a déterminé la dépendance du poids moléculaire de la poly(vinylpyrrolidone) par rapport à la dose de même que la dépendance de la pénétration de la couche greffée dans le polymère de base par rapport à la dose ainsi que la teneur en eau des solutions de monomères. Les copolymères greffés sont hydrophiles et leur hydrophilie est proportionnelle à la quantité de polyvinylpyrrolidone greffée dans la silicone. L'emplacement du copolymère greffé a été déterminé par des techniciens de teinture et de sectionnement. Le greffage varie depuis le greffage en surface jusqu'au greffage apparemment homogène; cela dépend de la teneur en eau de la solution du monomère et de la dose totale.

Zusammenfassung

Pfropfcopolymere von Poly(vinylpyrrolidon) (PVP) auf Poly(dimethylsiloxan) wurden nach dem Wechselbestrahlungsverfahren mit hochenergetischen (3 MeV) Elektronen aus einer Van-de-Graaf-Anlage dargestellt. Wasser besitzt einen beschleunigenden Einfluss auf die Polymerisation von Vinylpyrrolidon und setzt das Eindringen der Monomerlösung in das Polymere herab. Die Abhängigkeit des Molekulargewichtes von Poly(vinylpyrrolidon) von der Dosis und die Abhängigkeit der Penetration der aufgepfropften Schicht in das Stammpolymere von der Dosis und dem Wassergehalt in der Monomerlösung würde bestimmt. Die Pfropofcopolymeren sind hydrophil und ihre Hydrophilität ist der Menge des auf das Silikon aufgepfropften Poly(vinylpyrrolidon) proportional. Die Lage des Pfropfcopolymeren wird durch Färbe- und Schnittverfahren bestimmt. Die Aufpfropfung variiert von der Oberflächenaufpfropfung bis zu einer offenbar homogenen Aufpfropfung, je nach dem Wassergehalt in der Monomerlösung und der Gesamtdosis.

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Processus de l'Ecoulement Visqueux des Hauts Polymères

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Synopsis

Two recent theories concerning the viscosity of high polymers are summarized: the first one, by Bueche, is based on a complex activation process; the other one, established by Cohen and Turnbull to explain the empirical equation of Williams, Landel, and Ferry, is based on the value of the free volume. The discrepancies with the experimental values are emphasized. A mechanism of deformation is proposed which implies that the displacement of a segment of a macromolecule requires the localization of n_0 holes, at least, in a volume which contains N_0 segments Then, the variation of the number of holes with the temperature is computed, with account of the flex energy of the backbone chain and the formation energy of holes (like Flory, and Gibbs and di Marzio). The theoretical results are in good agreement with the experimental values of the variation of the viscosity with the temperature, the second-order transitions (thermal expansion and heat capacity), and the variation of the glass temperature with the molecular weight. A simple activation process can also produce the deformation and has the most important contribution at low temperature. It is believed that similar mechanism of diffusion of holes can also explain the viscosity of mineral glasses.

La variation de la viscosité des hauts polymères en fonction de la température ne peut s'expliquer par un processus d'activation simple, c'est pourquoi diverses théories ont été émises afin de rendre compte du comportement observé.

THÉORIE FONDÉE SUR UN PROCESSUS COMPLEXE D'ACTIVATION

Bueche[1] suppose que la coopération de plusieurs degrés de liberté est nécessaire pour produire le déplacement d'un segment de macromolécule, déplacement qui est le processus élémentaire de l'écoulement visqueux.

La concordance avec l'expérience est bonne pour $T > T_g + 20°\text{C}$, T_g étant la température de vitrification, lorsqu'on choisit les nombres de degrés de liberté suivant: $n = 29 \pm 5$ pour le polyisobutylène, $n = 220$ pour le polystyrène.

L'équation à laquelle il aboutit est une somme d'un grand nombre de termes, ce qui limite son application pratique.

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Nous avons refait les calculs par d'autres méthodes et une intégration approchée nous a permis d'obtenir l'équation

$$\log \eta = C + 1{,}3(E/RT)^{0{,}4\sqrt{n}} \tag{1}$$

η, E et n étant respectivement le coefficient de viscosité, l'énergie d'activation moyenne par degré de liberté, et le nombre de degrés de liberté.

Cette équation est identique à la formule empirique de Fox et Flory[2]

$$\log \eta = C + (A/T^{\alpha}) \tag{1'}$$

En prenant les valeurs de proposées par Fox et Flory: $\alpha = 2$ pour le polyisobutylène, $\alpha = 6$ pour le polystyrène, nous trouvons les nombres de degrés de liberté qui sont respectivement 25 et 225, nombres qui concordent avec ceux trouvés par Bueche, ce qui justifie nos approximations.

Cette théorie a cependant des lacunes. En effet, elle ne concorde plus bien avec les résultats expérimentaux pour les températures proches de T_g, et ne rend pas compte des transitions du second ordre observées à cette température (volume et chaleur spécifique). En outre, elle ne peut expliquer pourquoi la viscosité dépend de la vitesse de refroidissement, car cette théorie implique un équilibre thermodynamique quasi instantané.

THÉORIE FONDÉE SUR LE VOLUME LIBRE

Un autre traitement théorique plus récent a été proposé par Cohen et Turnbull[3] afin de justifier l'équation empirique de W.L.F. (Williams, Landel et Ferry):[4]

$$\log (\eta/\eta_g) = 17{,}44(T - T_g)/(51{,}6 + T - T_g) \tag{2}$$

Cohen et Turnbull ont d'abord démontré l'équation empirique de Doolittle:[5]

$$\log \eta = C + (v/\phi) \tag{3}$$

où v est le volume libre que nécessite le déplacement d'un segment, et ϕ le volume libre moyen par segment. Leur raisonnement est d'ailleurs analogue à celui de Boltzmann.

Ils ont ensuite considéré[6] que la fonction liant l'énergie interne E et l'accroissement de volume α était du type Lenard-Jones (Fig. 1) et que par conséquent, le volume libre ϕ pouvant être redistribué sans changement d'énergie interne n'apparaissait qu'à partir d'une valeur α_0, d'où:

$$\phi = \alpha - \alpha_0$$

et en prenant

$$d\alpha/dT = A$$

on obtient

$$\phi = A(T - T_0) = A(T - T_g + T_1) \tag{4}$$

soit, en tenant compte d'éq. (3),

$$\log(\eta/\eta_g) = [(v/AT_1)(T - T_g)]/(T_1 + T - T_g) \qquad (2')$$

équation identique à celle de W.L.F.

Nous pensons que le raisonnement statistique précédent ne peut convenir à des molécules non sphériques, car le volume libre total est la somme de volumes libres partiels; il faudrait alors appliquer un raisonnement analogue à celui déjà tenu par Bueche.[1] En outre, Cohen et Turnbull n'expliquent pas de quelle facon l'accroissement de volume est lié à la température; enfin, l'équation de W.L.F. ne concorde plus avec les résultats expérimentaux pour les températures supérieures de plus de 100 °C à T_g.

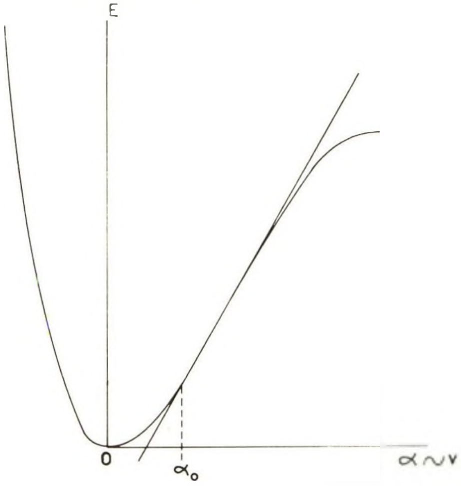

Fig. 1. Energie de liaison en fonction de l'accroissement de volume.

PROCESSUS DE DÉFORMATION PROPOSÉ

Nous considérons que le pseudo-réseau constitué par les maillons de chaîne d'un haut polymère peut contenir des lacunes.

Pour que le déplacement permanent d'un segment se produise, nous supposons qu'il est nécessaire que dans un volume contenant N maillons, se trouvent rassemblées au moins n_0 lacunes.

Soit

$$\alpha = n_1/n_2$$

n_1 et n_2 étant respectivement les nombres de lacunes et de maillons de haut polymère contenus dans le réseau.

La probabilité qu'au moins n_0 lacunes se trouvent localisées sur un groupe déterminé de N maillons est:

$$P = \sum_{n=n_0}^{n=\infty} [\alpha^n/(1 + \alpha)^N] \cdot [(N + n)!/N!n!] \qquad (5)$$

Lorsque $n_0 \gg 1$, nous avons sensiblement:

$$P = \frac{(N + n_0)!\cdot \alpha^{n_0}}{N!n_0!\cdot (1 - \alpha)^{N-(N+n_0)/n_0}} \tag{5'}$$

soit, pour les petities valeurs de α:

$$\log P = C + n_0 \log \alpha - \left[\frac{N_0 - (N + n_0)/n_0}{2{,}3}\right] \alpha \tag{5''}$$

en prenant

$$C = \mathrm{Log}_{10} \frac{(N + n_0)!}{N!n_0!}$$

Pour les valeurs $n_0 = 12$ et $N = 15$, nous avons représenté graphiquement la fonction $\log P = f(\alpha)$.

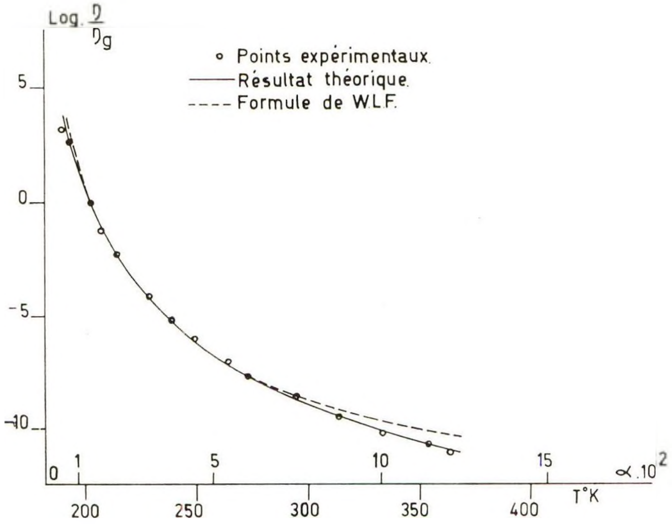

Fig. 2. Logarithme du coefficient de viscosité du polyisobutylène en fonction de l'accroissement du volume spécifique et de la température.

La courbe coincide parfaitement avec celle qui représente la variation du logarithme de la viscosité du polyisobutylène en fonction de la température, ainsi que le montre la Figure 2. Nous avons choisi ce haut polymère, car son coefficient de viscosité a été l'objet de nombreuses mesures.

La coïncidence a été obtenue en reliant α et T par l'équation linéaire:

$$\alpha = 6{,}66 \times 10^{-4}(T - 182{,}5) \tag{6}$$

Nous voyons que l'on n'observe pas de divergences entre la courbe théorique et les valeurs expérimentales pour les températures élevées; la courbe de W.L.F. est tracée à titre de comparaison.

MÉCANISME DE FORMATION DES LACUNES

Nous avons repris le raisonnement que Flory[7] a tenu pour calculer la proportion de liaisons carbone–carbone fléchies, dans les hauts polymères en solution.

Soit n_2 chaînes dont chacune est formée de x maillons, et n_1 molécules de solvant. Il existe donc n_0 sites:

$$n_0 = n_1 + xn_2$$

Soit Z la valence du carbone; chaque liaison comporte $Z - 1$ positions dont l'une est plus stable que les $Z - 2$ autres que nous applerons fléchies.

Soit f la proportion de liens fléchis; le nombre de configurations possibles des: n_2 chaînes est:

$$W = \left\{\frac{n_0! n_0^{-n_2(x-1)}}{n_1! n_2!\, 2^{n_2}}\right\} \left\{\frac{Z^{n_2}(Z-2)^{fn_2(x-2)}[n_2(x-2)]!}{[fn_2(x-2)]![(1-f)n_2(x-2)]!}\right\} \tag{7}$$

Nous considérons, ainsi que Gibbs et di Marzio[8] que le même traitement peut s'appliquer si l'on suppose qu'il n'existe pas de solvant, mais n_1 lacunes.

En appliquant la formule de Stirling, nous trouvons:

$$\frac{1}{W^{n_2(x-2)}} = \left(\frac{Zx}{2e}\right)^{1/(x-2)} \left[\left(\frac{2}{f}\right)^f \frac{1}{(1-f)^{1-f}} \left(\frac{(\alpha+1)}{\alpha}\right)^\alpha \left(\frac{1}{e}\right)\right] \tag{8}$$

en prenant:

$$\alpha = n_1/n_2x$$

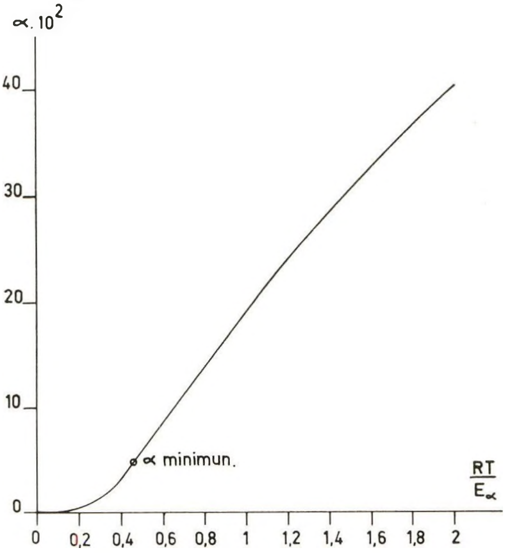

Fig. 3. Proportion de lacunes en fonction de la température.

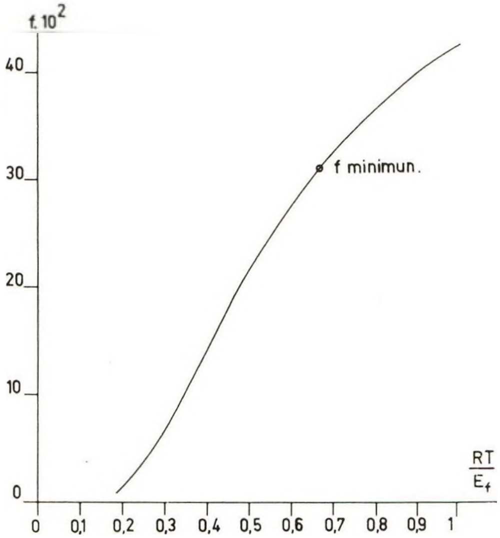

Fig. 4. Proportion de liens carbone–carbone fléchis, en fonction de la température.

Soit E_α l'énergie de formation d'une mole de lacunes et E_f l'énergie de flexion d'une mole de liens carbone-carbone; l'énergie libre est:

$$F = \alpha E_\alpha + fE_f - RT \log W$$

Le minimum de F qui correspond à l'équilibre est réalisé pour:

$$\alpha = R^{-E\alpha/RT}/(e - 2e^{-E\alpha/RT}) \tag{9}$$

$$f = 2e^{-E_f/RT}/(1 + 2R^{-E_f/RT}) \tag{10}$$

Les représentations graphiques des éq. (9) et (10) correspondent respectivement aux Figures 3 et 4.

Le nombre de configurations W ne peut être inférieur à l'unité, ce qui détermine, d'après l'éq. (8) des valeurs minimales de α et f indépendantes de la température.

Nous avons trouvé pour le polyisobutylène, en tenant compte de l'éq. (6):

$$E_\alpha = 780 \text{ cal/mol}$$

$$\alpha_{\text{minimum}} = 4{,}7 \times 10^{-2}$$

et

$$E_f = 550 \text{ cal/mole}$$

$$f_{\text{minimum}} = 0{,}31$$

en prenant $x = \infty$ (poids moléculaire très élevé).

Il existe donc un certain nombre de lacunes et de segments fléchis dépendant de la configuration désordonnée de l'amas de macromolécules; leurs positions sont donc déterminées, et pour une configuration donnée des macromolécules, de telles lacunes ne peuvent subir de changement de position et ne contribuent donc pas au processus de l'écoulement visqueux que nous venons de décrire.

Par conséquent, dans l'éq. (5), nous devons remplacer α par:

$$\alpha' = \alpha - \alpha_{\text{minimum}}$$

La fonction $\alpha(T)$ est quasi linéaire pour:

$$0{,}2 > \alpha > 0.047(=\alpha_{\text{minimum}})$$

et on a dans ce domaine:

$$\alpha' = 0{,}26(R(T - T_{\text{minimum}})/E_\alpha \qquad (11)$$

or, pour le polyisobutylène $E_\alpha = 780$ cal., d'ou:

$$\alpha' = 6{,}66 \times 10^{-4}(T - 182.5) \qquad (6')$$

Nous obtenons bien une équation identique à éq. (6) et il existe donc une parfaite correspondance entre les résultats théoriques et les valeurs mesurées de la viscosité du polyisobutylène (Fig. 2).

VARIATION DE LA TEMPERATURE DE VITRIFICATION EN FONCTION DU POIDS MOLÉCULAIRE

L'éq. (8) permet de calculer les valeurs de $\alpha_{\min}$ et $f_{\min}$ en fonction du nombre x de maillons des chaînes, c'est à dire du poids moléculaire M:

$$M = M_0 x/2$$

(M_0 étant le poids moléculaire du monomère), α étant une fonction de la température, à chaque valeur de $\alpha_{\min}$ correspond une température $T_{\min}$.

Nous obtenons en linéarisant l'éq. (8) dans le domaine étudié (autour des valeurs $\alpha_{\min}$ et $f_{\min}$ correspondant á $x = \infty$):

$$\frac{1}{x-2} \log 0{,}75x = 1{,}480\ \Delta f_{\min} + 2{,}15\ \Delta\alpha_{\min} \qquad (12)$$

soit, en tenant compte éqs. (9) et (10)

$$\frac{M_0}{2(M - M_0)} \log \frac{1{,}5M}{M_0} = \left(\frac{1{,}12}{E_\alpha} + \frac{1{,}48}{E_f}\right) \Delta T_{\min} \qquad (12')$$

Pour le polystyrène dont les valeurs expérimentales de T_g en fonction de M ont été déterminées par Fox et Flory[9], nous avons obtenu une concordance satisfaisante (Fig. 5) en prenant:

$$T_g = T_{\min} + 14°\text{C}$$
$$M_0 = 104$$
$$E_\alpha = 1.530 \text{ cal/mol}$$
$$E_f = 1.080 \text{ cal/mol}$$

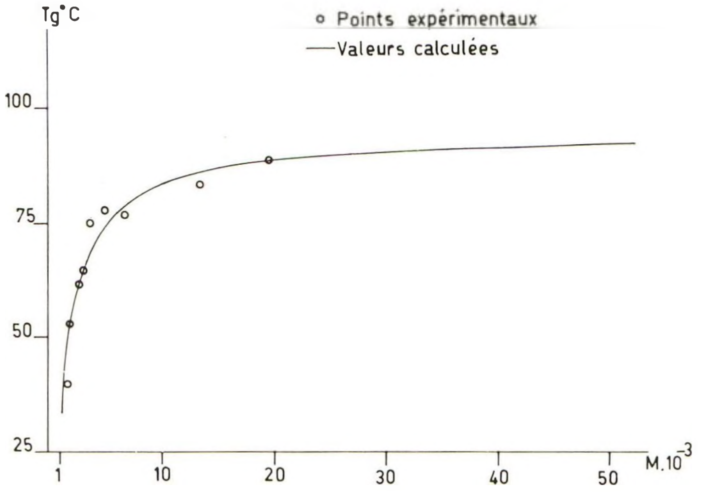

Fig. 5. Variation de la température de vitrification en fonction du poids moléculaire.

Les valeurs théoriques et expérimentales du coefficient de viscosité concordent également pour $n_0 = 10$ et $N = 15$.

A la température de vitrification nous obtenons d'ailleurs:

$$d \log\eta/dT \simeq n_0/2{,}3(T_g - T_{\min}) = 10/2{,}3 \times 14 = 0{,}31$$

valeur qui est exactement celle mesurée par Kovacs.[10]

DISCONTINUITÉS DU SECOND ORDRE

Accroissement de Volume

La discontinuité du coefficient d'expansion cubique doit être:

$$\Delta(dv/dT) = d\alpha/dT$$

or, nous obtenons pour le polystyrène, en tenant compte de l'éq. (11):

$$d\alpha/dT = 0.26R/E\alpha = 0{,}52/1530$$

il en résulte:

$$\Delta(dv/dT) = 3{,}4 \times 10^{-4}$$

valeur qui concorde exactement avec les mesures de Kovacs.[10]

Chaleur Spécifique

La discontinuité de la chaleur spécifique a pour amplitude:

$$\Delta C = (2/M_0)[E_\alpha(d\alpha/dT) + E_f(df/dT)] = 0{,}03 \text{ cal/gr. degré}$$

La valeur mesurée est pour le polystyrène:[11]

$$\Delta C = 0.035 \text{ cal/gr. degré}$$

Les valeurs théoriques et expérimentales sont donc assez proches; l'écart provient peut être du fait que le traitement que nous proposons est un schéma fort simplifié.

CONTRACTION ISOTHERME

Lorsque la température est inférieure à T_g, les temps de relaxation sont longs par rapport à la durée d'observation, et l'équilibre thermodynamique ne s'établit donc que lentement, ainsi que l'ont déjà mesuré et constaté maints auteurs.[10,12,13]

Selon notre théorie, cette contraction doit effectivement se produire pour $T < T_g$, car α_g qui est supérieur à $\alpha_{\min}$ n'est donc pas une limite inférieure.

L'extrapolation aux basses températures du volume spécifique calculée d'après les variations aux températures supérieures à T_g fait apparaitre que les hauts polymères atactiques amorphes devraient avoir á l'état d'équilibre un volume spécifique inférieur à celui des polymères isotactiques cristallins, si l'on considère que la discontinuité de ce coefficient est due au fait que l'équilibre thermodynamique n'est plus atteint car ce processus devient très lent.

Cette contradiction est levée, car nous avons vu que α ne décroît plus lorsque la température est inférieure à $T_{\min}$; l'extrapolation n'est donc pas justifiée.

VERRES INORGANIQUES

Nos résultats sont numériquement proches de ceux de W.L.F. qui ont montré que leur équation permettait également de rendre compte de la variation de la viscosité des verres inorganiques en fonction de la température.

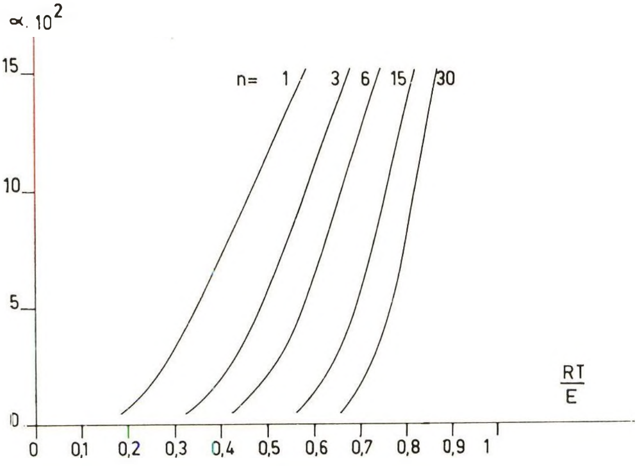

Fig. 6. Proportion de lacunes en fonction de la température, lorsque n degrés de liberté participent au processus.

Il est évident que le mécanisme de formation des lacunes ne peut être identique à celui des hauts polymères. Nous pensons qu'alors la formation des lacunes est due à la coopération de plusieurs degrés de liberté.

La variation de α fonction de la température pour divers nombres de degrés de liberté est représentée sur la Figure 6 (n est le nombre de degrés de liberté et nE est l'énergie de formation d'une lacune).

Nous voyons que α est également une fonction quasi linéaire de T dans un domaine de températures étendu. Il n'existe cependant pas de points de transition du second ordre marqués nettement.

MÉCANISME DE LA DÉFORMATION DANS LE DOMAINE DES TEMPÉRATURES INFÉRIEURES À T_g

Lorsque les hauts polymères sont à l'état vitreux, un processus d'activation simple rend compte de la variation des phénomènes de relaxation avec la température.

La probabilité de transition est alors:

$$P_E = e^{-E/RT}$$

Pour des températures proches de T_g, deux processus peuvent donc produire la déformation: la localisation d'énergie thermique sur les groupements qui participent à la déformation, ou bien la localisation de lacunes au voisinage de ces mêmes groupements. On a donc:

$$P_{\text{total}} = P_E + P_\alpha$$

En tenant compte de ces deux processus à la fois, on met en évidence l'accroissement de l'énergie apparente d'activation au voisinage de T_g.[13]

Il est à remarquer que la valeur P_α qu'il faut choisir aux températures inférieures à T_g dépend de la vitesse de refroidissement et de la contraction isotherme. La variation de l'énergie apparente d'activation au voisinage de T_g dépend donc de l'histoire de l'éprouvette, ainsi que l'a constaté Bueche.[14]

CONCLUSION

Le mécanisme de déformation que nous proposons permet de rendre compte de la variation de la viscosité et des phénomenes de relaxation, en fonction de la température, ainsi que des différentes transitions du second ordre observées.

Cependant, le processus de formation des lacunes ne peut s'appliquer qu'aux matières qui ne cristallisent pas; dans les matériaux cristallins, la proportion de lacunes est quasi nulle aux température inférieures au point de fusion, la fusion correspondant à la création d'une proportion considérable de lacunes,[15] création qui se manifeste par la présence de points de transition du premier ordre.

Ces travaux ont été faits à l'Université Libre de Bruxelles dans les laboratoires du Professeur Georges A. Homes à qui nous tenons à exprimer notre gratitude et nos remerciements pour l'aide et les précieux conseils qu'il nous a prodigués tout au long de ces recherches. Nous tenons également à remercier Mademoiselle Lucia de Brouckére, professeur à l'Université Libre de Bruxelles, avec qui nous avons eu des entretiens fructeux.

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Résumé

L'auteur résume deux théories récentes sur la viscosité des hauts polymères; la première, élaborée par Bueche, est basée sur un processus d'activation complexe; la seconde, établie par Cohen et Turnbull pour expliquer l'équation empirique de Williams Landel et Ferr, est basée sur la valeur du volume libre. On a fait ressortir les écarts par rapport aux valeurs expérimentales. L'auteur propose alors un mécanisme de déformation que implique que le déplacement d'un segment d'une macromolécule exige la localisation de n. cavités au moins dans un volume qui contient N. segments. Par la suite il a calculé la variation du nombre de cavités avec la température, ainsi que l'énergie de flexion de la chaîne principale et l'énergie de formation des cavités (suivant Flory, Gibbs et di Marzio). Les résultats théoriques concordent bien avec les valeurs expérimentales de la variation de la viscosité avec la température, les transitions de second ordre (l'expansion thermique et la capacité calorifique) ainsi que la variation de la température de transition vitreuse avec le poids moléculaire. Un simple processes d'activation peut aussi produire la déformation et contribue de la façon la plus importante aux basses températures. L'auteur pense qu'un mécanisme analogue de diffusion des cavités peut aussi expliquer la viscosité des verres mineraux.

Zusammenfassung

Der Autor fass zwei neuere Theorien der Viskosität von Hochpolymeren zusammen. Die erste, von Bueche, beruht auf einem komplexen Aktivierungsprozess, die andere, von Cohen und Turnbull, zur Deutung der empirischen Gleichung von Williams, Landel und Ferry aufgestellt, beruht auf dem Wert des freien Volumens. Die Diskrepanzen mit den experimentellen Werten werden betont. Sodann schlägt der Autor einen Deformationsmechanismus vor, welcher annimmt, dass die Verrückung eines Segmentes eines Makromolekuüls die Lokalisierung von zumindest n_0 Löchern in einem Volumen, das N_0 Segmente enthält, erfordert. Sodann wird die Abhängigkeit der Zahr der Löcher von der Temperatur berechnet, mit Berücksichtigung der Biegungsenergie der Hauptkette und der Bildungsenergie der Löcher (ähnlich wie Flory, und Gibbs und di Marzio). Die theoretischen Ergebnisse stimmen gut mit den experimentellen Werten für die Temperaturabhängigkeit der Viskosität, für die Umwandlung zweiter Art (thermische Ausdehnung und Wärmekapazität) und für die Abhängigkeit der Glastemperatur vom Molekulargewicht überein. Ein einfacher Aktivierungsprozess kann ebenfalls die Deformation erzeugen und liefert den wichtigsten Beitrag bei tiefer Temperatur. Der Autor ist der Meinung, dass ein ähnlicher Löcherdiffusionsmechanismus auch die Viskosität mineralischer Gläser erklären kann.

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Study of Crosslink Formation by Partial Conversion Properties I. Copolymerization of Poly(ethylene Fumarate) and Styrene

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Synopsis

The copolymerization reaction of poly(ethylene fumarate) and styrene has been studied in dilute solution by the change in number-average molecular weight with conversion. The partial conversion molecular weight is found to vary with conversion and to be a guide to the overall reaction mechanism, which is that of crosslink formation.

INTRODUCTION

Many polymerization reactions involving the formation of crosslinks have been studied by measurement of some macroscopic property, e.g., solubility, gel density, elastic modulus, and melt viscosity, of the polymer sample as a function of conversion. In such a complex system, with changing environmental conditions, these properties are not necessarily an exact guide to the nature of the crosslinking reaction, or to the structure of the crosslinked polymer produced over each extent of conversion, since these properties are cumulative. However, Wall[1,2] has defined the concept of "partial conversion" properties which do relate the changing properties with changing environment. For the purpose of studying crosslink formation in a reaction, Wall[2] considers that the most important property of the system is the partial conversion number-average molecular weight ($\bar{\bar{M}}_n$), since it measures the change in number of polymer molecules over each unit of conversion,

i.e.,
$$\bar{\bar{M}}_n = dW/dN \tag{1}$$

where W is the weight of polymer, and N the corresponding number of molecules.

Since
$$\bar{M}_n = W/N$$

$\bar{M}_n$ is the number-average molecular weight,

as
$$dN/dW = [\bar{M}_n - W(d\bar{M}_n/dW)]\bar{M}_n^2$$

then
$$\bar{\bar{M}}_n = \bar{M}_n^2/[\bar{M}_n - W(d\bar{M}_n/dW)] \tag{2}$$

It can readily be seen that when crosslinking, or gelation, is taking place the quantity (dN/dW), i.e., $1/(\bar{M}_n)$ will become negative, since the number of molecules is decreasing with conversion, as the molecular weight increases. The value of (dN/dW) should then be a sensitive guide to the nature of the overall polymerization process, particularly at each stage of conversion.

The present paper deals with the application of this analytical method to the copolymerization reaction of poly(ethylene fumarate) and styrene, ebulliometry being used to measure the number-average molecular weight $(\bar{M}_n)$. This linear condensation polymer was used since it could readily be made to any desired molecular weight. This allowed molecular weights and conversions to be studied in solution to appreciable extents before gelation occurred without resort to very high dilutions.

EXPERIMENTAL

Reagents

Ethylene glycol, maleic anhydride, styrene, and benzoyl peroxide were used after the normal standard purification.

Dioxane was used throughout as a solvent for the copolymers. Special precautions had to be taken since it readily absorbed water from the atmosphere, and it formed an azeotrope. The solvent was partially dried and then allowed to stand in an atmosphere of nitrogen, over anhydrous magnesium sulfate. It was then fractionally distilled in a nitrogen atmosphere in an efficient column, and in the presence of stannous sulfate to destroy peroxides. It was stored under nitrogen and in dark bottles.

Polymerizations and Copolymerizations

The poly(ethylene fumarate) (PEF) was prepared from maleic anhydride and ethylene glycol at 195°C. by the method described by Gordon et al.[3] In the condensation reaction all the *cis* maleic anhydride double bonds were converted to the more stable *trans* fumarate.[4] The polymer showed no trace of *cis* double bond peaks in its infrared spectrum (Fig. 1).

The polymer was purified by repeated precipitations with methanol from chloroform solutions, and dried under vacuum. The number-average molecular weight used throughout this present series of experiments was found to be 1600 ± 200, as measured in dioxane solution.

The copolymerization reactions were carried out in dioxane solutions at 60°C. with the use of 0.164 g. monomer mole/l. of PEF and 1.4×10^{-6} g.-mole/l. of benzoyl peroxide, activated with dimethylaniline, as initiator, under an atmosphere of air-free nitrogen. Samples were withdrawn at various intervals from the reaction mixture, and the copolymer samples precipitated immediately from methanol at 0°C., then filtered, washed, and dried under high vacuum.

The copolymer samples were analysed by weight increase, and also by infrared spectroscopy. The PEF content was measured from optical den-

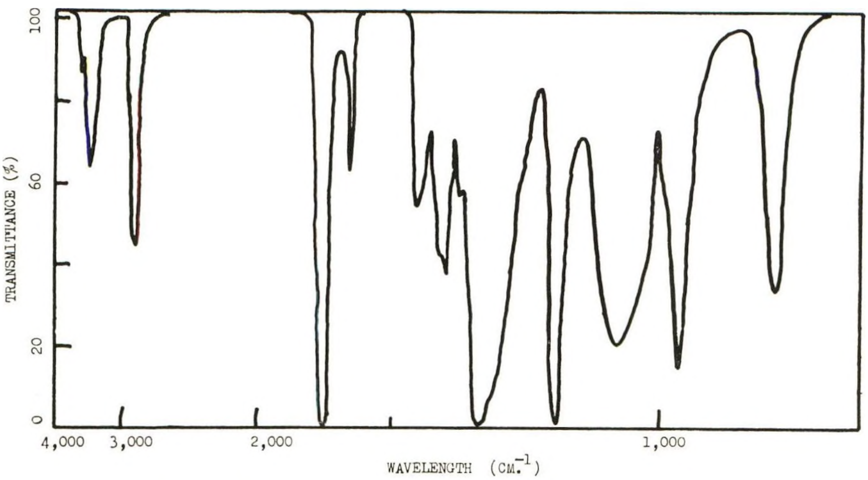

Fig. 1. Infrared spectrum of poly(ethylene fumarate).

sity of the double-bond peaks at 1640 and 977 cm.$^{-1}$, a standard solution in chloroform and 1 mm. NaCl cells being used. The two sets of measurements were found to agree to well within the experimental error (±5%), and to be more accurate and reproducible than any other physical or chemical method which was tried.

Molecular Weight Determinations

The number-average molecular weights were determined by a modified Lehrle and Majury ebulliometer.[5] Highly purified dioxane was used as a solvent since it was found to be the only suitable one for both the polymer and copolymer. Unfortunately, substantial foaming of some of the solutions took place on boiling. This added considerable "noise" to the background in the detecting circuit, reducing the accuracy of the molecular weight measurement to almost 10%. Since dioxane readily formed an azeotrope, considerable care had to be taken to ensure complete elimination of water.

The ebulliometer was calibrated for dioxane as solvent with tristearin, poly(propylene oxide), and poly(ethylene glycol) samples. We are indebted to Shell Chemical Co., for the two latter samples and their characterization.

RESULTS

The system, PEF and styrene, was characterized by a series of copolymerizations with different initial concentrations of styrene. In each case the concentration of PEF was kept constant (0.164 g. monomer moles/l.), and the extent of conversion was measured by residual double bond content. The experimental conditions for a few typical copolymerization runs are listed in Table I.

TABLE I

Copolymerizations

Run no.	Initial Concn. of styrene, g.-mole/l.	Monomer mole fraction of styrene
5	2.040	0.944
9	0.670	0.845
10	0.388	0.758

TABLE II

Copolymer Analysis for Run No. 5

Molecular weight $\bar{M}_n$	Conversion W of PEF, %	$d\bar{M}_n/dW$	$\bar{\bar{M}}_n \times 10^{-3}$	$dN/dW \times 10^4$
1,800	7.5	19.35	1.95	5.14
2,100	20.0	35.00	3.14	3.19
2,300	25.0	60.00	6.62	1.51
2,700	30.0	100.0	−24.30	0.41
3,300	35.0	140.0	−6.22	−1.61
4,100	40.0	200.0	−4.31	−2.32
5,400	45.0	290.0	−3.80	−2.64
7,000	50.0	310.0	−5.76	−1.79
8,500[a]	55.0	330.0	−7.30	−1.36
10,400[a]	60.0	350.0	−10.10	−0.99

[a] Small amount of insoluble material present in molecular weight determinations.

The extent of copolymerization and crosslinking was followed by the molecular weight until gel formation began. No attempt was made to follow the reaction after this point. A series of experimental details and their

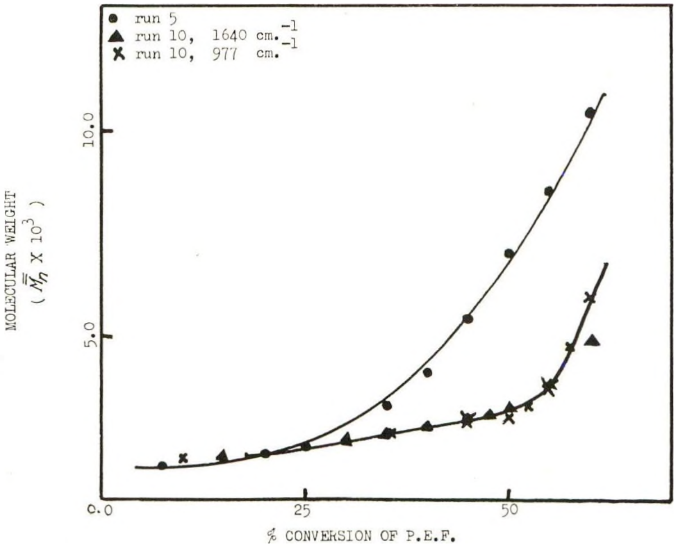

Figure 2,

TABLE III

Copolymer Analysis for Run No. 9

Series	Molecular weight $\bar{M}_n$	Conversion W of PEF, %	$d\bar{M}_n/dW$	$\bar{\bar{M}}_n \times 10^{-3}$	$dN/dW \times 10^4$
A[a]	1,950	15.0	11.66	2.14	4.68
	2,100	27.5	11.65	2.69	3.72
	2,300	37.5	21.67	3.56	2.81
	2,320	40.0	30.00	4.82	2.07
	2,500	45.0	60.00	−31.30	−0.32
	2,900	50.0	90.00	−5.25	−1.91
	3,400	55.0	110.0	−4.35	−2.30
	4,000	60.0	146.0	−3.40	−2.94
B[b]	2,000	15.0	21.65	2.39	4.19
	2,350	30.0	25.00	3.44	2.91
	2,480	35.0	50.00	8.42	1.19
	2,820	40.0	90.0	−10.15	−0.99
	3,400	45.0	135.0	−4.29	−2.33
	4,200	50.0	180.0	−3.66	−2.74
	5,150	55.0	200.0	−4.50	−2.22

[a] Per cent conversion (W) calculated from 1640 cm.$^{-1}$ band.

[b] Per cent conversion (W) calculated from 977 cm.$^{-1}$ band.

TABLE IV

Copolymer Analysis for Run No. 10

Series	Molecular weight $\bar{M}_n$	Conversion W of PEF, %	$d\bar{M}_n/dW$	$\bar{\bar{M}}_n \times 10^{-3}$	$dN/dW \times 10^4$
A[a]	2,100	15.0	23.33	2.55	3.93
	2,500	30.0	30.00	3.13	3.22
	2,650	35.0	35.00	4.90	2.04
	2,800	40.0	40.00	6.52	1.53
	2,950	45.0	45.00	10.87	0.92
	3,050	47.5	70.00	−33.30	−0.30
	3,200	50.0	85.00	−9.72	−1.03
	3,800	55.0	170.0	−2.58	−3.88
	4,900	60.0	215.0	−3.00	−3.33
B[b]	2,000	10.0	18.30	2.20	4.55
	2,600	35.5	40.00	5.73	1.75
	2,900	45.0	45.00	9.67	1.04
	3,150	50.0	50.0	15.22	0.58
	3,300	52.5	100.0	−5.59	−1.79
	3,800	55.0	200.0	−5.00	−2.00
	4,800	57.5	300.0	−1.85	−5.41
	6,000	60.0	400.0	−2.00	−5.00

[a] Per cent conversion (W) calculated from 1640 cm.$^{-1}$ band.

[b] Per cent conversion (W) calculated from 977 cm.^{1} band.

analysis by eq. (2) are listed in Tables II–IV for the experimental runs listed in Table I. These tables include the per cent conversion as calculated from infrared analysis based on the 1640 and 977 cm.$^{-1}$ fumarate double-bond absorption bands. Both sets of values are included in Tables III and IV, since considerable agreement was found between them, unlike some recent work.[6]

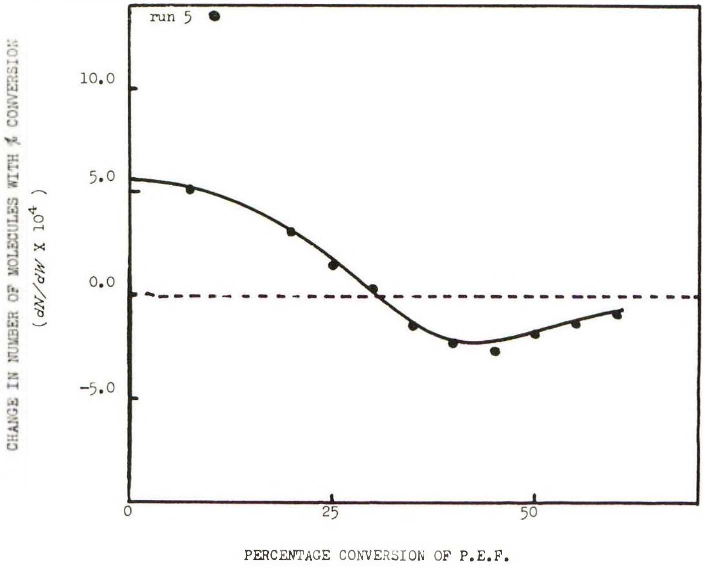

Figure 3*a*.

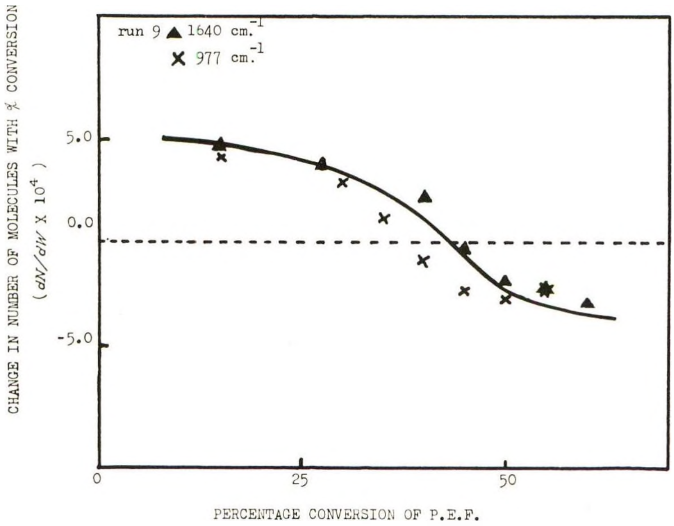

Figure 3*b*.

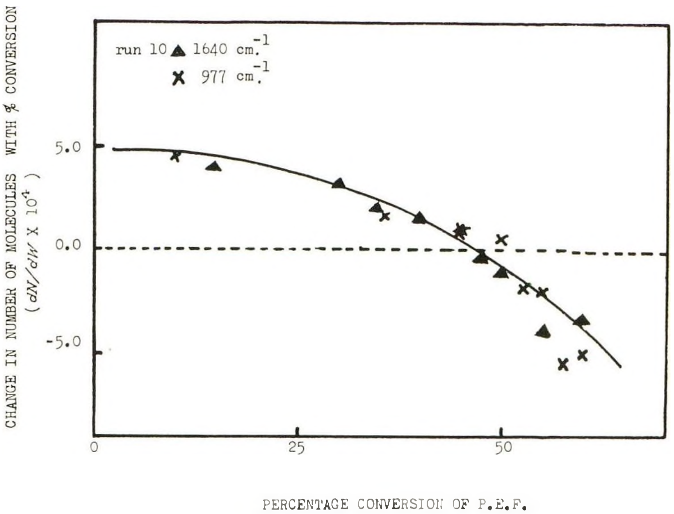

Figure 3*c*.

For the calculations by use of eq. (2), smoothened values of $\bar{M}_n$ are quoted. These are derived from the plots of $\bar{M}_n$ against per cent conversion, similar to those shown in Figure 2, for runs 5 and 10. In Figures 3 and 4, dN/dW and the partial conversion molecular weight ($\bar{\bar{M}}_n$) are plotted against per cent conversion for all three runs. All the curves show a general decrease in dN/dW with conversions, until it becomes negative. The partial conversion molecular weight, ($\bar{\bar{M}}_n$), which is the reciprocal of dN/dW, changes from large positive to negative values as dN/dW becomes negative, and asymptotically approaches zero as dN/dW decreases.

DISCUSSION

Since the rate of change of the number of molecules of polymer with conversion is a decreasing function of the conversion, the predominant reaction in this copolymerization system must be that of forming crosslinks between styrene and PEF molecules. The formation of polystyrene branches or separate molecules would not reduce the number of polymer molecules present and dN/dW would not be a decreasing function. This reduction in number of polymer molecules can be more readily seen from Figure 5, where the number of copolymer molecules, as calculated from the weight, is plotted against conversion. The initial positive value of dN/dW, indicating an initial rise in number of molecules has no significance, arising partly from equating W with percentage conversion, which does not take into account the number of PEF molecules initially present, but does make the analysis by eq. (2) more sensitive to changes in PEF units, and also from errors in each individual molecular weight determinations. Absolute values of dN/dW have only relative significance.

The conclusions that the predominant reaction is that of crosslink formation is confirmed to some extent by the fact that no polystyrene fraction, or even a much enriched styrene copolymer fraction was ever extracted from the copolymer precipitate. Indeed, the reactivity ratios for the system, which have recently been measured[7] show clear evidence that the styrene radical prefers to add to a fumarate double bond rather than to another styrene monomer unit. This, it must be stressed, is only true for PEF units and not for the simpler diethyl fumarate itself. Hence the formation of long styrene branches or polystyrene chains is highly unfavored, and the

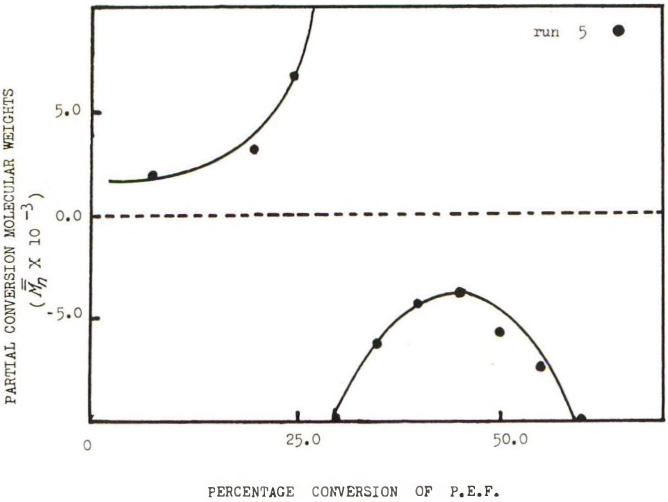

Figure 4*a*.

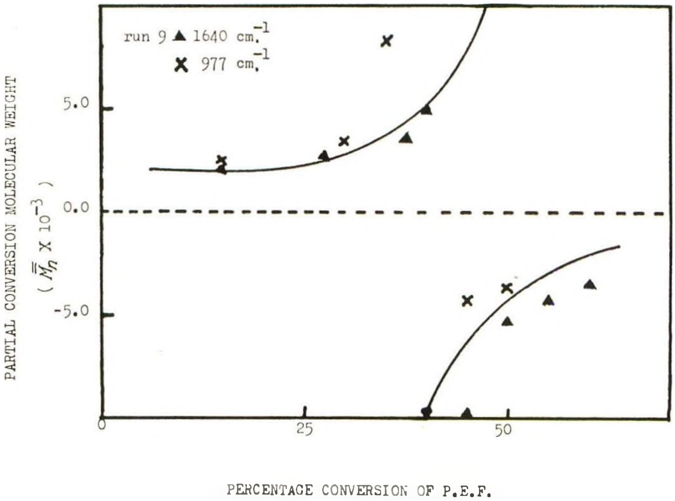

Figure 4*b*.

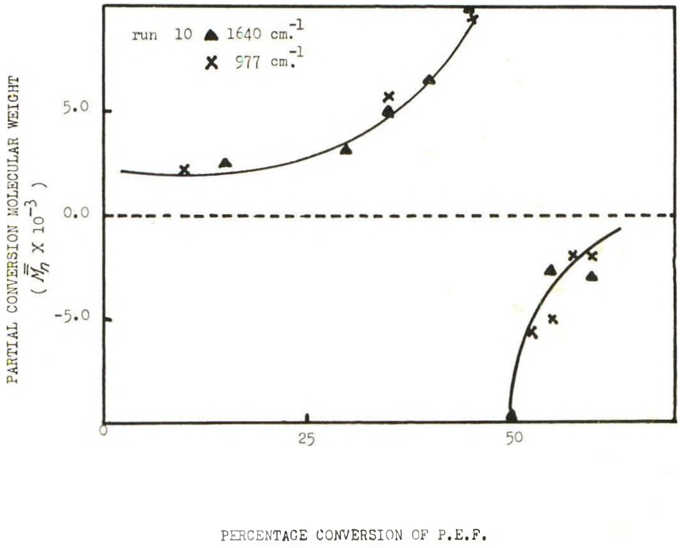

Figure 4c.

copolymerization is predominantly that of a crosslinking reaction between PEF units.

For run 5, at high conversions, the value of dN/dW as plotted against per cent conversion of PEF units (see Fig. 2), shows a marked change to increasing values. This is not evident to any appreciable extent in any of the other copolymerization experiments, nor is it in the dN/dW values, for run 5, calculated for the per cent weight conversion based on the styrene analysis. Wall, however, has also noted a similar change for a styrene–butadiene copolymerization.[2] This decrease in rate of disappearance of PEF units with conversion must indicate some change in reaction mechanism. Reactions competing with the crosslinking one which increase the number of molecules present, that is, produce polystyrene or cause chain degradation, are unlikely. No polystyrene is isolated from the copolymer samples, and no degradation is detectible in the other copolymerizations. The change in value of dN/dW must then either reflect a reduction in the crosslink formation with conversion or the production of polystyrene branches (or possibly larger polystyrenes segments between PEF units in a crosslink). Both seem equally likely. As the molecules become larger and more crosslinked, the polymer network becomes more rigid, segmental motion becomes greatly reduced, and the large molecules, in these dilute solutions, more isolated from one another. The reactivity of the PEF double bonds to radical addition will then appear to decrease. The conversion of PEF units to copolymer still occurs, however, but to a reduced extent. The activity of the styrene monomer units is not reduced to the same degree, and so small polystyrene branches (or larger crosslinks) are produced. The copolymer samples, however, show only a small increase in styrene content with conversion, (from 0.6 to 0.7 mole fraction throughout experiment).

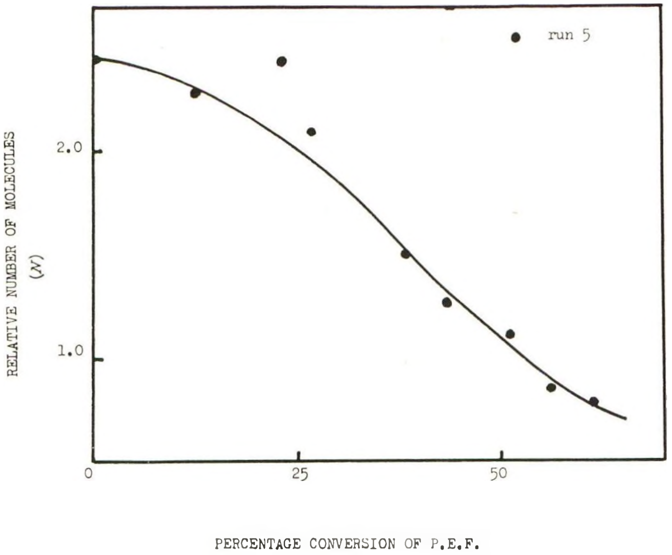

Figure 5*a*.

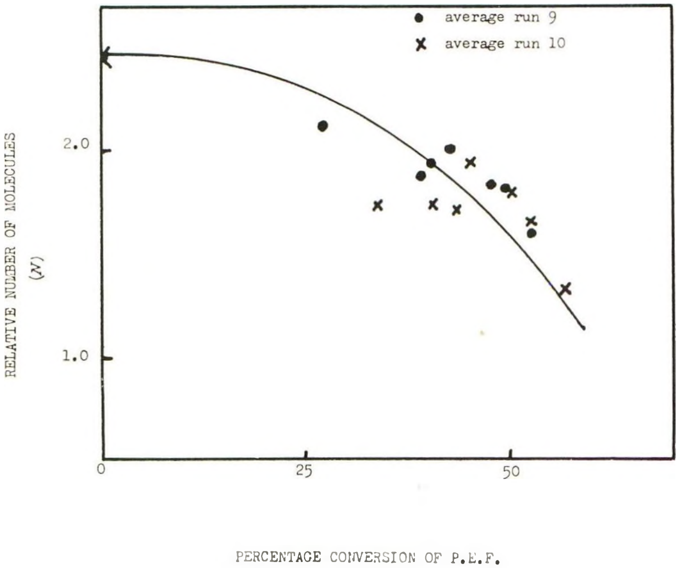

Figure 5*b*.

At high degrees of conversion, intermolecular crosslinking will be reduced but not to the same extent as intramolecular crosslinks, and the changing value of dN/dW with increasing conversion of PEF units will be higher (more positive) than expected.

The fundamental reaction in the copolymerization of styrene and PEF is that of producing crosslinks. There is no evidence of production of poly-

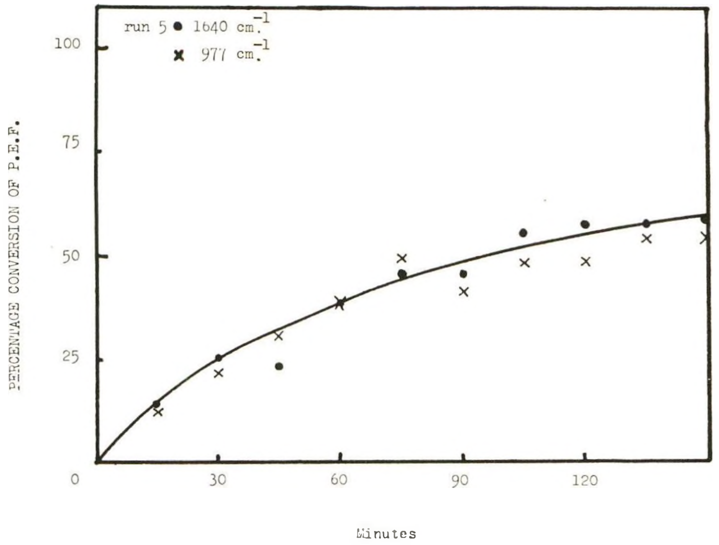

Fig. 6. Rate of crosslink formation.

styrene branches in any appreciable amounts, (except in presence of large excess of styrene and at high conversion), so that the rate of PEF units copolymerizing must be a measure of the rate of production of crosslinks. The rate of disappearance of PEF units can be seen, in Figure 6, to fall off with conversion. Unfortunately, this measure of the rate of crosslink formation does not differentiate between intramolecular and intermolecular crosslinks.

The plot of the dN/dW, or its reciprocal, the partial conversion molecular weight against conversion, can be used as a guide to the overall type of reaction which is occurring in a copolymerization reaction at various extents of reaction. Because of the errors inherent in each individual experimental determination, and the assumptions made concerning the weight of copolymer and its conversion, the absolute values of these partial conversion properties have no significance, but the general trend and shape of the above plots do. In general, for a crosslinking reaction, dN/dW is a decreasing function of conversion, and $(\overline{\overline{M}}_n)$ is a tangent-like function. Any reaction altering the rate of crosslinking with conversion will alter the shape of these curves.

One of us (J. D. B. S.) is grateful to D. S. I. R. for the award of a studentship in support of this work.

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Résumé

La copolymérisation du fumarate de polyéthylène et du styrène a été étudiée en solution diluée en examinant le changement du poids moléculaire moyen en nombre avec le taux de conversion. Le poids moléculaire pour un taux de conversion partiel change avec le taux de conversion et conduit au mécanisme de la réaction globale, qui est un mécanisme de pontage.

Zusammenfassung

Die Copolymerisationsreaktion von Polyäthylenfumarat mit Styrol wurde in verdünnter Lösung durch Messung der Änderung des Zahlenmittels des Molekulargewichts mit dem Umsatz untersucht. Das Molekulargewicht bei teilweisem Umsatz hängt vom Umsatz ab und bildet einen Schlüssel zum Bruttoreaktionsmechanismus, welcher derjenige einer Vernetzungsbildung ist.

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Synthesis and Cyclopolymerization of 4,4-Dimethyl-1,6-heptadiene-3,5-dione*

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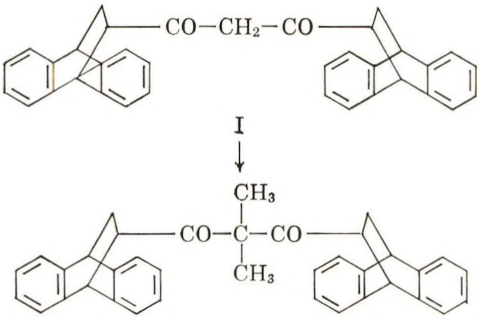
Synopsis

Dimethyldiacrylylmethane has been synthesized and polymerized to yield a soluble polymer which has the cyclic 1,3-diketone structure. It has not been possible to prepare a polydioxime of this polyketone, but a monooxime with only 90% oximated structure was obtained. This monooxime underwent the Knoevenagel reaction to yield a partial ladder polymer which had interesting thermal stability.

Polydiacrylylmethane[1] proved to be an insoluble and intractable polymer which was unsuited to conversion to the ladder-type polymer through the Knoevenagel reaction. We describe in this paper the synthesis of dimethyldiacrylylmethane (4,4-dimethyl-1,6-heptadiene-3,5-dione) which yields a soluble polymer, and some ring closing experiments on the oxime are also recorded.

Methylation of 1,3-bis(9,10-dihydro-9,10-ethano anthracenyl-11)-1,3-propandione (I),[2] by successive treatment with sodium hydride and methyl iodide, gives 2,2-dimethyl-1,3-bis(9,10-dihydro-9,10-ethano anthracenyl-11)-1,3-propandione (II) in 95% yield. Compound II was characterized by infrared spectroscopy and elementary analysis.



II

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* The work discussed herein was supported by Contract AF 33(657)-9969 with the Materials Laboratory, WADD, Wright-Patterson Air Force Base, Ohio.

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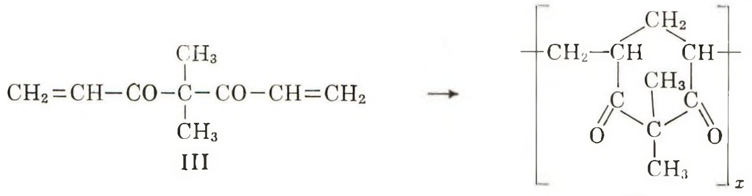
III

IV

Pyrolysis of compound II in the presence of *tert*-butyl hydroquinone, gives 4,4-dimethyl-1,6-heptadiene-3,5-dione (III) and anthracene by a reverse Diels-Alder reaction in 60–70% yield. The dione III is a pale yellow liquid with an intense acrylic odor and lachrymatory properties. It can be stored, in the absence of polymerization inhibitors, at temperatures below −20°C. It was characterized by infrared and NMR spectroscopy* (Fig. 1) and by elemental analysis.

When 4,4-dimethyl-1,6-heptadiene-3,5-dione (III) is allowed to stand at room temperature, it polymerizes slowly to yield a hard, insoluble, intractable polymer.

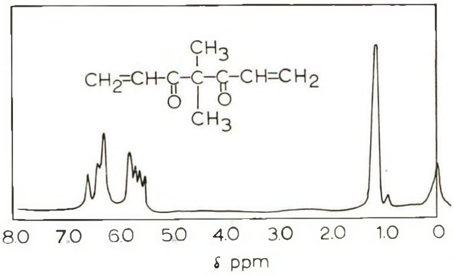

Fig. 1. Nuclear magnetic resonance spectrum of 4,4-dimethyl-1,6-heptadiene-3,5-dione.

Free radical polymerization at 65°C. with 2,2′-azobisisobutyronitrile as an initiator, in various organic solvents, yields up to 95% of a white, powdery polymer, which is soluble in the most common organic solvents. The molecular weight of the polymer depends upon the initial concentration of the monomer in the polymerization reaction, as shown in Table I. For concentrations of monomer exceeding 20%, a partly insoluble polymer is obtained. The melting point of the polymers of $[\eta]^{30°\text{C.}} = 0.12$ fluctuates around 220°C., while the polymers of $[\eta]^{30°\text{C.}} = 0.3$ do not melt below 350°C., but they shrink and turn brown after 250°C.

Attempts to increase the molecular weight of the polymer by varying the initiator concentration resulted only in changing the yield of polymer (expts. 7–11, Table I).

The cyclic structure (IV) is assigned to the polymer on the basis of absence of vinyl and enol absorption in the infrared spectrum and on the fact that the polymer was readily soluble in the common organic solvents.

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* The NMR spectra were obtained on a Varian A-60 spectrometer by Dr. J. H. Griffith at the University of Arizona.

TABLE I

Free Radical Polymerization of 4,4-Dimethyl-1,6-heptadiene-3,5-dione in Benzene[a]

Expt. no.	Initiator (AIBN), mg.	Monomer, mg.	Reaction time, hr.	$[\eta]^{30°C.}$	Yield	
					mg.	%
1	3	512	24	0.10	122	25
2	4	794	70	0.11	198	20
3	7	1450	100	0.12	432	30
4	10	1861	20	0.33[b]	1503	80
5	12	2500	15	0.32[b]	1910	75
6	15	2902	24	0.30[b]	2787	95
7	24	831	30	0.09	795	95
8	8	774	20	0.11	385	50
9	4	794	70	0.11	198	20
10	2.5	731	56	0.10	111	15
11	1	802	24	0.11	93	12

[a] All polymerizations were carried out in 10 ml. of benzene.

[b] The polymer is only 50% soluble in dimethyl sulfoxide; this solvent is used to determine the viscosity of the soluble portion in experiments 4, 5, and 6; for the other viscosities benzene was used.

TABLE II

Oximation of the Polycyclic Diketone, All Run with 304 mg. of Polymer

Run no.	$NH_2OH \cdot HCl$ mg.	Base	Amt. base, g.	Time, hr.	Solvent	N content of resulting polymer, %[a]
OxP_1	560	NaOAc	0.660	2	THF/EtOH	0.63
OxP_2	560	NaOAc	0.660	8	THF/EtOH	1.4
OxP_3	560	NaOAc	0.660	20	THF/EtOH	1.6
OxP_6	560	Pyridine	0.640	8	THF/EtOH	0.9
OxP_7	560	KOH	0.450	8	THF/EtOH	1.7
OxP_8	1020	KOH	1.120	8	THF/EtOH	4.92
OxP_9	1020	KOH	1.120	20	THF/EtOH	5.62
OxP_{11}	280	KOH	11.200	20	THF/EtOH	6.11
OxP_{14}	280	KOH	11.200	24	THF/EtOH	7.61
OxP_{16}	280	KOH	11.200	48	THF/EtOH	7.32
OxP_{20}	280	Pyridine	48.000	24	Pyridine	7.41
OxP_{21}	280	Pyridine	48.000	24	Pyridine	7.46
OxP_{23}	280	Quinoline	48.000	24	Quinoline	9.51[b]

[a] The calculated N content for a monooxime is 8.3%.

[b] Black polymer, insoluble in most organic solvents; some cyclization is apparent.

Some noncyclic polymer may be present, since high yield polymers show some insoluble portion due to crosslinking.

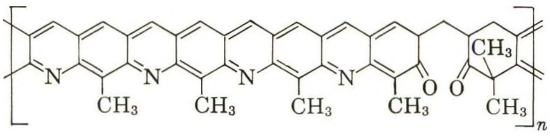
Attempts to prepare the dioxime[3,4] derivative of polymer IV in weak acid or weak alkaline medium gave almost no conversion of ketone to oxime functions. However, when the reaction is carried out in a strongly alkaline medium, an orange-yellow polymer is obtained, which is soluble in the same solvents as the starting material. Infrared absorption at 1720 cm.$^{-1}$ (>C=O), 1650 cm.$^{-1}$ (>C=N—), and 3400 cm.$^{-1}$ (—OH) and elemental analysis indicate a monooxime derivative of polymer IV with some remaining carbonyl groups. Complete conversion to a monooxime could not be obtained (Table II). Repeated oximation of the previous reaction product also failed to give 100% conversion to a monooxime (Table III).

TABLE III
Repeated Oximation of Polycyclic Diketone

Run no.	Times oximation was carried out	Base	N content of resulting polymer, %[a]
OxP$_{14}$	1	KOH	7.61
	2	KOH	7.64
OxP$_{16}$	1	KOH	7.32
	2	KOH	7.59
	3	KOH	7.70
OxP$_{21}$	1	Pyridine	7.46
	2	Pyridine	7.49
	3	Pyridine	7.49

[a] Calculated N content for 100% conversion to a monooxime is 8.3%.

Dehydration reactions on monooxime derivatives of polymer IV have been carried out in the solid state and in solution. When the polymers are heated under vacuum to 220°C. for several hours, completely black, insoluble polymers are obtained, which still contain a high percentage of oxygen. When the oximated polymers are heated at reflux temperature in quinoline for several hours, black metallic polymers can be recovered by precipitation in 1:1 methanol–water. The polymers are soluble in hot quinoline, dimethyl sulfoxide, and dimethylacetamide. Analysis of these polymers suggests structure V, viz., a ladder sequence of nine rings, alternating with one "open" segment.



V

Infrared spectra of polymer IV, the oximated derivative, and polymer V are given in Figure 2. The intrinsic viscosity at 30°C. of polymer V is $[\eta]^{30^\circ\text{C.}} = 0.12$, indicating no degradation.

The thermographic analysis curve (Fig. 3) for this polymer shows a weight loss of about 20% between 300 and 500°C. and then very little additional loss up to 900°C. This might indicate that the unaromatized ring is broken out of the chain, leaving the ladder section of the polymer essentially unaltered by this heating. The 20% weight loss corresponds rather closely to what would be expected if this type of decomposition took place.

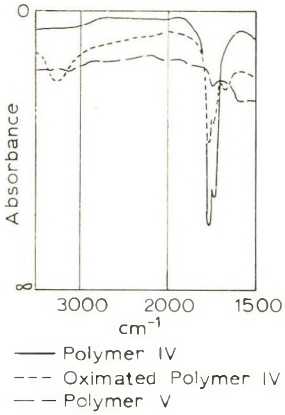


Fig. 2. Infrared spectra: polymer IV; oximated polymer IV; polymer V.

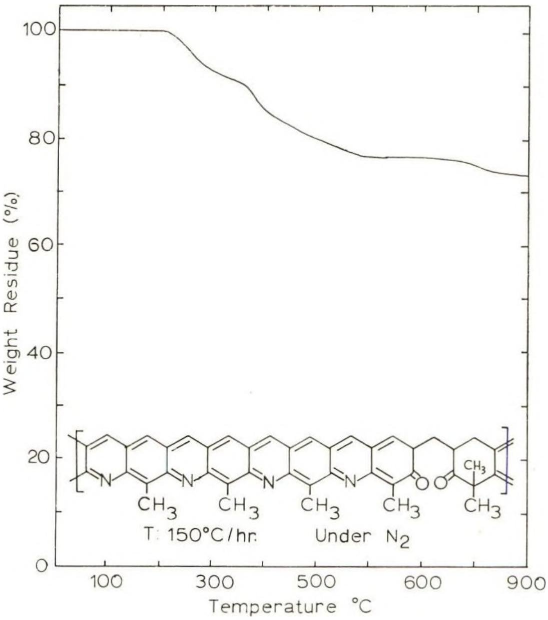


Fig. 3. Thermogravimetric analysis.

Oximation of polymer IV in quinoline at temperatures of 235–240°C., with an excess amount of hydroxylamine hydrochloride gives black, insoluble polymers which show the presence of free ketone functions (absorption band in the infrared spectrum at 1720 cm.$^{-1}$).

Further treatment of polymer V with hydroxylamine hydrochloride in quinoline or dimethylacetamide does not diminish the amount of ketone functions in the polymer.

Experimental

Methylation of 1,3-Bis(9,10-dihydro-9,10-ethano anthracenyl-11)-1,3-propandione (I). Sodium hydride (0.76 g.) was dissolved in 50 ml. of dimethyl sulfoxide and the solution was put in a 250-ml., three-necked flask, fitted with an all-glass Trubore type stirrer, a dropping funnel, and a condenser. The mixture was cooled in a crushed-ice bath, and under stirring, a solution of 7.6 g. of I, dissolved in 50 ml. of a mixture of benzene and dimethyl sulfoxide (50/50) was added within 15 min. The mixture was stirred for 15 min., then 3 ml. of methyl iodide was added within 20 min., and the slurry was stirred for 6 hr. at room temperature. The reaction product (II) was precipitated in water, washed, dried, and analyzed.

Anal. Calcd. for $C_{37}H_{32}O_{32}$: C, 86.7%; H, 7.0%. Found: C, 86.9%; H, 6.9%.

The infrared spectrum has bands at 1740 (s), 1720 (s), 1380 (m), 1330 (m), 1280 (w), 1260 (w), 1180 (m), 1150 (m), 1060 (s), 1030 (m), 990 (m), 950 (m), 915 (w), 880 (w), 850 (w), and 760 (vs) cm.$^{-1}$.

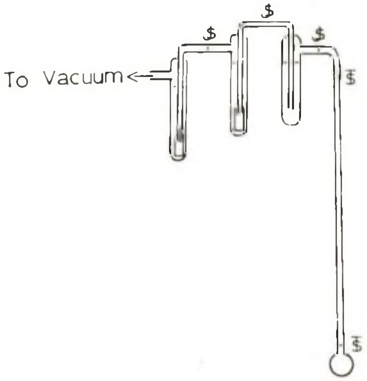


Fig. 4. Diagram of the pyrolysis apparatus.

Pyrolysis of 2,2-Dimethyl-1,3-bis(9,10-dihydro-9,10-ethano anthracenyl-11)-1,3-propandione (II). *tert*-Butyl hydroquinone (100 mg.) and 10 g. of II were placed in a 100-ml., round-bottomed flask which was connected to an upward directed Vycor tube, 20 mm. in diameter. The exit of this tube was attached by a ball-and-socket joint to an outside wall of a trap cooled at −80°C. This trap was connected by ball-and-socket joints to two other traps in series, each containing a weighed vial (Fig. 4). The end of the third trap was connected to a vacuum pump and a nitrogen inlet (see Fig. 4). After evacuating the system several times to a pressure of 0.05 mm., prepurified nitrogen was allowed to bleed into the system at a pressure of about 5 mm. Hg. Pyrolysis of II was accomplished by heating the flask for 30 min. by an open flame. The 4,4-dimethyl-1,6-heptadiene-3,5-dione (III) produced in the pyrolysis, was distilled, solidified in the first trap, and then allowed to come to room temperature; it was then redistilled twice under a pressure of 0.5 mm. and collected in the vial of the third trap. The yield was 70%.

The infrared spectrum of the product has bands at 1650 (s), 1430 (s), 1320 (s), 1020 (s), 955 (s) cm.$^{-1}$, and some broad absorption in the range of 800–650 cm.$^{-1}$.

The NMR shows peaks at τ 8.7 (methyl H), τ 4.3 (vinyl CH), and τ 3.6 (vinyl CH_2).

The refractive index of the pure product was n_D^{30} 1.4596 (compared to n_D^{30} 1.5698 for diacrylylmethane). The product was not analyzed but used directly for polymerization studies.

Free Radical Polymerization of 4,4-Dimethyl-1,6-heptadiene-3,5-dione (III). To a solution of 2.5 g. of triply distilled monomer (III) in 10 ml. of benzene was added 12 mg. of α,α'-azobisisobutyronitrile as an initiator, and the whole was frozen in a 50-ml. reaction tube. The flask was evacuated to very low pressure several times to remove the oxygen and then sealed under vacuum. The flask and contents were slowly heated in an oil bath to a temperature of 65°C. and maintained at this temperature for several hours (see Table I). The viscous solution was then cooled to room temperature and the contents poured into methanol, where the polymer precipitated. The polymer was dissolved in benzene and reprecipitated in methanol several times.

ANAL. Calcd. for $C_9H_{12}O_2$: C, 71.0%; H, 7.9%; O, 21.0%; Found: C, 70.5%; H, 8.0%; O, 21.1%.

The infrared spectrum of the polymer has absorption bands at 1750 (s), 1720 (s), 1380 (m), 1270 (m), 1265 (s), 1095 (m), 1030 (m), 805 (s), and 725 (m) cm.$^{-1}$.

Preparation of an Oxime Derivative of Polymer IV in Strongly Alkaline Medium. A 300-mg. portion of polymer IV was dissolved in 20 ml. of tetrahydrofuran. The solution was added dropwise, within 20 hr., to a boiling solution of 1 g. hydroxylamine and 5 g. of potassium hydroxide in 30 ml. of ethanol and 30 ml. of tetrahydrofuran. A purple color appeared immediately and then turned reddish after several hours. The solution was refluxed for 4 hr. more, cooled, and the solvent was removed by freeze-drying. The residue was redissolved in water, and the polymer was precipitated by adding dilute hydrochloric acid. The polymer was slightly orange-brown colored.

ANAL. Calcd. for $C_9H_{13}O_2N_1$ (monooxime): C, 64.7%; H, 7.7%; N, 8.3%; O, 19.1%. Found: C, 63.1%; H, 7.8%; N, 7.3–7.6%; O, 20.5–21.0%.

The infrared spectrum of the polymer has bands at 3040 (m), 1740 (s), 1720 (s), 1650 (m), 1380 (m), 1270 (s), 1095 (m), 1030 (m), 805 (s), and 725 (m) cm.$^{-1}$.

Oximation of Polymer IV in Quinoline at High Temperatures. Hydroxylamine hydrochloride (3 g.) and 600 mg. of polymer IV were dissolved in 60 ml. of quinoline and the solution was heated to reflux temperature for 48 hr. After cooling, the resulting black insoluble polymer was filtered off, washed and dried. The infrared spectrum of the polymer still showed the presence of free ketone functions.

ANAL. Calcd. for C_8H_5N (ladder polymer): C, 83.4%; H, 4.3%; N, 12.3%; O, ——. Found: C, 72.0%; H, 6.3%; N, 9.5%; O, 10.8%.

The infrared spectrum of this polymer has bands at 1740 (s), 1720 (s), 1650 (s), 1380 (w), 1265–1270 (s), 1059 (m), 1030 (m), 805 (m), and 725 (m) cm.$^{-1}$.

Dehydration of the Oximated Polymer IV. In the *in vacuo* procedure, 200 mg. of oximated polymer IV (N content 7.6%) was heated under vacuum at 220°C. for 48 hr.; 158 mg. of an insoluble black-brown polymer was recovered after washing.

Dehydration was also carried out in quinoline. A 200 mg. portion of oximated polymer IV (N content 7.6%) was dissolved in 100 ml. of quinoline. The solution was heated to reflux temperature for 48 hr. During the reaction the solution turned black. The black polymer was recovered by precipitation in a mixture of 200 ml. water and 250 ml. methanol.

ANAL. Calcd. for $(C_8H_5N)_n$ (ladder polymer): C, 83.4%; H, 4.3%; N, 12.3%. Calcd. for $(C_{40}H_{29}N_4O_2)_n$ (structure V): C, 80.3%; H, 4.8%; N, 9.4%; O, 5.4%. Found: C, 80.2%; H, 4.6%; N, 9.6%; O, 5.9%.

The infrared spectrum of this cyclized polymer has bands at 1710–1730 (m), 1380 (w), 1140–1160 (w), 880–900 (w), 805 (w), and 725 (m) cm.$^{-1}$.

We are indebted to Dr. G. Ehlers of the Materials Laboratory, WADD, Wright-Patterson Air Force Base, Ohio, for the thermogravimetric curve on polymer V.

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Résumé

On a synthétisé le diméthyldiacrylylméthane, et après polymérisation on a obtenu un polymère soluble possédant une structure cyclique 1,3-dicétonique. Il a été impossible d'obtenir une polydioxime de cette polycétone, mais on a obtenu une monooxime possédant seulement 90% de fonction oxime. Par la réaction de Knoevenagel, la monooxime donne un polymere en échelle G, qui présente des propriétés intéressantes du point de vue de la stabilité thermique.

Zusammenfassung

Dimethyldiacrylylmethan wurde synthetisiert und unter Bildung eines löslichen Polymeren mit der zyklischen 1,3-Diketonstruktur polymerisiert. Es war nicht möglich, ein Polydioxim dieses Polyketons darzustellen, es konnte aber ein Monooxim mit nur 90% oximierter Struktur erhalten werden. Dieses Monoxim wurde der Knoevenagel-Reaktion unterzogen und lieferte ein partielles Leiterpolymeres mit interessanter thermischer Stabilität.

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Polymerization of Styrene with $TiCl_3$–$Al(C_2H_5)_3$ and VCl_3–$Al(C_2H_5)_3$ Catalysts

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Synopsis

The polymerization of styrene was studied in benzene solution with two catalyst systems: $TiCl_3$–$Al(C_2H_5)_3$ and VCl_3–$Al(C_2H_5)_3$. The reaction was carried out at atmospheric pressure, temperatures of 40–70°C., [monomer] = 0.695–5.75 moles/l., [$TiCl_3$] = 0.12–1.2 g./l., and [alkyl] = 0.001–0.016 mole/l. For polymerizations with $TiCl_3$–$Al(C_2H_5)_3$ catalyst, the rate of polymerization was found to be first-order with respect to $TiCl_3$, proportional to $[\text{monomer}]^{1.5}$ and for $[Al(C_2H_5)_3] > 0.002$ mole/l., proportional to $[Al(C_2H_5)_3]^{-1/2}$. For $[Al(C_2H_5)_3] < 0.002$ mole/l., the rate passed through a maximum and decreased rapidly to a negligible value as the alkyl concentration decreased. The apparent activation energy was 8.1 kcal./mole. The rate of polymerization with VCl_3 as catalyst component was generally faster than the rate obtained with $TiCl_3$. A reaction scheme has been postulated to account for the influence of monomer and catalyst on the steady state rate. The model suggests that $TiCl_3$ activation consists of surface alkylation and removal of Cl^- ions by reaction with $Al(C_2H_5)_3$. Monomer adsorption occurs on vacant sites, neighboring alkylated surface sites, in competition with the adsorption of metal alkyl. Vacant and alkylated sites partake in the first coordination sphere of Ti^{+3} ions in $TiCl_3$. Polymerization follows by monomer insertion into the Ti—C bond at the alkylated site.

In recent years many investigations have been carried out on the kinetics of polymerization of relatively simple monomer molecules in the presence of several homogeneous and heterogeneous catalysts. This latter group included a large number of combinations between a transition metal halide and a light metal alkyl compound. These studies have brought to light the influence on the polymerization rate and on the structure of the polymer formed of the concentration of monomer, the metal halide/metal alkyl ratio, the temperature, the nature of solvent, and the extent of polymerization. This knowledge has provided the basis for speculations on the mechanism of the polymerization reaction. In order to verify the suggested reaction schemes and better to understand the effect of some of the above variables on catalytic polymerization, we have conducted experiments on the polymerization of styrene on $TiCl_3$–$Al(C_2H_5)_3$ and VCl–$Al(C_2H_5)_3$ catalysts, in the temperature range 40–70°C., together with observations on the degree of polymerization and on the steric composition of the polymer

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formed as evidenced by the amount of polymer insoluble in methyl ethyl ketone.

The polymerization of styrene on $TiCl_3$–$Al(C_2H_5)_3$ catalysts has been studied previously.[1–4] In benzene and toluene solvents, the rate of polymerization was found to be dependent upon the first power of the concentration of styrene, while in heptane the rate was found to be dependent upon the second power of the monomer concentration for monomer concentrations <3.6 mole/l.

In one study,[1] a maximum in the value of the polymerization rate was found for Al/Ti mole ratios of 0.3–0.4; the rate, however, became independent of the Al/Ti ratio when $TiCl_3$ was sufficiently ground up. Other studies[2,3] showed that the rate of polymerization was essentially independent of the alkyl concentration for concentrations of alkyl >0.01 mole/l. Actual molar values for the Al/Ti have no immediate significance in terms of catalyst compositions, since the catalysts are heterogeneous and the amount of alkyl adsorbed on the halide surface is dependent upon the degree of dispersion of the solid phase.

EXPERIMENTAL

Materials and Reactor

Styrene (Dow Chemical Company) was distilled at approximately 40°C./17 mm. Hg in an atmosphere of dry nitrogen. Benzene, reagent grade, was purged with dry nitrogen and dried by passing it through a column containing Linde type 4A Molecular Sieves. $TiCl_3$ (Stauffer Chemical) was reduced with hydrogen and activated; VCl_3 (Stauffer Chemical) was obtained as a deep purple crystalline powder. $Al(C_2H_5)_3$ (Texas Alkyls) was contained in a 25% solution in benzene. It was used as received. Nitrogen (Airco, prepurified) was used for providing inert gas atmospheres, and was purified by passing it over hot copper, Drierite, Molecular Sieves, phosphorus pentoxide, and calcium hydride.

The glass reaction vessel had a capacity of approximately 2000 ml. and included a stainless steel cover with special openings for reagent addition and atmosphere control. Stirring was accomplished by a stirrer operated by a variable speed hydraulic motor. Constant temperature (±0.2°C.) was maintained inside the reactor by circulating water from a controlled temperature bath through stainless steel coils. The temperature was measured by a submerged stem thermometer placed in a well in the cover of the reactor.

Procedure

All solvent, monomer, and catalyst transfers were carried out in an atmosphere of dry nitrogen. $TiCl_3$ and VCl_3 were stored in a dry box under nitrogen. The oxygen content of the dry box was reduced to <80 ppm, that of water to <100 ppm by continuous recycling of purified nitrogen. Quantities of catalyst were weighed into small test tubes in the dry box.

The general procedure for carrying out a polymerization experiment was as follows: the reactor was evacuated and heated for several hours and subsequently purged with dry nitrogen. Known amounts of benzene were forced into the reactor by means of nitrogen pressure. A known quantity of $Al(C_2H_5)_3$ was added by means of a measuring buret. The mixture of solvent and alkyl was stirred and heated to the desired temperature, while weighted amounts of $TiCl_3$ or VCl_3 were added. Freshly distilled styrene was introduced, and the time of addition of styrene was recorded as the starting time for the polymerization reaction. The total volume of the reaction mixture was generally about 800 ml. The mixture reached a constant temperature in about 5 min. after the styrene addition and remained under continuous stirring. By forcing some of the mixture out by means of nitrogen pressure, 25 ml. samples of the reaction mixture were removed periodically. The sample was immediately poured into 100 ml. of methanol containing a small amount of hydrochloric acid. The precipitated polymer was left in the methanol solution overnight, filtered on a sintered-glass filter, washed with methanol, and dried under vacuum at 70°C. to a constant weight. The polymerizations were generally carried out for durations of 1–20 hr.

The amount of polymer soluble in methyl ethyl ketone was used as a measure of the atactic fraction in the polystyrene.[5] Viscosity-average molecular weights were determined in toluene solutions. The polymer was not completely soluble in boiling toluene but it was possible to dissolve the polymer completely by heating the polymer–solvent mixture in a 75 ml. pressure bomb to a temperature ≤ 150°C. Viscosity measurements were made in a modified Ubbelhode suspended-level viscometer and viscosity-average molecular weights were calculated using the equation:[5]

$$[\eta] = 1.10 \times 10^{-4} M^{0.725}$$

RESULTS

The same batch of $TiCl_3$ was used for all $TiCl_3$–$Al(C_2H_5)_3$ polymerization runs, but kinetic observations were recorded during two time periods separated by a four-month interval (initial experiments, group A runs; later experiments, group B runs). Although $TiCl_3$ was stored in a sealed bottle kept in the dry box during this interval, there was a 14% decrease in the activity of the catalyst between the two sets of runs. However, the decrease in activity did not change the relations between the variables influencing the rate of polymerization. The degree of conversion for any given run was generally <8%, so that the concentrations of monomer and catalyst components could be assumed to remain constant, and volume changes in the reaction mixture were neglected. A small yield of low molecular weight, oily polymer was obtained when either $TiCl_3$ or VCl_3 were used alone. The $TiCl_3$–$Al(C_2H_5)_3$ catalyst appeared to be eight to ten times as active as the $TiCl_3$–$Al(C_4H_{10})_3$ catalyst used previously.[6] The melting point of the polymer formed was 231°C.

$TiCl_3$–$Al(C_2H_5)_3$ Catalyst

Typical results at 40°C. are plotted in Figure 1. These curves are characterized by a period of increasing rate of polymerization followed by a constant rate period (up to 20 hr.). The length of the variable rate period decreased as the temperature increased and was generally <200 min. at 40°C. and <100 min. at 60°C. The unsteady rate period was slightly longer for group B runs. The rates determined from the steady state por-

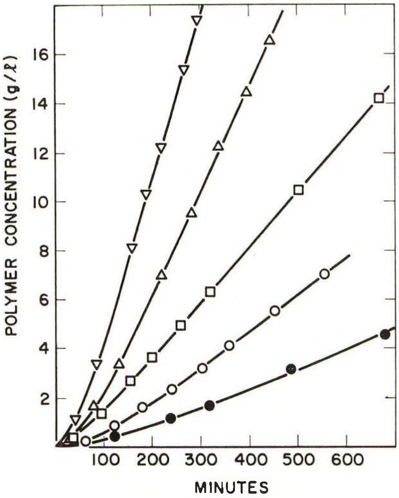


Fig. 1. Styrene polymerization in benzene at 40°C.: (●) [styrene] = 1.061 mole/l., [$TiCl_3$] = 1.47 × 10^{-3} mole/l., [$Al(C_2H_5)_3$] = 6.75 × 10^{-3} mole/l.; (○) [styrene] = 1.07 mole/l., [$TiCl_3$] = 3.72 × 10^{-3} mole/l., [$Al(C_2H_5)_3$] = 11.7 × 10^{-3} mole/l.; (□) [styrene] = 1.082 mole/l., [$TiCl_3$] = 6.70 × 10^{-3} mole/l., [$Al(C_2H_5)_3$] = 20.5 × 10^{-3} mole/l.; (△) [styrene] = 2.20 mole/l., [$TiCl_3$] = 3.73 × 10^{-3} mole/l., [$Al(C_2H_5)_3$] = 10.5 × 10^{-3} mole/l.; (▽) [styrene] = 2.15 mole/l., [$TiCl_3$] = 8.04 × 10^{-3} mole/l., [$Al(C_2H_5)_3$] = 22.6 × 10^{-3} mole/l.

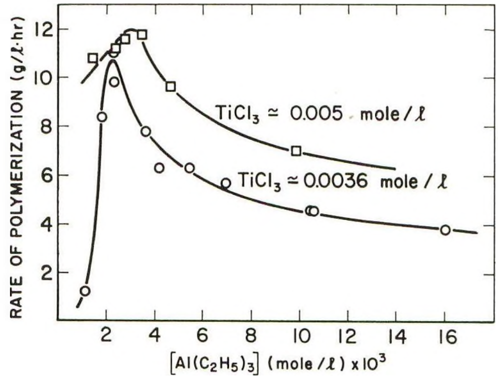


Fig. 2. Effect of $Al(C_2H_5)_3$ concentration on the rate of polymerization of styrene with $TiCl_3$–$Al(C_2H_5)_3$ catalyst. [Styrene] = 2.15 mole/l.; T = 60°C.

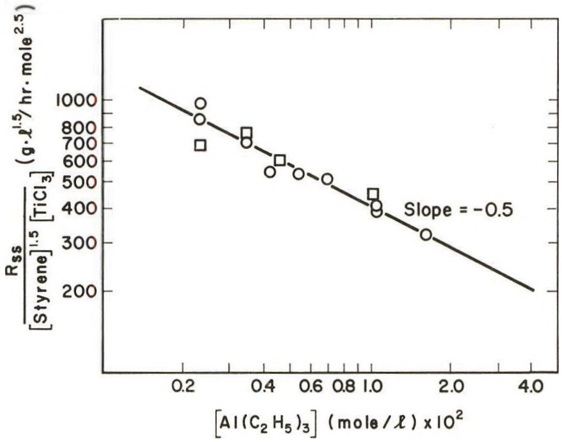


Fig. 3. Dependence of the rate R_{ss} of polymerization of styrene on $[Al(C_2H_5)_3]$: (○) $[TiCl_3] \simeq 0.0036$ mole/l.; (□)$[TiCl_3] \simeq 0.0050$ mole/l. [Styrene] $\simeq 2.15$ mole/l.; $T = 60$°C.

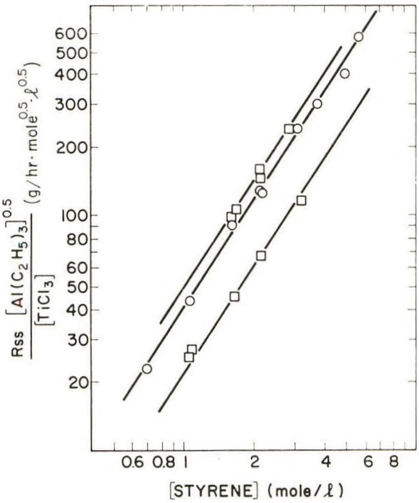


Fig. 4. Dependence of the rate R_{ss} of polymerization of styrene on [styrene]: (□) group A runs; (○) group B runs. $[TiCl_3] = 0.0036$ mole/l.; $[Al(C_2H_5)_3] = 0.0105$ mole/l.; $T = 60$°C. Slope = 1.5.

tion of the concentration versus time curves were used to investigate the effect of reaction variables on the rate of polymerization.

In the range of concentrations studied, $[Al(C_2H_5)_3]$ had a pronounced effect on the polymerization rate. This effect is shown by the results presented in Figure 2, where the rate of polymerization is plotted versus [alkyl] for two concentrations of $TiCl_3$ at constant [monomer]. The maximum rate occurred at a mole ratio Al/Ti of $\sim$0.6. For concentrations of $Al(C_2H_5)_3$ above that at which the maximum rate occurred, the rate of polymerization was proportional to $[Al(C_2H_5)_3]^{-1/2}$ (Fig. 3). There were also indications that the polymer formed under conditions of maximum rate was of a higher molecular weight. However, the polymer formed at [alkyl] = 1.0×10^{-3} mole/l. contained a large amorphous fraction. The rates of polymerization obtained at constant concentrations of $TiCl_3$ and $Al(C_2H_5)_3$ are given in Figure 4. They indicate that the rate was proportional to $[styrene]^{1.5}$. The polymerization rate was found to be linearly dependent upon $[TiCl_3]$ (Fig. 5). The results from group B runs at 60°C. were obtained at constant [monomer] and $[Al(C_2H_5)_3]$, while those from group A runs at 40°C. and 60°C. were recorded at two different monomer concentrations and varying $Al(C_2H_5)_3$ concentrations.

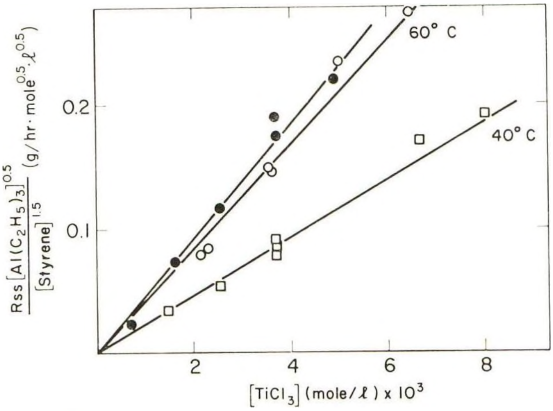


Fig. 5. Dependence of the rate R_{ss} of polymerization of styrene on $[TiCl_3]$: (●, □) group A runs; (O) group B runs.

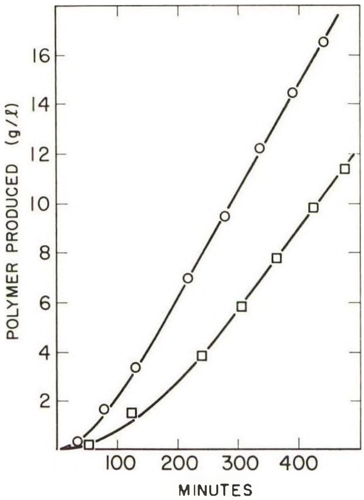


Fig. 6. Effect of premixing $TiCl_3$ and $Al(C_2H_5)_3$ on the unsteady-rate period: (O) no premixing; (□) premixing for 5 hr. $[TiCl_3]$ = 0.0037 mole/l.; $[Al(C_2H_5)_3]$ = 0.0105 mole/l., T = 40°C.

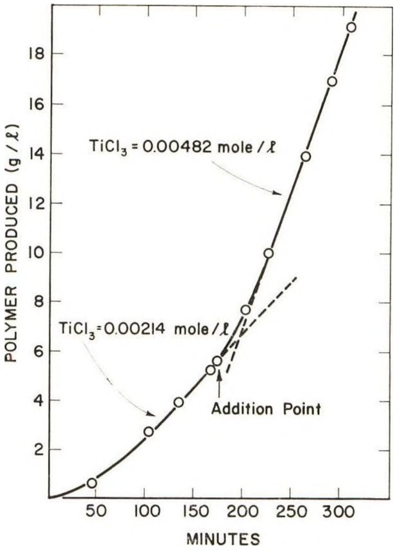


Fig. 7. Effect of additions of TiCl$_3$ during polymerization. [Styrene] = 2.14 mole/l., [Al(C$_2$H$_5$)$_3$] = 0.0105 mole/l., T = 60°C.

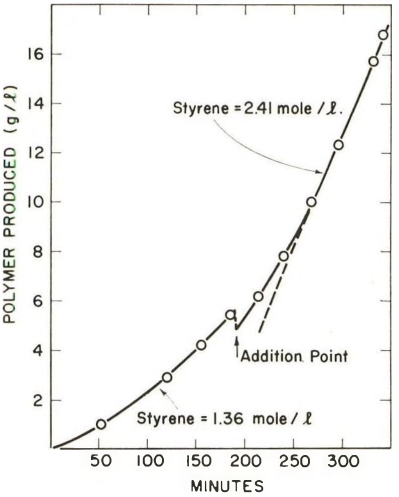
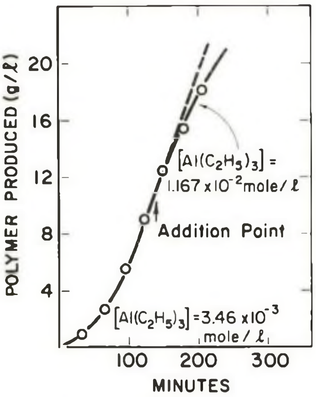


Fig. 8. Effect of additions of styrene to the reaction mixture during polymerization. [Al(C$_2$H$_5$)$_3$] = 0.0105 mole/l., [TiCl$_3$] = 0.0364 mole/l., T = 60°C.

As indicated by the above results, the steady state polymerization rate, R_{ss}, obtained using concentrations of Al(C$_2$H$_5$)$_3$ greater than those at the peaks shown in Figure 3, can be represented by:

$$R_{ss} = k[\text{styrene}]^{1.5}[\text{TiCl}_3]/[\text{Al}(\text{C}_2\text{H}_5)_3]^{0.5} \qquad (1)$$

From the temperature dependence of k, an apparent activation energy of 8.1 kcal./mole was computed. When R_{ss} is expressed as grams of polymer per



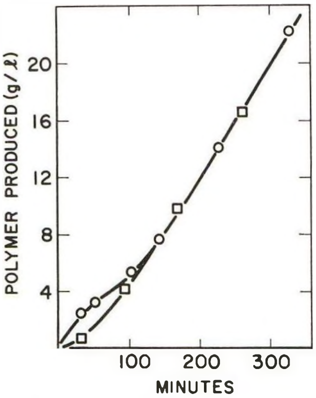


Fig. 9 (left). Effect on the rate of polymerization of adding $Al(C_2H_5)_3$. [Styrene] = 2.11 mole/l., $[TiCl_3]$ = 0.00363 mole/l., T = 60°C.

Fig. 10 (right). Effect of the order of addition on the rate of polymerization: (□) styrene added last; (O) $Al(C_2H_5)_3$ added last. [Styrene] = 2.14 mole/l., $[TiCl_3]$ = 0.00355 mole/l., $[Al(C_2H_5)_3]$ = 0.0106 mole/l., T = 60°C.

liter per hour and the concentrations are in moles per liter, the value of the preexponential factor for the group A runs is 1.07×10^7 and 0.91×10^7 for the group B runs.

Several experiments were carried out with the aim of gaining further insight into the nature of the nonsteady-state rate period. Two runs were made after premixing $Al(C_2H_5)_3$ and $TiCl_3$ for periods of 5 hr. (group A) and 90 min. (group B). A comparison of the courses of two runs in which all experimental conditions were similar, except for premixing of $TiCl_3$ with $Al(C_2H_5)_3$, is shown in Figure 6. It is clear from these results that premixing did not eliminate the unsteady rate, but slightly reduced the steady-state rate. This could probably be adscribed to some deactivation of the catalyst by impurities.

Addition of $TiCl_3$ during the course of the polymerization resulted in a new unsteady-state period with the rate gradually increasing to a new steady-state value (Fig. 7). This supports the contention that the unsteady-state period is connected with phenomena occurring on the surface of the $TiCl_3$. The influence of additional monomer on the polymerization rate is shown in Figure 8. After addition of styrene the rate showed an approximate first-order dependency on monomer when compared to the steady state rate before addition. The influence of the introduction of $Al(C_2H_5)_3$ during reaction is shown in Figure 9.

In most of the experiments reported the monomer was the last addition during the charging of the reactor. For some runs the order of addition was reversed to benzene, styrene, $TiCl_3$, and $Al(C_2H_5)_3$. The effect of the reversal in the sequence of additions before polymerization is shown in Figure 10. The steady-state rate was not influenced by the order of addition, but the unsteady-state rate was found to be dependent upon the addition sequence.

VCl_3–$Al(C_2H_5)_3$ Catalyst

The polymerization of styrene with VCl_3–$Al(C_2H_5)_3$ was studied at 60°C. The polymerization exhibited a period of increasing rate similar to that observed for polymerization with the $TiCl_3$–$Al(C_2H_5)_3$ catalyst. The

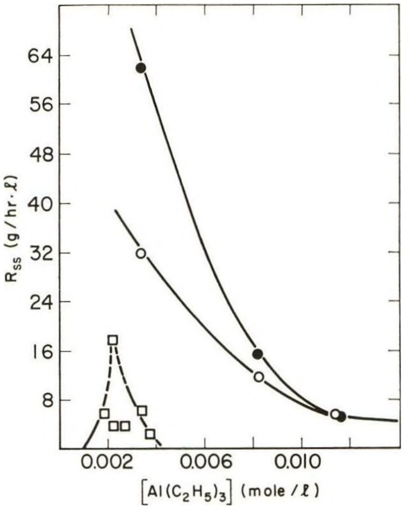


Fig. 11. Effect of $[Al(C_2H_5)_3]$ on the rate R_{ss} of polymerization of styrene with VCl_3 and $Al(C_2H_5)_3$: (□) $[VCl_3] \simeq 0.00395$ mole/l., (○) $[VCl_3] \simeq 0.0155$ mole/l., (●) $[VCl_3] \simeq 0.031$ mole/l., [styrene] $\simeq 2.15$ mole/l., $T = 60$°C.

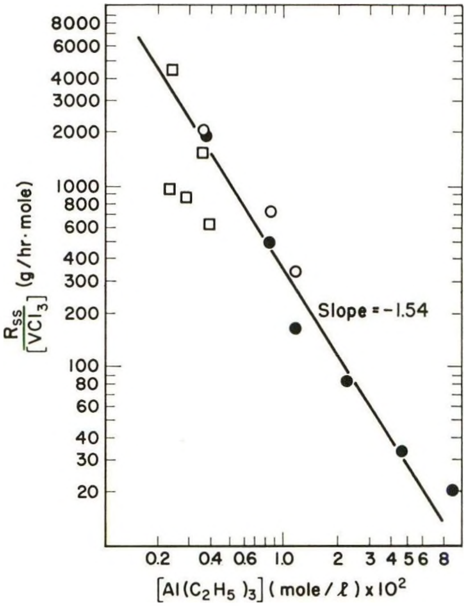


Fig. 12. Dependence of the rate R_{ss} of polymerization of styrene with VCl_3–$Al(C_2H_5)_3$ catalyst on $[Al(C_2H_5)_3]$: (●) $[VCl_3] = 0.031$ mole/l., (○) $[VCl_3] = 0.0155$ mole/l., (□) $[VCl_7] = 0.00395$ mole/l., [Styrene] = 2.15 mole/l., $T = 60$°C.

effect of $[Al(C_2H_5)_3]$ on the rate of polymerization at three different concentrations of VCl_3 is shown in Figure 11. For $[VCl_3] = 3.95 \times 10^{-3}$ mole/l., significant rates were obtained over a very narrow range of alkyl concentrations. The rate achieved a maximum value at approximately the same alkyl concentrations for which maximum rate values were found when using the $TiCl_3$–$Al(C_2H_5)_3$ catalyst.

The dependence of the polymerization rate on $[Al(C_2H_5)_3]$ is shown in Figure 12. The plot indicates that the rate was proportional to $[\text{alkyl}]^{-1.5}$. A first-order dependence on $[VCl_3]$ is also shown. The effect of monomer concentration was not studied.

Molecular Weight and Insoluble Fraction

The dependence of the intrinsic viscosity $[\eta]$ of the polymer on $[TiCl_3]$, $[Al(C_2H_5)_3]$, and [monomer] is presented in Figures 13, 14, and 15 and Table I. Generally, $[\eta]$ increased with the degree of conversion, as it can be seen from the results collected in Table I, where information on the fraction insoluble in methyl ethyl ketone is also included.

Increasing temperatures resulted in polymers with lower molecular weights. The viscosity-average molecular weight ranged from 2×10^6 to 11

TABLE I

Reaction Variables in the Polymerization of Styrene and Intrinsic Viscosity and Solubility in Methyl Ethyl Ketone of the Polymer Formed

Polymerization temperature, °C.	Conversion, %	$[Al(C_2H_5)_3]$, mole/l.	[Styrene], mole/l.	$[TiCl_3]$, mole/l.	% of polymer insoluble in MEK	$[\eta]$, dl./g.	$M \times 10^{-6}$
60	2.0	0.00696	2.11	0.00363	91	6.00	3.42
	4.8				92	6.32	3.66
	61				88	7.20	4.39
	5.0	0.01025	0.695	0.00352	94	4.34	2.19
	9.3				97	4.16	2.06
	13.0				97	4.90	2.59
	3.4	0.00234	2.6	0.00512	77	12.4	9.30
	8.4				85	13.9	10.87
	1.0	0.0105	2.17	0.00363	83	5.7	3.18
	7.5				78	6.7	3.98
	2.7	0.0103	3.80	0.00355	91	6.63	3.92
	4.6				83	6.84	4.09
	4.7	0.0104	1.055	0.00362	70	4.90	2.59
	8.9				80	5.45	3.00
	3.2	0.0104	2.10	0.00503	87	5.74	3.22
	8.7				75	7.10	4.31
40	6.3	0.0105	2.20	0.00373	96	8.3	5.34
50.8	6.9	0.0105	2.16	0.00360	86	7.05	4.27
60	5.9	0.0105	2.16	0.00371	92	6.5	3.82
70	6.7	0.0107	2.12	0.00404	78	5.7	3.18

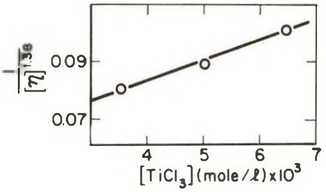


Fig. 13. Dependence of the intrinsic viscosity on [$TiCl_3$]. [Styrene] = 2.15 mole/l., [$Al(C_2H_5)_3$] = 0.0105 mole/l., T = 60°C.

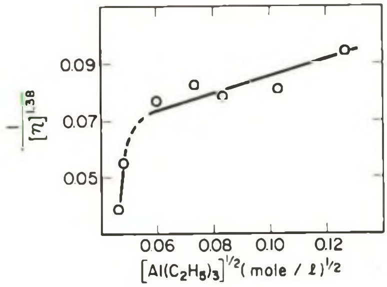


Fig. 14. Dependence of the intrinsic viscosity on [$Al(C_2H_5)_3$]. [Styrene] = 2.15 mole/l., [$Al(C_2H_5)_3$] = 0.0036 mole/l., T = 60°C.

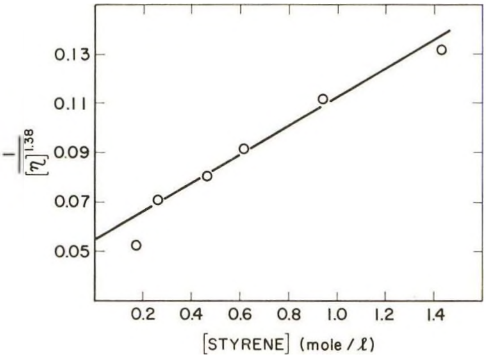


Fig. 15. Dependence of the intrinsic viscosity on [styrene]. [$Al(C_2H_5)_3$] = 0.0105 mole/l., [$TiCl_3$] = 0.0036 mole/l., T = 60°C.

$\times 10^6$. The molecular weights of the polymer obtained with the VCl_3–$Al(C_2H_5)_3$ catalyst also increased with decreasing concentration of $Al(C_2H_5)_3$.

DISCUSSION

Rate of Polymerization

The significant results reported in the previous section show that the constant temperature rate of polymerization of styrene in benzene solutions with $TiCl_3$–$Al(C_2H_5)_3$ catalysts was dependent upon monomer concentration to a power >1, while it showed a maximum value as the alkyl concentration was increased at constant monomer concentration. In addition, a period of increasing rate preceded the stage of steady-state rate. This initial, increasing rate period has been previously recorded for styrene polymerization in *n*-heptane with $TiCl_3$–$Al(C_2H_5)_3$ while a decreasing rate period was found with $TiCl_3$–$Al(C_2H_5)_2Cl$. It has also been reported that the unsteady rate was influenced by the solvent used for polymerization.[3]

The general uniformity of the unsteady-state periods, observed during the present study, and their reproducibility lends support to the suggestion that the nonsteady rate is related to chemical reactions among the components of the catalyst system.[3] Furthermore, the facts that a new period of increasing rate results when monomer was added to the reacting mixture and that premixing of the catalyst components did not eliminate the unsteady-rate period do not conflict with the above assumption.

The experimentally observed relation between the rate of polymerization and monomer concentration indicates that two monomer units are involved in the activated complex whose formation controls the observed rate of polymerization. Several kinetic schemes based on this consideration can be visualized, and the choice among them is made difficult by the lack of direct information on the structure of the activated complex. In order to indicate some types of reactions which could be held responsible for the reported results, it is instructive to briefly review the structure of the $TiCl_3$ surface. The most likely surface planes of the layer structure of α-$TiCl_3$ are perpendicular to the trigonal axis and formed by a close packed layer of Cl^- ions, with Ti^{+3} ions lying directly underneath the surface layer. Each

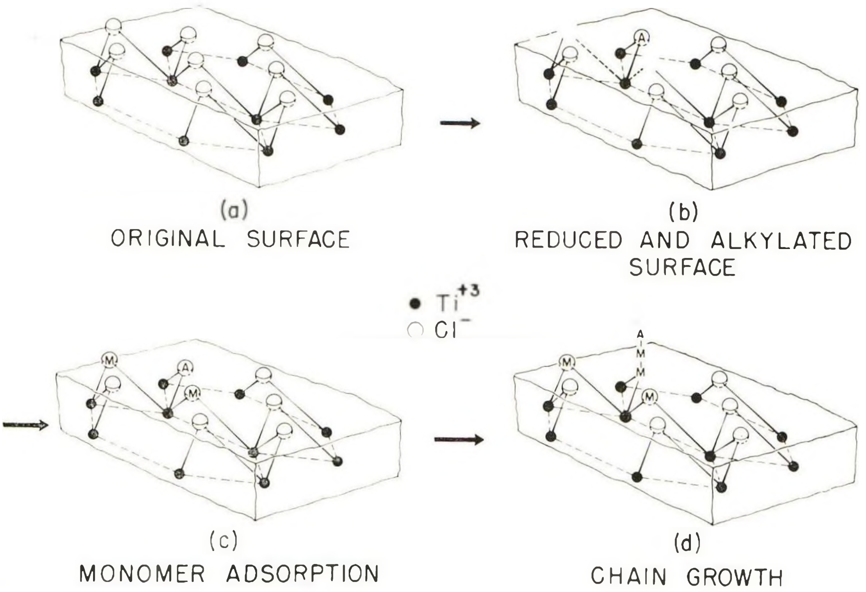


Fig. 16. Schematic representation of alkylation, reduction, adsorption of monomer, and polymerization at the surface of $TiCl_3$. A = C_2H_5, M = monomer.

Ti^{+3} is surrounded by an octahedral coordination shell of Cl^- ions. Thus, for the present discussion we shall consider in a simple fashion the reactions of "surface groups" $Ti^{+3}\ (Cl^-)_6$ as the steps of catalyst activation and surface polymerization take place. We shall assume that the reaction between surface groups and adsorbed $Al(C_2H_5)_3$ results in the formation of surface reduced and alkylated groups, $Ti^{+3}\ (Cl^-)_xA$, where A is an alkyl group, and $x = 3, 4,$ or 5. As a result, vacant octahedral positions are formed in the first coordination sphere of Ti^{+3}. It is possible that a similar reduction can be achieved by cleaving $TiCl_3$ crystals under a reducing atmosphere (grinding). The extent of surface reduction obtained by treatment with the aluminum alkyl is not known and it is probably dependent on temperature, concentration of alkyl, and surface conditions. The reduced and alkylated surface groups can be viewed as forming a cluster of one or more anionic vacancies in whose proximity a carbon ion is located.[7] In this manner the aliphatic anion is stabilized with the help of the electron affinity of the neighboring vacancies. We assume that surface groups $Ti^{+3}\ (Cl^-)_xA$ are the active sites for monomer adsorption and polymerization. The representation of these groups as isolated entities is, of course, a crude approximation, since in the actual crystal structure of $TiCl_3$ each Cl^- is shared by two Ti^{+3} ions. An essentially similar picture of an active surface site has already been suggested for the polymerization of propylene.[8]

If adsorption of monomer takes place in the vacant sites, adjacent to the alkylated surface site, an activated polymerization complex could result with the participation of monomer from neighboring sites (Fig. 16). Through interaction of one of the electrons of the anion, situated in the field of the defect, with π-electrons of the olefin, the formation of a σ-electron bond between the carbon atom of the anion and a neighboring carbon atom of the monomer may take place. It has been shown that in this type of process selection of the stereoconfiguration of the chain is possible.[7] It should be noted that according to the above mechanism $Al(C_2H_5)_3$ would not only induce the alkylation of the $TiCl_3$ surface, but would also act as a reducing agent for the latter. The activation reaction, therefore, is not viewed as equivalent to the formation of alkyl titanium compounds. This is consistent with the observation that the latter, when in pure state, are not able to readily polymerize olefins.

According to the type and conditions of monomer adsorption, the polymerization mechanism just outlined yields a rate proportional to $[\text{monomer}]^y$, where $0 < y \leqslant 2$. In fact, assuming a degree of surface reduction corresponding to $x = 3$, monomer adsorption at a surface vacancy can be schematically represented by

$$Ti^{+3}(Cl^-)_3A + M \rightleftharpoons Ti^{+3}(Cl^-)_3AM \quad (2)$$

and at a second vacancy of the same active site:

$$Ti^{+3}(Cl^-)_3AM + M \rightleftharpoons Ti^{+3}(Cl^-)_3AM_2 \quad (3)$$

If reactions (2) and (3) take place faster than the polymerization reaction:[9]

$$\mathrm{Ti}^{+3}(\mathrm{Cl}^-)_3\mathrm{AM}_2 \xrightarrow{k_4} \mathrm{Ti}^{+3}(\mathrm{Cl}^-)_3\mathrm{A} + \text{polymer} \tag{4}$$

the rate of polymerization can be represented by:

$$d[\text{polymer}]/dt = k_4[\mathrm{Ti}^{+3}(\mathrm{Cl}^-)_3\,\mathrm{AM}_2] \tag{5}$$

The detailed reactions leading to the formation of the active groups Ti^{+3}-$(\mathrm{Cl}^-)_3$ are not known, but conceivably involve the adsorption of the metal alkyl dimer from the liquid phase in competition with the monomer. Thus, it is possible to set:

$$[\mathrm{Ti}^{+3}(\mathrm{Cl}^-)_3\mathrm{A}] \cong \frac{b_\mathrm{A}K^{1/2}[\mathrm{A}_2]^{1/2}[\mathrm{TiCl}_3]}{1 + b_\mathrm{A}K^{1/2}[\mathrm{A}_2]^{1/2} + b_\mathrm{M}[\mathrm{M}]} \tag{6}$$

where b_A, b_M, K, A_2 are the adsorption coefficients of the alkyl and monomer, the dimerization constant, and the dimeric form of the metal alkyl, respectively. $[\mathrm{TiCl}_3]$ is assumed to be proportional to $[\mathrm{Ti}^{+3}(\mathrm{Cl}^-)_6]$. Equation (6) assumes that the Langmuir formalism can be used in the present case and that no reaction products other than those appearing in the adsorbed phase are present. The expression for $[\mathrm{Ti}^{+3}(\mathrm{Cl}^-)_3\mathrm{AM}_2]$ can be obtained in a similar manner from eqs. (2) and (3). The experimental results on the effect on the rate of the Al/Ti ratio (Fig. 2) require, however, that equilibria (2) and/or (3) be established under conditions of competitive adsorption with the metal alkyl. From the present results it is not possible to distinguish between the two alternatives. Therefore we shall assume that only equilibrium (2) is appreciably influenced by alkyl adsorption. Thus, from eqs. (2), (3), (6), and (5):

$$\frac{d[\text{polymer}]}{dt} = k_4 \times \left\{\frac{b_2b_3b_\mathrm{A}K^{1/2}[\mathrm{M}]^2[\mathrm{A}_2]^{1/2}}{(1 + b_2[\mathrm{M}] + b_\mathrm{A}K^{1/2}[\mathrm{A}_2]^{1/2})(1 + b_3[\mathrm{M}])(1 + b_\mathrm{M}[\mathrm{M}] + b_\mathrm{A}K^{1/2}[\mathrm{A}_2]^{1/2})}\right\} \tag{7}$$

In this expression b_2, b_3 are the adsorption coefficients of reactions (2) and (3). Equation (7) predicts a rate directly proportional to $[\mathrm{A}_2]^{1/2}$ at low $[\mathrm{A}_2]$, becoming inversely proportional at high $[\mathrm{A}_2]$. This is consistent with the results of Figure 2. In addition, eq. (7) shows that at low [M] the rate of polymerization should become dependent upon $[\mathrm{M}]^2$ and independent at high [M].

Degree of Polymerization

Taking the reciprocal of the number-average degree of polymerization, $\bar{x}_n$, as

$$1/\bar{x}_n = \sum_i (R_t)_i/R_p$$

where R_p, R_t are the rates of propagation and termination, respectively, the relation between $\bar{x}_n$, $[\eta]$, $[M]$ and the concentrations of reagents contributing to chain propagation and termination processes is of the form

$$1/\bar{x}_n = K'(1/[\eta])^{1/a} = A + (B/[M]) \tag{8}$$

where K' is a constant, $a = 0.725$, and A and B are combinations of rate constants and concentrations of reagents, other than monomer, that contribute to chain termination processes. Figures 13, 14, and 15, support the validity of eq. (8) except at high values of the intrinsic viscosity. This effect may be the result of a change in the value of a in eq. (8).

It is not possible to arrive at a definite form for the expression relating the concentration variables to $[\eta]$. The data can be satisfactorily described by empirical expression of the type:

$$\frac{1}{[\eta]^{1.38}} = 0.054 + 165\,\frac{[Al(C_2H_5)_3]^{1/2}\,[TiCl_3]}{[\text{Styrene}]}$$

which indicates that the degree of polymerization is given by an equation of the form:

$$\frac{1}{\bar{x}_n} = k_{tm}\,\frac{[M] + k_{tTA}\,[TiCl_3][Al(C_2H_5)_3]^{1/2}}{k_p[M]}$$

where k_{tm} is a rate constant for termination reactions involving monomer and k_{tTA} is a rate constant for termination reaction depending on $TiCl_3$ and $Al(C_2H_5)_3$.

The fact that the $TiCl_3$ influences the molecular weight is difficult to explain. Probably an organotitanium compound whose concentration depends on that of $TiCl_3$ takes part in a chain transfer process. It is well known[10] that the molecular weight of polypropylene formed with a $TiCl_3$–$Al(C_2H_5)_3$ catalyst depends upon $[TiCl_3]^{1/2}$.

CONCLUSIONS

Over the range of conditions studied, the polymerization of styrene with $TiCl_3$–$Al(C_2H_5)_3$ catalysts in benzene solution showed an initial period during which the rate increased with time followed by a period of constant rate. The nature of the increasing rate period was a function of [monomer] as well as the concentration of the catalyst components. The time necessary to reach a steady state depended upon temperature, [monomer], and [catalyst].

The course of the steady-state period can be satisfactorily described by a model which assumes that the formation of active sites occurs by alkylation and reduction of $TiCl_3$ following reaction with $Al(C_2H_5)_3$. The concentration of active sites gradually increases to a constant value. Polymerization occurs upon adsorption of monomer molecules on the active sites with subsequent addition to the growing chains. The activated complex contains two monomer units.

A maximum in the value of the polymerization rate was found as the Al/Ti ratio varied. This may result from competitive adsorption between metal alkyl and monomer, and/or deactivation of sites due to termination reactions involving alkyl. The per cent of polymer insoluble in methyl ethyl ketone varied from 70 to 97%. The polymer formed under the conditions used for this investigation had a high molecular weight, with $[\eta]$ from 4.2 to 13.9 dl./g. The effect of the reaction variables upon $[\eta]$ indicated that monomer, $Al(C_2H_5)_3$, and some agent dependent upon $[TiCl_3]$ took part in chain termination processes.

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Résumé

On a étudié la polymérisation du styrène en solution benzénique en présence de deux systèmes catalytiques: $TiCl_3$–$Al(C_2H_5)_3$ et VCl_3–$Al(C_2H_5)_3$. La réaction a été réalisée à pression atmosphérique et à des températures variant de 40 à 70°C, une concentration en monomère de 0.695 à 5.75 moles/litre, $[TiCl_3] = 01.2$ à .12 g/l et [alcoyl] = 0.001 à 0.016 moles/litre. Pour les polymérisations initiées par le système $TiCl_3$–$Al(C_2H_5)_3$, on a trouvé que la vitesse de polymérisation était du premier ordre par rapport à $TiCl_3$, proportionnelle au $[\text{monomère}]^{1.5}$ et pour une concentration en $[Al(C_2H_5)_3] > 0.002$ mole/l elle est proportionnelle à $[Al(C_2H_5)_3]^{-1/2}$. Pour $[Al(C_2H_5)_3] < 0.002$ mole/l, la vitesse passe par un maximum et décroît rapidement jusqu'à une valeur négligeable quand la concentration en alcoyle décroit. L'énergie d'activation apparente est de 8.1 Kcal/mole. La vitesse de la polymérisation catalysée par VCl_3 est généralement plus grande que celle de la polymérisation catalysée par $TiCl_3$. On a proposé un schéma de réaction pour expliquer l'influence du monomère et du catalyseur sur la vitesse à l'état stationnaire. Le modèle suggère que l'activation par $TiCl_3$ consiste en une alcoylation en surface et en un enlèvement d'ions Cl^- par réaction avec $Al(C_2H_5)_3$. L'absorption du monomère a lieu sur des sites libres proches des surfaces occupées par les groupes alcoyles en compétition avec l'adsorption du dérivé métallique. Les sites libres et alcoylés font partie de la première sphère de coordination des ions Ti^{3+} dans $TiCl_3$. La polymérisation a lieu par insertion du monomère entre le lien Ti–C sur le site alcoylé.

Zusammenfassung

Die Polymerisation von Styrol wurde in Benzollösung mit zwei Katalysatorsystemen $TiCl_3$–$Al(C_2H_5)_3$ und VCl_3–$Al(C_2H_5)_3$ untersucht. Die Reaktion wurde bei Atmosphärendruck, Temperaturen von 40 bis 70°C, [Monomeres] = 0,695 bis 5,75 Mol/l, [$TiCl_3$] = 0,12 bis 1,2 g/l und [Alkyl] = 0,001 bis 0,016 Mol/l ausgeführt. Bei Polymerisation mit $TiCl_3$–$Al(C_2H_5)$-Katalysator war die Polymerisationsgeschwindigkeit von erster Ordnung in Bezug auf $TiCl_3$, proportional zu $[\text{Monomeres}]^{1,5}$ und bei $[Al(C_2H_5)_3] >$ 0,002 Mol/l proportional zu $[Al(C_2H_5)_3]^{-1/2}$. Bei $Al(C_2H_5)_3 <$ 0,002 Mol/l ging die Geschwindigkeit durch ein Maximum und nahm mit fallender Alkylkonzentration rasch auf einen vernachlässigbar kleinen Wert ab. Die scheinbare Aktivierungsenergie betrug 8,1 kcal/Mol. Mit VCl_3 als Katalysatorkomponente war die Polymerisationsgeschwindigkeit im allgemeinen grösser als die mit $TiCl_3$ erhaltene Geschwindigkeit. Ein Reaktionsschema zur Erklärung des Einflusses von Monomerem und Katalysator auf die stationäre Geschwindigkeit wird aufgestellt. Das Model lässt eine $TiCl_3$-Aktivierung durch Oberflächenalkylierung und Entfernung von Cl^--Ionen durch Reaktion mit $Al(C_2H_5)_3$ als wahrscheinlich erscheinen. Monomeradsorption findet an freien Plätzen in der Nachbarschaft alkylierter Oberflächenplatze in Konkurrenz mit der Adsorption von Metallalkylen statt. Freie und alkylierte Plätze beteiligen sich an der ersten Koordinationssphäre von Ti^{+3}-Ionen in $TiCl_3$. Die Polymerisation erfolgt durch Monomerinsertion in die Ti–C-Bindung in den alkylierten Plätzen.

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Study of the Preparations of a Piperazine Polyurea and Polyamide by Low Temperature Solution Polymerization

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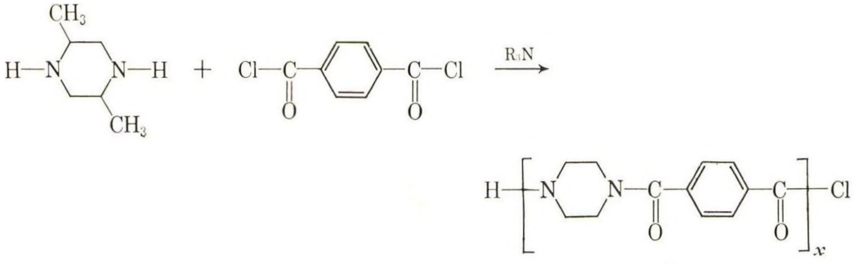
Synopsis

The preparations of two condensation polymers by low temperature solution polymerization are compared for the effect of reactant imbalance upon molecular weight. In addition, other variables, such as solvent selection, reaction time, and stirring rate are examined. The polymers are the polyamide from *trans*-2,5-dimethylpiperazine and terephthaloyl chloride and the alternating polyurea from *trans*-2,5-dimethylpiperazine and methylene bis(4-phenyl isocyanate). In contrast to the polyamide-forming reaction, the polyurea polymerization does not require acid acceptors and produces no by-products. The investigation led to the preparation of extremely high molecular weight polyureas by use of the inert solvent mixture, tetramethylene sulfone–chloroform. Poly(*N*,*N*,-terephthaloyl-*trans*-2,5-dimethylpiperazine) was previously shown to have an unusual lack of sensitivity to reactant imbalance as compared to melt polycondensation when excess diamine was used as the acid acceptor. Similar behavior is found for the polyurea as well as the polyamide when tertiary amine is used as the acid acceptor. However, under certain conditions, side reactions can cause the formation of polyamides with lower inherent viscosity values than calculated. In both cases the insensitivity to reactant imbalance is ascribed to an extremely fast reaction.

INTRODUCTION

A previous publication on the preparation of the polyamide (I) from *trans*-2,5-dimethylpiperazine and terephthaloyl chloride, by low temperature solution polymerization revealed the lack of sensitivity of this reaction to react imbalance as compared to melt polycondensation.[1] This system employed excess diamine as the acid acceptor and produced piperazine dihydrochloride as a by-product.

In contrast to the poly(terephthaloyl dimethylpiperazine) preparation by solution polycondensation, polyurea formation from a diamine and diisocyanate represents a simple system with no need for acid acceptors and no by-product formation. For this reason, the polycondensation yielding alternating poly(*trans*-2,5-dimethylpiperazine/4,4′-methylenediphenylurea) (II) was selected for a further study of reactant imbalance upon molecular weight. This polymer had previously been made by Katz.[2]



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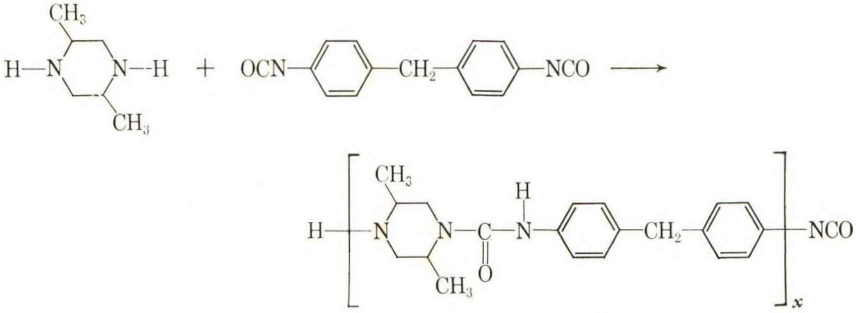

II

EXPERIMENTAL

Materials

The following chemicals, which are available commercially, were purified further as indicated and stored in amber bottles.

trans-2,5-Dimethylpiperazine, (DMePip), was recrystallized from acetone, m.p. 118°C.

Methylene bis(4-phenyl isocyanate), (DDMDI), was subjected to two vacuum distillations. The colorless fraction which distilled at 163–166°C. at 0.3 mm. was used.

Tetramethylene sulfone (TMS), was distilled under reduced pressure through a 15-in. Vigreaux column. The desired fraction distilled at 101–102°C. at 0.3 mm. and the $n_D^{31.8}$ was 1.4813.

Chloroform was A.C.S. reagent grade which was freed of alcohol stabilizer by washing three times with an equal volume of water. It was dried over anhydrous calcium chloride for several hours, filtered, and then stored over a mixture of approximately equal parts of anhydrous calcium chloride and potassium carbonate. Washed chloroform required at least an overnight drying period before use. Hydrogen chloride and phosgene, which are present in decomposing chloroform, may be detected by the development of a precipitate upon the addition of a drop or so of an aliphatic diamine or by the insertion of moist litmus paper into the vapors.

Polymer Preparation

The alternating polyurea (II) was prepared in a variety of solvents from *trans*-2,5-dimethylpiperazine and methylene bis(4-phenyl isocyanate).

This polyurea is abbreviated DMePip-1-DDM-1 following polyamide nomenclature in which 1 denotes carbonic acid or one-carbon diacid and the diamine portions are designated by DMePip and DDM (for diaminodiphenylmethane). The polyamide (I) from *trans*-2,5-dimethylpiperazine and terephthaloyl chloride is coded DMePip-T.

The rate of formation of DMePip-1-DDM-1 polyurea is fast enough to result in a polymer with very high molecular weight in a few minutes.[1] Therefore, this polyurea was successfully prepared in a home blender with fast stirring in 5 min. or less, even when the polymer precipitated. The initial temperature was 25°C., but the temperature was allowed to rise spontaneously from the heat of reaction and stirring.

Regardless of the order of mixing of the reactants, polymer with high inherent viscosity was obtained when equivalents of intermediates were used. Generally, *trans*-2,5-dimethylpiperazine was added to the methylene bis(4-phenyl isocyanate) solution.

The concentration was varied between 3 g. and 10 g. of polymer per 100 ml. of solvent. However, 3–5 g. of polymer per 100 ml. is the preferred range. The lower range of concentration permits more effective stirring, especially when polymer precipitates or the solvent is viscous. More dilute solutions introduce a higher proportion of impurities, while more concentrated solutions make temperature control more difficult.

The polymerization reaction was quenched with ammonium hydroxide or *n*-butylamine. The polymer was then washed with acetone–water (1:1 by volume) or water.

The following examples illustrate the preparation of DMePip-1-DDM-1 polyurea and DMePip-T polyamide. Procedure A employs fast stirring with fast addition of reactants and short reaction time. Procedures B and C illustrate polyurea and polyamide preparations with slow addition of the second reactants and long reaction periods in solution. These procedures were used to study the effect of reactant imbalance on the molecular weight of polymer.

DMePip-1-DDM-1 polyureas were characterized by solubility tests and by determination of inherent viscosity ($\eta_{\text{inh}} = [\ln \eta_{\text{rel}}]/c$ in sulfuric acid at 30°C. with $c = 0.5$ g./100 ml. solution). The inherent viscosity of DMePip-T polyamides was similarly determined in *m*-cresol.

A quart-size blender was used in procedure A. Prior to use, the blender was thoroughly dried and the stirrer bearing was lubricated with Celvacene medium vacuum grease (Distillation Products Industries). The top was covered with aluminum foil and over this was placed a plastic cap which had a $^3/_4$-in. hole in the center. A powder funnel was placed through this hole and a hole made directly below in the foil.

Procedure A. Methylene bis(4-phenyl isocyanate) (3.253 g.) was dissolved in 79 ml. of tetramethylene sulfone–chloroform (70:30 by volume) and placed in a home blender. *trans*-2,5-Dimethylpiperazine (1.484 g.) in 79 ml. of tetramethylene sulfone–chloroform (70:30 by volume) was added rapidly through the funnel while the stirrer was simultaneously speeded up to high speed by means of a rheostat. The viscous solution was stirred at high speed for seven minutes. The polymerization reaction was quenched by stirring for two minutes with 4 ml. of *n*-butylamine in 96 ml. of water. More water was added to precipitate the polymer which was collected by filtration on a medium-pore fritted glass funnel. The polymer was washed once with acetone–water (1:1 by volume) and several times with water by stirring in a blender. It was dried in a vacuum oven at 80°C. The yield of polymer was 100% and the inherent viscosity was 2.95.

When the chloroform portion of the solvent was increased to 80%, hexane was used to precipitate the polymer.

Procedure B. Methylene bis(4-phenyl isocyanate) (2.453 g.) was dissolved in 60 ml. of tetramethylene sulfone–chloroform (80:20 by volume) in a 500-ml. round-bottomed flask equipped with a stirrer and dropping funnel. While the above solution was vigorously stirred, 1.119 g. of *trans*-2,5-dimethylpiperazine in 50 ml. of tetramethylene sulfone–chloroform (80:20 by volume) was added dropwise. This was followed by a 9-ml. solvent rinse. The total time of addition of the diamine and rinse was 85 min. The reaction mixture was stirred an additional 5 min. and then was quenched with 4 ml. of *n*-butylamine in 96 ml. of water. The resulting oily dispersion was stirred for 15 min. The mixture was poured into a 1-qt. blender and stirred with more water. Only water was used in the precipitation and washing of polymer so as to prevent fractionation. The yield of polymer was 100% and the inherent viscosity was 2.34.

The experiments plotted in Figure 2 were carried out in this manner.

Procedure C. *trans*-2,5-Dimethylpiperazine (2.284 g., 0.02 mole) was dissolved in 150 ml. of chloroform and 5.55 ml. (0.04 mole) of triethylamine in a 500-ml. round-bottomed flask equipped for fast stirring. A solution of terephthaloyl chloride (4.061 g., 0.02 mole) in 100 ml. of chloroform was added dropwise over a period of 45 min. A 10-ml. rinse of chloroform was next added over a period of 5 min., and the stirring was continued an additional 5 min. The polymer and triethylamine hydrochloride remained in solution during this entire time. The polymer was precipitated with hexane in a home blender, collected, and washed with water three times.

The experiments plotted in Figure 3 on inherent viscosity versus reactant ratio were carried out in this manner. The initial volume of chloroform was always 150 ml. and contained either 0.02 mole of terephthaloyl chloride or 0.02 mole of *trans*-2,5-dimethylpiperazine with triethylamine equal to twice the molar quantity of acid chloride to be added. The volume of solution in the graduated dropping funnel was proportional to the amount of added reactant ($0.20M$ in acid chloride or diamine). When diamine was added dropwise, the solution also contained triethylamine equal to twice the molar quantity of diamine. The temperature of the flask was maintained at 25°C.

DISCUSSION

In order to study the preparations of DMePip-1-DDM-1 polyurea and DMePip-T polyamide for the effect of reactant imbalance upon molecular weight, it was necessary to examine solvents for polymerization media, reaction and stirring rates, and polymer molecular weights.

Solvent Selection

Preparations of polyureas from the diamine and diisocyanate in *m*-cresol, dimethylformamide, acetone, and alcohols have been described in the literature.[3-6] These and related solvents were used in the preparation of DMePip-1-DDM-1 polyureas, and the results are described in Table I. The inert solvent mixture, tetramethylene sulfone–chloroform, was selected for a more detailed study because polyurea was obtained with much higher than usual molecular weight.

TABLE I
Effect of Solvents on Molecular Weight of DMePip-1-DDM-1 Polyurea

Reaction intermediates[a]					
trans-2,5-Dimethylpiperazine		Methylene bis(4-phenyl isocyanate)		Product[b]	
Wt., g.	Solvent, ml.[c]	Wt., g.	Solvent, ml.	Yield, %	η_{inh}
2.672	$CHCl_3$, 48	5.844	$CHCl_3$, 116	98.4	1.04[d]
2.706	TMS–$CHCl_3$, 53:10	5.936	TMS, 105	94.4	2.06
2.329	TMU, 57	5.097	TMU, 85	94.6	0.41
2.250	NMP, 48	4.937	NMP, 90	90.5	0.35
2.638	DMF, 66	5.792	DMF, 95	90.0	0.35
2.250	*m*-Cresol, 52	4.931	*m*-Cresol, 85	90.5	0.88
1.975	*tert*-Butyl alcohol, 34	4.336	TMS, 86	100	2.52[e]
2.618	TMS–*tert*-Butyl alcohol, 50:17	5.737	TMS, 95	100	1.87
2.614	TMS–*sec*-Butyl alcohol, 51:16	5.728	TMS, 95	100	1.85

[a] The polymers were prepared by procedure A. Solution concentration was about 5.2 g. polymer/100 ml. solvent based on theoretical yield of polymer.

[b] All polymers were in solution except those indicated by notes (d) and (e).

[c] TMS = tetramethylene sulfone, TMU = tetramethylurea, NMP = *N*-methyl-2-pyrrolidone, DMF = dimethylformamide.

[d] Polymer precipitated immediately in reaction medium.

[e] Polymer precipitated in a highly swollen form in reaction medium.

A useful solvent, in addition to dissolving the intermediates and providing for their contact, also dissolves or swells the polymer sufficiently to permit completion of the polymerization. Tetramethylene sulfone is a good solvent for the polymer; however, a small quantity of chloroform or other liquid must be added to it to keep the intermediate *trans*-2,5-dimethylpiperazine in solution at 25°C.

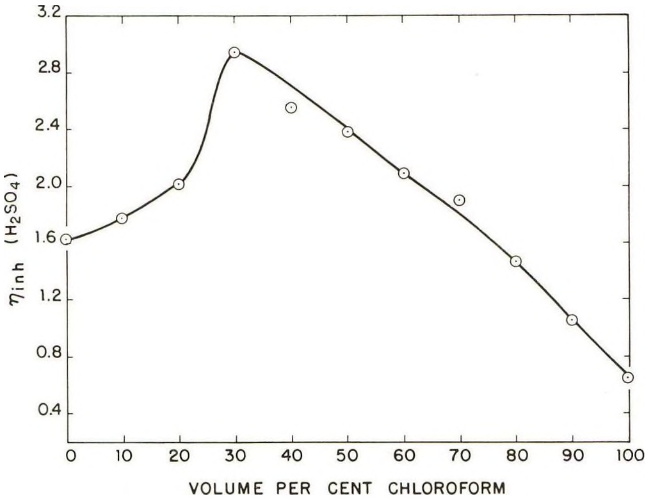

Fig. 1. Effect of tetramethylene sulfone–chloroform mixtures on molecular weight of DMePip-1-DDM-1 polyurea.

The importance of polymer solubility in relation to molecular weight obtained was demonstrated by a study of mixtures of a good solvent, tetramethylene sulfone, and a poor polymer solvent, chloroform. Figure 1 presents inherent viscosities for DMePip-1-DDM-1 polyurea prepared by procedure A with different volume ratios of the two solvents. High inherent viscosities were obtained over a wide solvent ratio range with the peak viscosity occurring at 30% chloroform and the lowest at 100% chloroform. The viscosities increased with increasing proportions of chloroform as long as the polymer was in solution, but when precipitation began to occur the inherent viscosities decreased concurrently. In addition to being a solvent for the diamine, chloroform improved the stirrability of the system by diluting the viscous tetramethylene sulfone and thus allowed for better contact between intermediates. This factor appears to be as important as solubility. At 100% tetramethylene sulfone, considerable heating was necessary to dissolve the *trans*-2,5-dimethylpiperazine. When the reactant addition was reversed so as to accommodate the use of solid diamine, the inherent viscosity of the polymer was increased to 2.5 as compared to 1.6.

Reaction and Stirring Rates

Our qualitative impression is that the rates of formation of DMePip-T polyamide and DMePip-1-DDM-1 polyurea are extremely rapid, but that the rate of formation of the polyurea is the slower of the two. Yet very high molecular weight polyurea was prepared in a few minutes at room temperature. In a tetramethylene sulfone–chloroform system in which the polymer was dissolved or highly swollen, polymer with high molecular weight was obtained even though the second reactant was added over an extended period of time and regardless of the speed of stirring. However, when polymer precipitates as a hard powder as, for example, in chloroform, the two reactants should be combined rapidly with high-speed stirring in order to obtain the maximum molecular weight permitted by the solvent.

Chain Extension and Network Formation

When equivalents of reactants were employed in the preparation of the polyurea, similar inherent viscosities were obtained regardless of the final work-up of the polymers. However, when excess isocyanate was used, the polymer increased in inherent viscosity and even became insoluble in sulfuric acid unless it was quenched with *n*-butylamine or ammonium hydroxide. Table II compares the inherent viscosities obtained from polymerization reactions which were and were not quenched.

TABLE II
Effect of Quenching upon the Molecular Weight of DMePip-1-DDM-1 Polyurea[a]

Excess methylene bis(4-phenyl isocyanate), mole-%	η_{inh} Quenched polymer[b]	η_{inh} Unquenched polymer
50	—	Insoluble
20	0.43	3.83
10	0.51	1.85
5	0.82	1.98
2	1.55	—
0	2.36	2.26

[a] Polymer was prepared by procedure C. Yields were 100%.

[b] The polymerization reaction was quenched with *n*-butylamine to inactivate any remaining methylene bis(4-phenylisocyanate).

The chain extension and crosslinking took place during the isolation step when water was added to precipitate the polymer. Other research has shown that water reacts with aryl isocyanates to produce as final products urea and biuret.[7] In addition, the hydrogen of the urea groups in the chain can react with excess diisocyanate to produce biuret groups and eventual crosslinking.

Reactant Imbalance and Molecular Weight

Like DMePip-T polyamide, DMePip-1-DDM-1 polyurea shows an unusual lack of sensitivity to reactant imbalance as compared to melt polycondensations. In the low temperature procedures, insensitivity to reactant imbalance is ascribed to the existence of a very fast reaction rate and a relatively slow mixing rate, with the result that there are zones in which the polymer attains high molecular weight by reacting with the complementary species without sensing the excess reactant. Thus, a drop of diamine solution in a large volume of diisocyanate solution reacts rapidly with the surrounding diisocyanate before it has a chance to disperse. This leads to

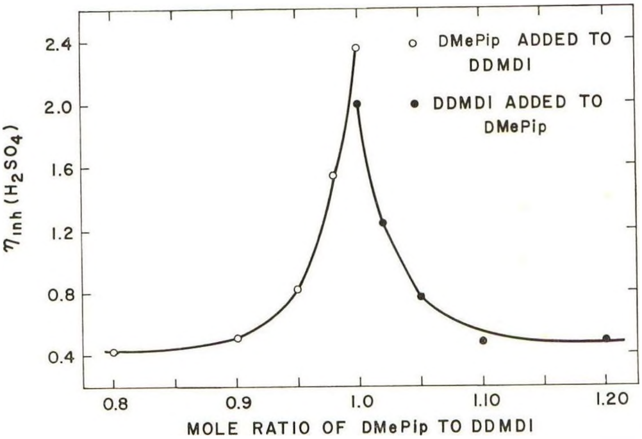

Fig. 2. Effect of reactant ratio on the molecular weight of DMePip-1-DDM-1 polyurea prepared in tetramethylene sulfone–chloroform (80:20 by volume).

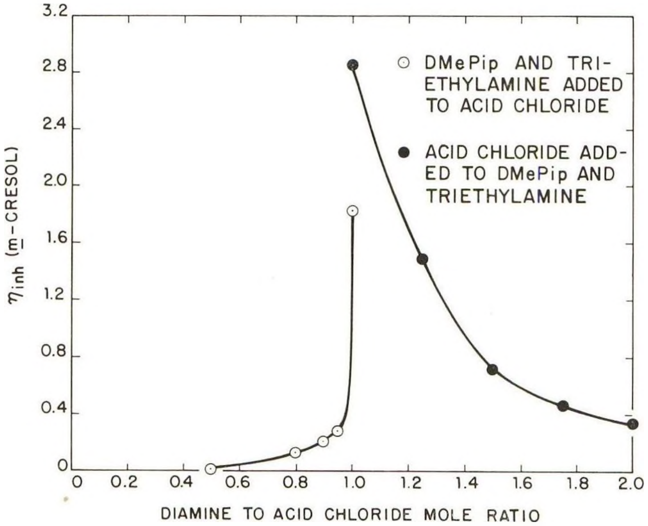

Fig. 3. Effect of reactant ratio on the molecular weight of DMePip-T polyamide prepared in chloroform.

higher molecular weight polymer than would be obtained by random reaction at the reactant ratio in the total system. Each successive drop of reactant continues this condition. It is only at the end of the reaction, when the concentration of the reactive groups is diminished and equivalence is approached, that a more random reaction can occur.

Figure 2 presents data showing the effect of reactant imbalance as well as mixing rate on polymer molecular weight. The polymer preparations represented by the two curves were carried out by procedure B in a tetramethylene sulfone–chloroform (80:20 by volume) system. The points to the left of the peak were obtained by slow addition of diamine to excess diisocyanate, while those on the right by addition of diisocyanate to excess diamine. Figure 2 shows that the highest inherent viscosity was obtained when molar equivalents of *trans*-2,5-dimethylpiperazine and methylene bis(4-phenyl isocyanate) were employed, regardless of the order of addition. When an excess of either reactant was employed the inherent viscosities (based on a 100% yield) decreased sharply to produce a symmetrical curve.

A similar plot of viscosity versus reactant mole ratio for DMePip-T polyamide did not produce a symmetrical curve.[1] This was due to the fact that excess diamine was used as the acid acceptor and the system was less sensitive to excess diamine than acid chloride. The lesser sensitivity to excess diamine was postulated to result from the reduction of the reactivity of the excess diamine while in the form of the monohydrochloride.

For comparison, DMePip-T was prepared by using triethylamine as the acid acceptor. The preparations represented by Figure 3 were carried out by procedure C in chloroform. The points to the left of the peak were obtained by slow addition of diamine and triethylamine to acid chloride. Here triethylamine was equal to twice the molar quantity of diamine. The points to the right of the peak were obtained by slow addition of acid chloride to diamine and triethylamine which was equal to twice the molar quantity of acid chloride. As reported for polymer prepared with excess diamine as the acid acceptor, the curve is unsymmetrical, and the system is less sensitive to excess diamine than acid chloride. The high inherent viscosities to the right of the peak indicate that some diamine must have been withheld from the reaction as the soluble diamine monohydrochloride, in which form the second amine group has greatly reduced basicity and reactivity.[1]

$$\text{DMePip} + \text{Et}_3\text{N}\cdot\text{HCl} \leftrightarrows \text{DMePip}\cdot\text{HCl} + \text{Et}_3\text{N}$$

If such is the case, the amount of diamine with maximum reactivity available at any given point above 1.0 on the mole ratio scale is less than indicated in Figure 3.

Further explanation is necessary for the low inherent viscosities obtained to the left of the peak. Here, the slow addition of diamine and triethylamine to excess acid chloride produced polymer with viscosities which are equal to or lower than calculated. For example, at the diamine to acid chloride mole ratio of 0.95, the calculated inherent viscosity is 0.44, while the observed value was 0.28. In experiments with rapid addition, inherent viscosities only as high as 0.45 were obtained. When polymer prepared at this mole ratio was held in the polymerization medium for one hour, no increase in viscosity was produced by adding diamine to attain the point of stoichiometric balance.[8] However, as seen in Figure 3, it is possible to obtain polymer with high viscosity at the stoichiometric balance if the addition is slow but continuous.

These experimental results are believed to be due to interfering side reactions which are the consequence of excessive contact between triethylamine and acid chloride. These side reactions are great enough to overcome any benefit derived from a high rate of the amide forming reaction and control of the polymerization by mixing.

Complex formation between triethylamine and diacid chloride is marked by yellow coloration. In the experiments to the left of the peak, the presence of the slightest excess of triethylamine over the ratio of 2 moles for each mole of diamine was accompanied by yellow color formation. No coloration was observed in experiments where excess diamine was present (right of Fig. 3).

The by-product of the polymerization reaction, triethylamine hydrochloride, may also dissociate to some degree into triethylamine which can then react with acid chloride. In an experiment where triethylamine hydrochloride was kept in contact with diacid chloride for one hour prior to use in a polymerization, DMePip-T polyamide with an inherent viscosity of 1.03 was obtained as compared to 1.75 for the control.

Molecular Weight Determination

Osmotic pressure determinations confirm the fact that DMePip-1-DDM-1 polyurea was obtained in very high molecular weight (Fig. 4).

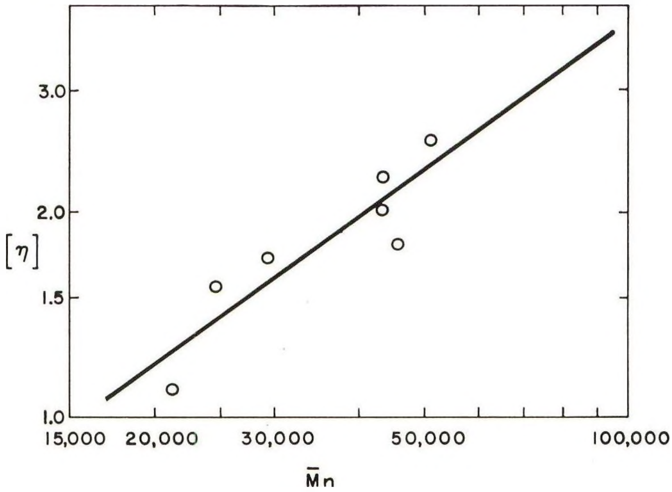

Fig. 4. Molecular weight–intrinsic viscosity relationship for DMePip-1-DDM-1 polyurea.

The number-average molecular weights versus intrinsic viscosity form a linear log–log plot which fits the equation:

$$[\eta] = 1.01 \times 10^{-3} \bar{M}_n{}^{0.715}$$

An average value for the k' factor in the Huggins equation[9]

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

was found to be 0.34.

It is possible to calculate the DP and molecular weight ($\bar{M}_n$) of polymer resulting from these unbalanced systems by using Flory's equation:[10] DP = moles of bifunctional reactants exclusive of any excess + 1 divided by moles of end-grouper. A balanced system consists of 1 mole of each reactant; any excess of this ratio is considered to be monofunctional end-grouper. One repeat unit has a DP of 2. Table III compares the calculated $\bar{M}_n$ with the observed $\bar{M}_n$ obtained from osmotic pressure measurements. These data are further evidence for claiming high molecular weights for polyureas prepared by unbalanced reactant systems.

TABLE III
Effect of Reactant Imbalance upon Molecular Weight of DMePip-1-DDM-1 Polyurea

Mole ratio, DMePip/DDMDI	[η]	Calcd. DP	$\bar{M}_n$ Calcd.	$\bar{M}_n$ Obs.
0.8	0.47	9	1,640	5,400
0.9	0.56	19	3,462	6,900
0.95	0.89	39	7,106	13,200
0.98	1.66	99	18,039	31,500
1.02	1.34	101	18,404	23,200
1.05	0.84	41	7,471	12,200
1.10	0.52	21	3,827	6,200
1.20	0.53	11	2,004	6,400

Properties of DMePip-1-DDM-1 Polyurea

DMePip-1-DDM-1 polyurea, even at an inherent viscosity of 0.4, was formed into tough and flexible films from dimethylformamide solution. This polymer has a melt temperature of 314°C.

Thanks are due to K. V. Sharp for excellent technical assistance.

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Résumé

On compare les préparations de deux polymères condensés obtenus par polymérisation en solution à basse température à l'effet des réactifs en quantités nonéquilibrées sur le poids moléculaire. De plus, on a examiné l'effet d'autres variables tels que le choix du solvant, le temps de réaction et la vitesse d'agitation. Les polymères sont des polyamides obtenus au départ de la *trans*-2,5-diméthylpipérazine et du chlorure de téréphtaloyle, les polyurées alternées obtenus de la *trans*-2,5-diméthylpipérazine et de l'isocyanate de bis-(4-phényl)-méthylène. Par opposition à la réaction de formation du polyamide, la polymérisation de la polyurée ne nécessite pas d'accepteurs d'acide et n'engendre pas de produits secondaire. Ces études ont conduit à la préparation de polyurées de poids moléculaire extrèment élevés par l'emploi d'un mélange inerte de solvants tétraméthylène-sulfone/chloroforme. On a montré précédemment que la poly(*N*,*N*-téréphtaloyl-*trans*-2,5-diméthylpipérazine) présentait une absence inhabituelle de sensibilité au rapport des quantités de réactifs comparativement à la polycondensation par fusion lorsqu'on utilisait un excès de diamine en guise d'accepteur d'acide. Un comportement similaire est trouvé pour la polyurée ainsi que pour le polyamide lorsqu'on emploie un amine tertiaire en guise d'accepteur d'acide. Cependant dans certaines conditions, des réactions secondaires peuvent produire des polyamides dont la viscosité inhérente est plus basse que celle calculée. Dans chacun des cas l'insensibilité aux proportions de réactif est attribuée à l'existence d'une réaction extrèmement rapide.

Zusammenfassung

Die Darstellung von zwei Kondensationspolymeren durch Tieftemperatur-Lösungspolymerisation wird in bezug auf den Einfluss des Verhältnisses der Reaktionsteilnehmer auf das Molekulargewicht verglichen. Zusätzlich werden andere Variablen, wie Lösungsmittelauswahl, Reaktionsdauer und Rührgeschwindigkeit überprüft. Die Polymeren sind das Polyamid aus *trans*-2,5-Dimethylpiperazin und Terephthaloylchlorid und der alternierende Polyharnstoff aus *trans*-2,5-Dimethylpiperazin und Methylenbis(4-phenylisocyanat). Im Gegensatz zur polyamidbildenden Reaktion erfordert die Polyharnstoffpolymerisation keine Säureakzeptoren und liefert keine anderen Nebenprodukte. Die Untersuchung führt zur Darstellung extrem hochmolekularer Polyharnstoffe durch Verwendung der inerten Lösungsmittelmischung Tetramethylensulfon/Chloroform. Für Poly(*N*,*N*,-terephthaloyl-*trans*-2,5-dimethylpiperazin) wurde früher geziegt, dass es im Vergleich zur Schmelzpolykondensation bei Anwendung eines Diamins als Säureakzeptor ungewöhnlich empfindlich gegen das Verhältnis der reagierenden Stoffe ist. Ein ähnliches Verhalten wurde sowohl für den Polyharnstoff als auch für das Polyamid bei Verwendung eines tertiären Amins als Säureakzeptor gefunden. Unter gewissen Bedingungen können jedoch Nebenreaktionen zur Bildung von Polyamiden mit niedrigeren Viskositätszahlenwerten als berechnet führen. In beiden Fällen wird die Empfindlichkeit gegen das Verhältnis der reagierenden Stoffe auf eine extrem rasche Reaktion zurückgeführt.

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Deuteration of Proteins and Polyamides in Deuterium Oxide Vapor

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Synopsis

This paper describes the H → D exchange reaction in proteins and polyamides immersed in saturated deuterium oxide vapor. Ten proteins (seven silk fibroins, wool, byssus, and Fibrolane BX) and the nylons 66, 6, and 11 were studied. With all the samples there was an initial rapid exchange followed by a slower exchange, this slow change gradually levelling off to give "equilibrium" values. The extent of the H → D exchange is discussed in relation to order and disorder in the polymer structures. The extent of exchange is shown to be related to the proportions of large side chains in the samples and also to the water sorption values. It is shown that the decrease in the absorbance of the 3300 cm.$^{-1}$ band of the polyamide films is a reasonably satisfactory measure of the extent of the H → D exchange in these films, provided that changes in band width are taken into account.

INTRODUCTION

This paper reports some measurements of the isotopic exchange reaction in several proteins and polyamides immersed in saturated deuterium oxide vapor. The materials studied (Table I) were seven silk fibroins, wool, byssus (a fiber from the Mediterranean lamellibranch *Pinna nobilis*), Fibrolane BX (a regenerated casein fiber), and the nylons 66, 6, and 11.

Few quantitative studies of the deuteration of these types of polymer have been reported. Speakman and his co-workers[1] studied the exchange reaction in wool, employing a gravimetric technique similar to that described below. Sutherland and his co-workers[2] estimated from the relative intensities of the 3300 cm.$^{-1}$ NH band and the 2410 cm.$^{-1}$ ND band the approximate degree of exchange in silkworm gut, keratin, gelatin, and other proteins. Fraser and Macrae[3] calculated exchange values for keratin from infrared spectra in the overtone region. Cannon[4] lists values for the extent of the exchange in various nylons, as derived from changes in the intensity of the 3300 cm.$^{-1}$ NH band. Wood and King[5] describe some measurements of the NH band of nylon 6 and the effect of deuteration treatments on this band.

EXPERIMENTAL

Materials

The fibroins and the byssus were obtained in a purified form from F. Lucas and J. T. B. Shaw of this Institute. The wool and Fibrolane BX were the samples studied in a recent investigation of water sorption.[6] The nylon 66 was obtained from British Nylon Spinners Ltd; the nylons 6 and 11 were commercial samples, Enkalon and Rilsan respectively. The Rilsan contained particles of a delustring pigment, but in such small amounts as to be negligible.

Films of the fibroin *B. mori* (2–3μ thick) were prepared by two methods to give different accessibilities; the lower accessibility film was prepared from a solution of fibroin in a concentrated aqueous solution of lithium thiocyanate; a thin film of this fibroin solution on a glass plate was precipitated by 50/50 (v/v) ethanol–water, followed by washing in this solvent and finally in water. The higher accessibility film was prepared by drying an aqueous solution of fibroin taken from the silk gland on a glass plate at 70°C. Films of the nylons (4–6μ thick) were prepared from solutions of 0.6 g. nylon in 95 ml. formic acid, 5 ml. water, and 2 ml. concentrated hydrochloric acid solution; the nylons 66 and 6 were soluble at room temperature and the films were dried on glass plates at room temperature; the nylon 11 was soluble in the hot solvent only, and the films were formed as a skin on the solution during cooling.

Measurement of the Extent of the H → D Exchange

With proteins and polyamides the H → D exchange takes place in the main-chain peptide groups, at the chain ends, and, with proteins, on the amine, amide, hydroxyl, and carboxyl groups in the side chains. The fraction of the total exchangeable hydrogen atoms deuterated during a particular treatment (referred to below as the "exchange fraction") was determined by measuring the increase in the dry weight of the sample;[1,7,8] the fraction is simply the ratio of the measured increase in dry weight to the increase which would result if all the exchangeable hydrogen atoms were exchanged. Values for the increases in dry weight corresponding to complete exchange (Table I) were calculated from the amino acid compositions of the fibroins,[9] byssus,[10] and Fibrolane (casein),[11] and from the well-known formulae of the polyamides. The value used for wool was that calculated by Speakman and co-workers.[1]

Silica spiral spring balances were used in this work; the increase in the length of a spring resulting from the increase in the dry weight of the sample was measured on a calibrated scale in the eyepiece of a microscope focused on the lower end of the spring. Two samples were studied in each deuteration experiment; the samples weighed about 0.25 g. each. At the start of an experiment the samples were dried by prolonged evacuation through a liquid nitrogen trap with the samples first at 25°C. and finally at 85°C.; the lengths of the springs were then measured (to obtain the weights of the dry samples) and the positions of the lower ends of the springs on the calibrated eyepiece scales were noted. The samples were then cooled to 25°C. and about 1 ml. of deuterium oxide (99.7% pure) was distilled from the reservoir into the glass tubes containing the samples and springs; after 10–15 min. the deuterium oxide was removed by evacuation through the liquid nitrogen trap for a few minutes; the "dry lengths" of the spring balances were not measured after this initial deuteration, the purpose of which was to remove a large part of the readily exchangeable hydrogen, and thus prevent this hydrogen from "diluting" the deuterium oxide in the subsequent deuteration experiments. After this preliminary deuteration, another batch of at least 1 ml. of deuterium oxide was distilled into the sample tubes and the deuteration was allowed to proceed at 25°C. for 30 min.; the samples were then dried by evacuation at 25 and 85°C., and the increase in the length of the springs measured on the calibrated scales. This deuteration procedure was repeated with longer periods of deuteration.

The polyamides were investigated in the form of thin films so that the results could be directly compared with the infrared results.

Infrared Study of the Deuteration Process

All infrared measurements were done on films mounted in brass vacuum cells with calcium fluoride windows; the deuterations were effected in these cells in the absence of air, the deuteration procedure being essentially similar to that described above. The infrared measurements were made on films which had been freed from water or deuterium oxide by evacuation of the cells through a cold trap. The infrared spectra were measured on a Grubb-Parsons double-beam spectrometer with a lithium fluoride prism.

The decrease in the peak absorbance of the 3300 cm.$^{-1}$ band of the dry film resulting from a deuteration treatment was calculated as a fraction of the peak absorbance of the dry, undeuterated film; the baselines to the bands were drawn from 3500 to 3000 cm.$^{-1}$.

RESULTS AND DISCUSSION

Figure 1 gives the exchange fractions of the protein fibers and polyamide films after various periods of treatment in saturated deuterium oxide vapor at 25°C. The exchange reaction was initially rapid and then slowed down, tending towards equilibrium. The exchange fractions after 2 hr. and after 3 days treatment are listed in Table I; the 3-day result for wool (i.e., the "equilibrium" value) is somewhat lower than the values of Speakman and his co-workers[1] (0.82_4–0.87_3) and little higher than the "infrared-overtone" value of Fraser and Macrae[3] ($\sim$0.7). It should be noted that the values for the nylon films, obtained for comparison with the infrared results, have no "absolute" significance; the accessibility of nylon film depends upon the method of preparation.[4,5]

In assessing the value of these exchange fractions as an index of accessibility and molecular order it is necessary to distinguish the polyamides from

TABLE I

H → D Exchange Reaction in Proteins and Polyamides

Sample number	Sample[a]	Calculated increase in dry weight after complete exchange (A), g./100 g.	Measured increase in dry weight after 3 days treatment (B), g./100 g.	Exchange fraction after 3 days (B/A)	Exchange fraction after 2 hr. treatment	Number of large side chains as fraction of total side chains[b]	Water absorption (65% R.H. 25°C.), g./100 g. dry sample	
							Value	Reference[c]
1	*Bombyx mori*	1.634	0.89_5	0.548	0.486	0.261	9.65	17
2	*Thaumatopoea pityocampa*	1.848	1.25_8	0.681	0.554	0.623	8.2	10
3	*Pachypasa otus*	1.902	1.45_1	0.763	0.741	0.379	10.8	10
4	*Anaphe moloneyi*	1.561	0.68_7	0.440	0.324	0.048	9.3	10
5	*Antherea mylitta*	1.707	1.11_6	0.654	0.624	0.330	10.2	10
6	*Antherea pernyi*	1.666	1.06_3	0.638	. . .	0.293	10.08	10
7	*Philosamia cynthia*	1.627	1.14_2	0.702	0.651	0.208	10.1	10
8	Wool	1.615	1.28_0	0.793	0.763	0.843	14.4	6
9	Byssus	1.774	1.31_5	0.741	0.729	0.815	15.5	10
10	Fibrolane BX	1.554	1.20_3	0.774	0.684	0.925	14.8	6
11	Nylon 66	0.894	0.34_4	0.385	0.299	—	4.1	6
12	Nylon 6	0.894	0.41_6	0.465	0.271	—	3.8	18
13	Nylon 11	0.552	0.22_5	0.408	0.259	—	1.05	18

[a] Samples 1–10 are fibers; samples 11–13 are films.

[b] Side chains of residues other than the glycine and alanine residues.

[c] The sources of these values are indicated by the references quoted; the values for wool, Fibrolane and nylon 66 are the results published previously[6] with a small estimated correction to adjust these results to 65% R.H., 25°C.

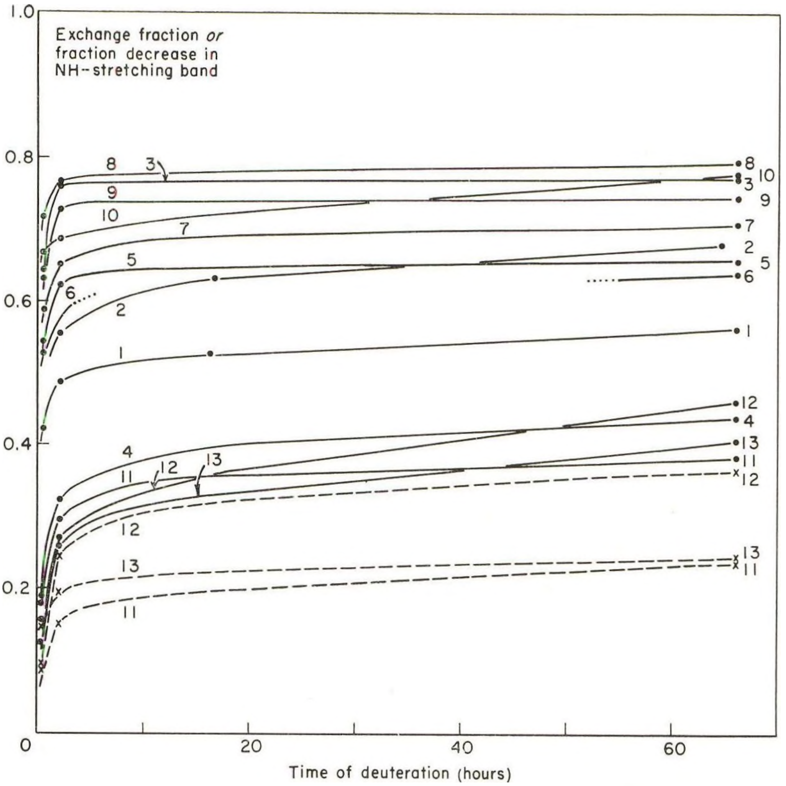
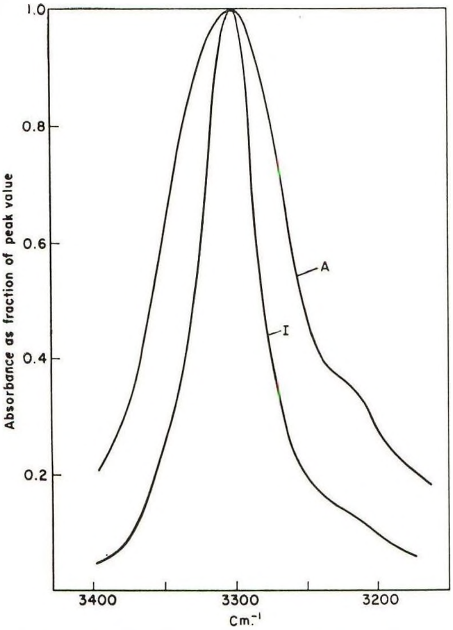


Fig. 1. Rate of H → D exchange with proteins and polyamides in saturated D_2O vapor at 25°C.: (——) fraction of the total exchangeable hydrogen atoms exchanged after various times of treatment ("exchange fraction"); (- -) fractional decrease in the peak absorbance of the NH bands of the three nylons as a function of time of deuteration. The numbers refer to samples as numbered in Table I.

the proteins. With the polyamides there is little doubt that the exchange fraction resulting from a particular deuteration treatment is a good measure of the degree of disorder in the polymer structure. In the first place the exchange fraction is quantitatively equivalent to the deuterium oxide accessible fraction of the structure, since the exchangeable atoms, apart possibly from the few at the chain ends, are evenly distributed throughout the structure. In the second place there is definite evidence that the accessibility of the accessible (exchangeable) fraction can be attributed to a lower degree of order in this fraction compared with the inaccessible fraction: the accessible part gives a broader NH band than the inaccessible fraction (Fig. 2), and in a "chemically uniform" polymer this can be reasonably interpreted as being due to differences in molecular order[4] (the NH band of the accessible fraction is obtained by subtracting the NH band remaining after deuteration from the NH band of the dry sample before deuteration). In any case, the mere fact of being more easily deuterated is evidence that the readily-exchanged regions are the more disordered, open,



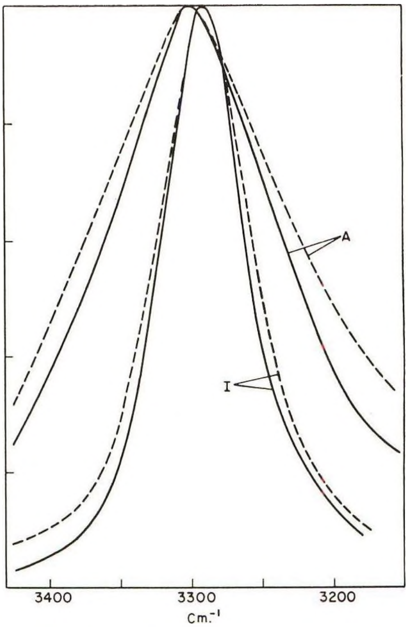
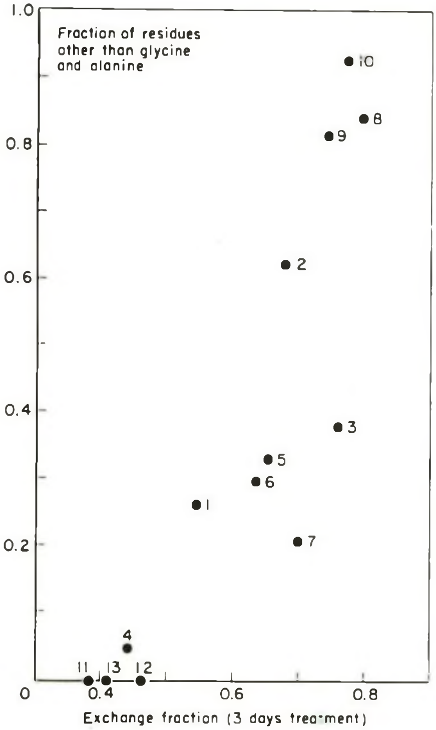


Fig. 2 (left). The 3300 cm.$^{-1}$ band of nylon 6 film: (*A*) "accessible" component (deuterated in saturated D_2O vapour at 25°C. for 3 days); (*I*) "inaccessible" component (not deuterated by this deuteration treatment). The ratio of the peak absorbance of the accessible component to that of the inaccessible component is 0.53.

Fig. 3 (right). The 3300 cm.$^{-1}$ band of films of *B. mori* fibroin: (——) low accessibility film; (- -) high accessibility film; (*A*) "accessible" component (deuterated in saturated D_2O vapour at 25°C. for 1 hr.); (*I*) "inaccessible" component (not deuterated by this deuteration treatment). The ratio of the peak absorbance of the accessible component to that of the inaccessible component is 0.76 and 2.77 for the films of low and high accessibility, respectively.

part of the structure. The usefulness of exchange fractions in the comparison of the order in different polyamides is less certain but even here they may serve as a rough guide.

Proteins are composed of several types of amino-acid residues; these residues contain from zero to four exchangeable hydrogen atoms in the side chain and are almost certainly distributed unequally between the accessible and inaccessible regions. As a result of this chemical heterogeneity the interpretation of the extent of the H → D exchange in terms of structural order is difficult; in the first place it is clearly not possible to interpret exchange fractions precisely in terms of the fraction of the structure accessible to deuterium oxide; secondly, the "accessibility" of a region is likely to depend upon its chemical composition as well as its molecular order; thirdly, changes in the width of the 3300 cm.$^{-1}$ band as a result of deuteration (Fig. 3) are not a completely reliable indication of differences in order between the deuterated and undeuterated material. Exchange fractions are therefore of limited use in comparing the molecular order in different proteins; however, despite the above difficulties of quantitative interpretation, it seems likely



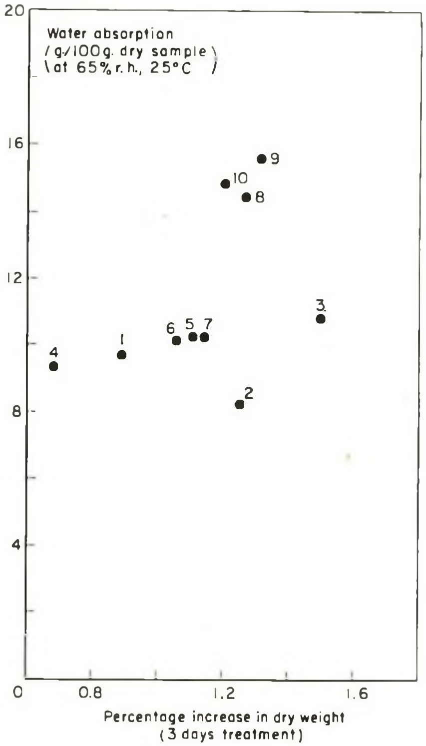


Fig. 4 (left). Relation between the exchange fraction after 3 days deuteration and the fraction of large side chains. The numbers refer to the samples as numbered in Table I.

Fig. 5 (right). Relation between the increase in dry weight after 3 days deuteration and the water absorption at 65% R.H. The numbers refer to the samples as numbered in Table I.

that, in general, increased molecular order in a given protein would lead to a decreased exchange fraction, and the latter should therefore be of some value in grading different samples of the same protein, e.g., in studying the effects of treatments, or of different methods of film or fiber preparation, on the molecular order in a protein. Figure 3, for instance, illustrates the deuteration of two films of *B. mori* prepared in different ways and quite different as regards the extent of the H → D exchange (compare the ratios of the peak absorbances of the accessible and inaccessible regions given in the legend to the figure); the more highly exchangeable film gives broader 3300 cm.$^{-1}$ bands than the less highly exchangeable film, presumably because of a lower degree of molecular order.

A relation exists between the exchange fractions of the proteins and the proportions of the larger side chains; Table I lists the number of amino acid residues other than glycine and alanine as a fraction of the total residues. These results are plotted in Figure 4; the relation is clear, although evidently complicated by other factors. The relatively high exchange fraction of the *P. otus* is thought to be due to the high proportion of arginine residues, which contain four exchangeable hydrogen atoms in the side chain. Simple considerations readily suggest reasons for this relation: large side chains, particularly when several varieties are present, will presumably pack into an ordered structure less easily than small side chains, and will therefore tend both to increase the amount of disordered material and also to be concentrated in this disordered material; this latter tendency will in itself lead to a higher exchange fraction since in general the larger side chains contain more exchangeable hydrogen atoms than the smaller side chains. A relation between the proportion of large side chains and the extension properties of fibroin fibers has been observed previously and was explained similarly.[16]

A relation would also be expected to exist between the extent of the H → D exchange in a protein and the water sorptivity of the protein, since chemical groups that contain exchangeable hydrogen atoms tend to be of a hydrophilic nature. Table I and Figure 5 indicate that this relation does exist, i.e., *A. moloneyi* and *B. mori* have comparatively low values for water sorptivity and isotopic exchange, while wool, Fibrolane, and byssus have high values; in Figure 5 the water absorption is plotted against the increase in dry weight on deuteration, this being a direct measure of the number of exchanged hydrogen atoms and presumably, therefore, a reasonable measure of the number of accessible hydrophilic groups. However, the range of water sorption values within the fibroins is small compared with the range of values of H → D exchange and it may be noted that in this group *T. pityocampa* has the lowest sorptivity despite its high degree of isotopic exchange; these complications reflect the fact that the sorption of water by a polymer depends upon the types and location, as well as the number, of the hydrophilic groups accessible to the water molecules.

The results in Figure 1 suggest that the exchange reaction can be regarded as being in two stages, a rapid stage followed by a slow stage. This type of deuteration behavior has been observed with cellulose.[8,12–14] With cellulose the rapidly-deuterated hydroxyl groups have been shown[13,14] to give a hydroxyl-stretching band different in character from the band of the remaining hydroxyl groups, namely a broad, featureless band compared with a band containing several characteristic peaks and shoulders; this infrared evidence indicates that the rapidly deuterated hydroxyl groups are hydrogen-bonded in a more or less irregular, disordered manner (i.e., are situated in the "infrared-amorphous" regions) whereas the remaining hydroxyl groups are hydrogen-bonded in a more regular, ordered system (i.e., are situated in the "infrared-crystalline" regions). With proteins and polyamides, however, there is no major difference in shape between the 3300 cm.$^{-1}$ band of the rapidly-deuterated NH and OH groups and that of the remaining material[15] (see Figs. 2 and 3), but only a difference in band width and, with the *B. mori* films, a slight difference in peak frequency. With the present samples, therefore, the significance of the changeover from rapid exchange to slow exchange is less clear than with cellulose; however, it may well represent, as with cellulose, a change from the deuteration of regions which are more or less disordered as regards intermolecular and intramolecular interactions to the deuteration of material of a distinctly higher level of order. With proteins an alternative explanation of two-stage deuteration behavior is conceivable, namely that the rapid stage is the result mainly of exchange in the side chains and the subsequent slow stage is the result of the exchange of peptide hydrogens; this simple explanation is, however, untenable, since with every protein the level of exchange at the end of the rapid stage is much higher than that which would be attained if all the exchangeable side chain hydrogens were exchanged. (This is particularly obvious with *A. moloneyi*, which has very few exchangeable hydrogen atoms in the side chains.)

Figure 1 (dashed lines) shows the effect of deuteration treatments on the peak absorbance of the 3300 cm.$^{-1}$ band of the three nylons. These values are in reasonable agreement with the infrared values given by Cannon[4] (0.28 for nylon 66, 0.26–0.37 for nylon 6). The decreases in the peak absorbances on Figure 1 are seen to be lower than the exchange fractions resulting from corresponding deuteration treatments, and on the basis of these results it is easy to calculate that the ratio of the peak extinction coefficient of the NH band of the inaccessible regions to that of the accessible regions is about 1.5–2.0 (Wood and King[5] report a ratio of about 5 for samples of nylon 6). However, with each of the three nylons the 3300 cm.$^{-1}$ band of the accessible fraction is about twice as broad as that of the inaccessible fraction (see e.g., Fig. 2) and this must account for much at least of the differences between the exchange fractions and the decreases in peak absorbances. Taking band widths into account, therefore, it would appear to be reasonably satisfactory to take changes in the absorbance of the 3300 cm.$^{-1}$ band as a measure of the exchange fraction.

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Résumé

Cette publication décrit la réaction d'échange H → D dans les protéines et les polyamides plongées dans la vapeur saturante d'oxyde de deutérium. On a étudié dix protéines (sept fibroïnes soyeuses, la laine "byssus" et le fibrolane BX) ainsi que les nylons 66, 6 et 11. Dans tous les cas, à une vitesse d'échange initialement rapide, succède un échange lent qui décroît progressivement pour atteindre une valeur d'équilibre. On discute de l'échange H → D en fonction de l'ordre et du désordre règnant au seine de la structure polymérique. L'importance de l'échange s'avère être en relation avec la proportion de chaînes longues présentes dans l'échantillon et aussi avec les valeurs de l'adsorption de l'eau. Il est montré que la décroissance de l'absorbance de la bande à 3300 cm^{-1} dans les films de polyamides est une mesure satisfaisante au degré d'échange H → D dans ces films, à condition de tenir compte de la variation de la largeur de bande.

Zusammenfassung

In der vorliegenden Mitteilung wird die H → D-Austauschreaktion von Proteinen und Polyamiden in gesättigtem Deuteriumoxyddampf beschrieben. Zehn Proteine (sieben Seidenfibroine, Wolle, Byssus und Fibrolan BX) und die Nylons 66, 6 und 11 wurden untersucht. Bei allen Proben trat anfangs ein rascher Austausch auf, dem ein langsamerer Austausch folgte; dieser langsame Austausch fällt langsam zum "Gleichgewichts"-Wert ab. Das Ausmass des H → D-Austausches wird in Beziehung auf die Ordnung und Unordnung in der Polymerstruktur diskutiert. Das Ausmass des Austausches steht in Beziehung zum Anteil an grossen Seitenketten in den Proben und auch zum Wassersorptionswert. Die Abnahme der Absorption der 3300 cm^{-1} Bande der Polyamisfilme bildet ein annehmbares Mass für das Ausmass des H → D-Austausches in diesen Filmen unter der Voraussetzung, dass der Änderung der Bandenbreite Rechnung getragen wird.

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Cationic Isomerization Polymerization of β-Methylstyrene and Allylbenzene

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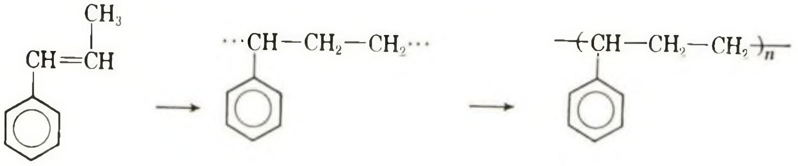
Synopsis

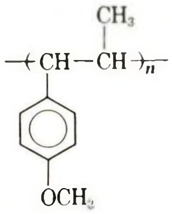
The structure of cationically obtained poly-β-methylstyrene and polyallylbenzene has been investigated by high resolution infrared spectroscopy. These studies indicate that under cationic conditions β-methylstyrene polymerizes by a conventional 1,2 mechanism, whereas allylbenzene partly isomerizes to β-methylstyrene prior to propagation and probably gives a "copolymer" of rearranged and unrearranged units.

Introduction

In 1935 Staudinger and Dreher[1] postulated that under cationic polymerization conditions ($SnCl_4$, BF_3, in toluene, at 0° to −78°C.) β-methylstyrene (propenylbenzene or 1-methyl-2-phenylethylene) and its *p*-methoxy derivative, anethole, rearrange prior to propagation. The polymerization mechanism was considered to be a "1,3"-process:



These experiments were re-examined in 1944 by a Hungarian group.[2] Significantly, chemical evidence for the presence of CH_3—C was found in the polymer. Consequently, Staudinger's proposition was repudiated and a conventional 1,2 enchainment was postulated for polyanethole:



The cationic polymerization of anethole has also been studied by others,[3-5] but the structure of the polymer was not elucidated further.

Strohmayer,[6] however, polymerized both β-methylstyrene and anethole and analyzed the polymer by infrared. He reported that poly-β-methylstyrene gave no evidence of methylene groups and abundant evidence for methyl groups. Thus, the polymer was formed by 1,2-addition. A similar conclusion was reached in the case of polyanethole though the spectra were more complicated. Moreover, Strohmayer found that the solubility of these polymers depended on the environmental conditions during polymerization apparently a result of alkylation side reactions.

In the course of our fundamental studies on cationic isomerization polymerization we re-examined these earlier findings by using modern spectroscopic techniques. Thus poly-β-methylstyrene was prepared by low temperature cationic polymerization technique, and the structure of the polymer was investigated by high resolution infrared spectroscopy. This paper describes our results and conclusions in this area.

Experimental

β-Methylstyrene was purchased from K. & K. Laboratories. The monomer was distilled before use. Gas chromatographic analysis (10 ft. Carbowax column) indicated the presence of seven minor impurities (total 1.87 wt.-%). Allylbenzene (Matheson, Coleman and Bell) after distillation showed four impurities by gas chromatography representing a total of 0.5 wt. -%.

The source and purity of $AlCl_3$ and methyl chloride together with general material handling technique and experimental procedures has been reported.[7]

Poly-β-methylstyrene was obtained by polymerizing 10 ml. (9.14 g.) monomer in 60 ml. methyl chloride with a solution of $AlCl_3$ in methyl chloride (7.2×10^{-2} mole/l.) at -60°C. A total of 110 ml. catalyst solution was introduced gradually over a period of 65 mins. into the monomer mixture. Polymerization initiation was apparent by the formation of white precipitate. Reaction was terminated by introducing cold methanol. The solvent was evaporated and the product washed with methanol. After drying at 50°C. in vacuum, 7.0 g. polymer (76.5%) was recovered. An additional 1.6 g. (1.75%) material was recovered from the combined methanol washings after evaporation. This latter product was not characterized further. The main product was Soxhlet-extracted with toluene, and the toluene-soluble fraction (37.7%) was investigated by infrared spectroscopy.

Polyallylbenzene was obtained by essentially the same technique. Total yield was 5.6 g. (61%).

Infrared spectra were obtained with a Perkin-Elmer 421 instrument. Conventional KBr technique was used for sample preparation.

Results

Figures 1 and 2 show the infrared spectra of cationically obtained poly-β-methylstyrene and polyallylbenzene, respectively.

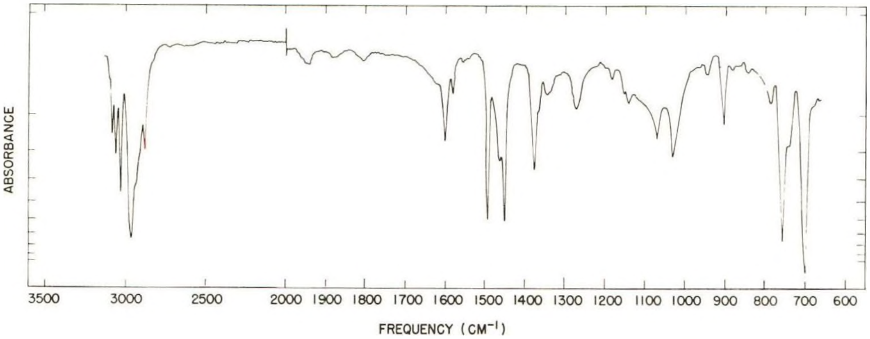


Fig. 1. Infrared spectrum of cationic poly-β-methylstyrene.

Strong absorptions at 2963, 2878, and 1378 cm.$^{-1}$ in the poly-β-methylstyrene spectrum are evidence for CH_3—C, i.e., methyl groups in the backbone of the polymer.

These results indicate that β-methylstyrene polymerizes by a conventional 1,2 head-to-tail process substantiating the proposition of the Hungarian workers. On the basis of infrared evidence it seems that cationic poly-β-methylstyrene consists largely, if not exclusively, of —$CH(CH_3)$-$CH(C_6H_5)$— repeat units.

Similarly, bands appearing at 2961, 2870, and 1373 cm.$^{-1}$ in the spectrum of cationic polyallylbenzene present strong and unmistakeable evidence for the presence of CH_3—C groups in the backbone of this polymer. In addition, however, the band at 2925 cm.$^{-1}$ indicates methylene —CH_2— groups in this spectrum, suggesting a mixture of structures. Again, on the basis of infrared analysis it seems that cationically obtained polyallylbenzene is a mixture of —$CH(CH_3)CH(C_6H_5)$— and —$CH_2CH(CH_2C_6H_5)$— units. The relative preponderance of these units cannot be assessed on the basis of available evidence, but it is clear that both structures are present in substantial amounts.

The small but definitive differences in frequencies assigned to the methyl groups in poly-β-methylstyrene and polyallylbenzene are significant and indicate that these methyl groups are in different environments in these two polymers.

Discussion

Evidence cited by Staudinger and Dreher[1] to substantiate the proposition that under cationic polymerization conditions β-methylstyrene gives a polymer with —$CH(C_6H_5)$—CH_2—CH_2— repeat unit is not convincing. Peculiarities in the viscosity constant led these early workers to postulate that no methyl groups were present in the polymer backbone. To corroborate this proposition, ozonization and pyrolytic experiments were carried out. The results of ozonization were inconclusive and could not be used to substantiate or to refute the postulate of 1,3 polymerization. Thermal cracking of poly-β-methylstyrene and polyanethole (the polymer

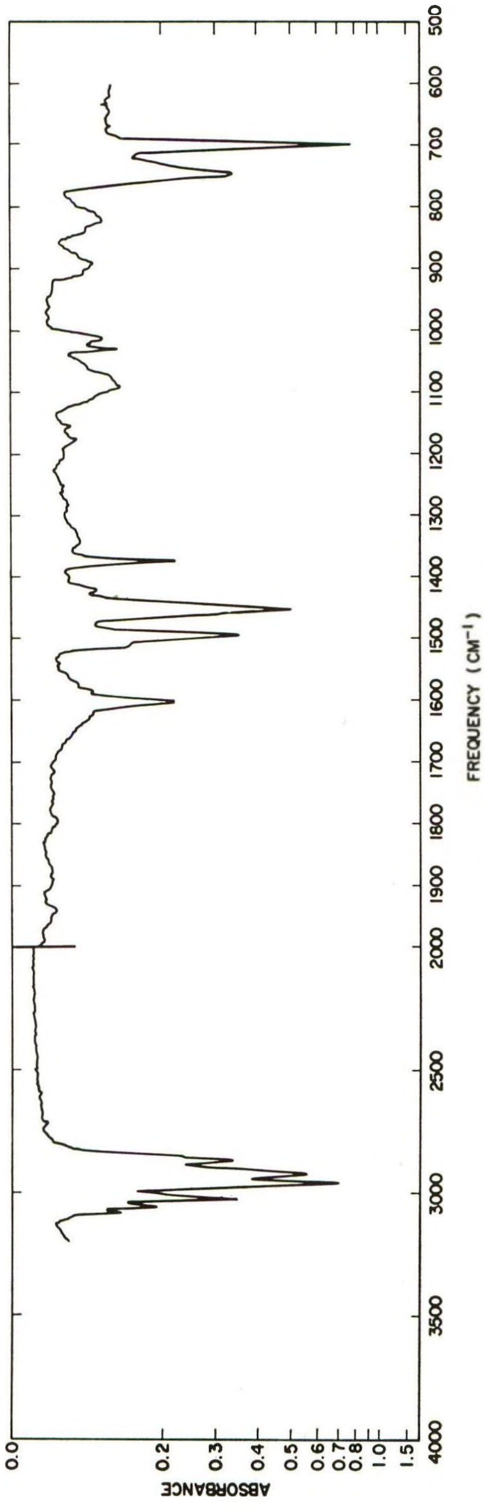
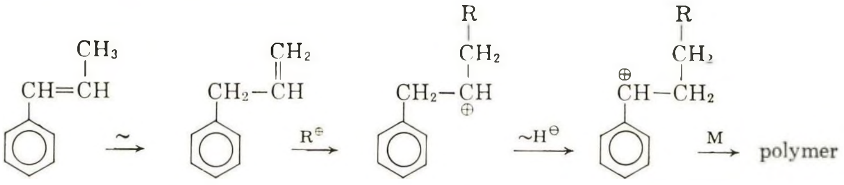


Fig. 2. Infrared spectrum of cationic polyallylbenzene.

of *p*-methoxy-β-methylstyrene) at 300°C. occurred readily, and unchanged monomer units were recovered. The occurrence of small amounts of 1,4-diphenylbutadiene among the cracking products of poly-β-methylstyrene was considered by the authors as conclusive evidence for their unusual polymerization mechanism. They admitted, however, that conventional 1,2-polymerization could have taken place, but it could not be demonstrated.

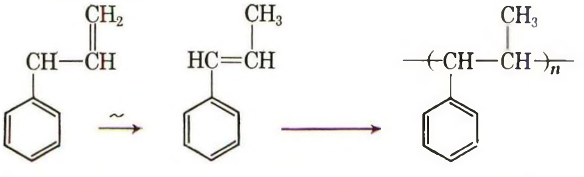
In 1944, Müller et al.[2] presented strong evidence obtained by conventional chemical group analysis for the presence of CH_3—C in the backbone of cationic polyanethole and refuted Staudinger's mechanism. Italian authors[4] determined the amount of CH_3—C groups by Kuhn's method in polyanetholes prepared by BF_3 catalyst under a variety of conditions. High resolution infrared studies carried out in these laboratories also suggest that the cationic polymerization of β-methylstyrene proceeds by a conventional olefin polymerization reaction.

In fact, it would be surprising if Staudinger's hypothesis of 1,3 polymerization would hold true. To explain a poly-β-methylstyrene molecule without pendant methyl groups in the backbone the following reaction sequence could be assumed:



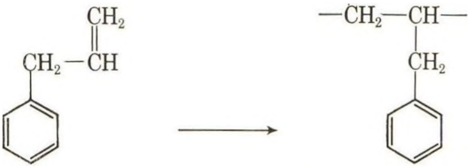
i.e., β-methylstyrene rearranges to allylbenzene which then interacts with the initiating or growing carbonium ion, $R^{\oplus}$, and a secondary carbonium is formed. Finally this carbonium ion rearranges to the energetically favored tertiary carbonium ion which is the true propagating species.

However, the first rearrangement, i.e., the conversion of an internal olefin to an external one, is quite unlikely to occur, particularly under the experimental conditions employed (small amount of catalyst, low temperatures). In fact it should be expected that this rearrangement will proceed in the opposite direction, i.e.,



To substantiate this mechanism allylbenzene was polymerized and the structure of the product was analyzed. High resolution infrared spectroscopy showed the presence of methyl groups in this polymer which is strong indication for the correctness of this mechanism. D'Alelio et al.[8] came to similar conclusions.

On the other hand, the presence of methylene groups in the polymer also suggest some measure of simple 1,2-type polymerization to occur:



Apparently, under the experimental conditions employed, the rate of isomerization of allylbenzene to β-methylstyrene and the rate of polymerization are not too dissimilar and a mixture of these structures is obtained. Further infrared evidence, i.e., the shifts in frequencies assigned to the methyl groups in the backbone as described above seem to indicate random copolymerization of rearranged and unrearranged allylbenzene units.

If polyallylbenzene were a block copolymer of rearranged and unrearranged structures, most of the backbone CH_3 groups would be in an identical environment in this polymer and in poly-β-methylstyrene. However, the small but significant methyl shifts suggest that these groups were in slightly different environment in these polymers. These shifts, therefore, could be an indication for random copolymerization of the two possible structures in polyallylbenzene.

The author is grateful to J. J. Elliott and J. W. Harrison, Analytical Research Division, for the competent help in interpreting infrared spectra.

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Résumé

On a démontré par spectroscopie infra-rouge à haute résolution les structures du poly (bèta-méthylstyrène) et du polyallyl-benzène, obtenus par polymérisation cationique. Ces études démontrent que dans des conditions cationiques le béta-méthylstyrène polymérise par un mécanisme 1,2-conventionnel, tandis que l'allylbenzène s'isomérise en partie en bèta-méthylstyrène plutôt que de propager et donne un copolymère composé d'unités réarrangées et non-réarrangées.

Zusammenfassung

Die Struktur von kationisch erhaltenem Poly(β-methylstyrol) und Polyallylbenzol wurde durch Hochauflösungsinfrarotspektroskopie untersucht. Es zeigt sich, dass unter kationischen Bedingungen β-Methylstyrol nach dem konventionellen 1,2-Mechanismus polymerisiert, während sich Allylbenzol vor dem Wachstum zum Teil zu β-Methylstyrol isomerisiert und ein "Copolymeres" der umgelagerten und der ursprünglichen Einheiten liefert.

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Heats of Mixing of Polymers with Ester and Ether Solvents

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Synopsis

Heats of mixing at infinite dilution have been obtained for polydimethylsiloxane in four series of ester solvents: the methyl and ethyl esters of the aliphatic acids, and the acetic and propionic esters derived from the normal alcohols. Heats have also been obtained in certain ethers including the dialkyl ethers. The solvent molecules are considered to be chains of two types of segments: —CH_2—CH_2— and —CO—O—, or —CH_2—O—. The heat of mixing is ascribed to two contributions: I, a difference in force fields between segments of polymer and solvent molecules, and II, a difference in the Prigogine structural factors of the molecules. Contribution II has been assumed to be approximately the same as with *n*-alkane solvents of corresponding chain lengths. By subtracting heats found with *n*-alkane solvents from those with esters or ethers II is eliminated and the resulting difference in I may be treated using a lattice model and assuming random mixing. This approach is successful for the ester solvents but somewhat less so for the ethers, where some departure from randomness due to steric factors may be present.

INTRODUCTION

The excess heat at constant pressure of a mixture of chain molecules contains two contributions[1,2] of which the first (I), is due to the difference in force fields and sizes between segments of the molecules of the two components A and B. These two differences are expressed by the parameters δ and ρ of the Prigogine[2] theory of solutions as defined by:

$$\delta = \epsilon_{BB}^*/\epsilon_{AA}^* - 1$$

$$\rho = r_{BB}^*/r_{AA}^* - 1$$

where $-\epsilon_{ij}^*$ is the minimum in the interaction potential of segments of types i and j occurring at distance r_{ij}^*. The effect of δ can be predicted by using a theory based on a rigid lattice model.[3] However, the second contribution (II) to ΔH_M arises from changes of volume of the component liquids as they mix, and hence cannot be treated by a rigid lattice model. For a solution of spherical molecules, II also depends on δ and ρ, but for a mixture of chain molecules the effect of these parameters is usually small compared with that of the difference in structural factors of the two mole-

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cules,[1,2] namely $(c_A/q_A) - (c_B/q_B)$. The structural factor of a chain molecule is a function of its length and flexibility and is connected with the thermal expansion coefficient of the liquid. The contribution I is the same for a polymer A and any solvent drawn from a homologous series such as the n-alkanes, where all segments of the solvent molecule are identical, i.e., the solvent is of formula $(B)_n$. The observed variation of ΔH_M with the length of the solvent molecule for such polymer–solvent systems[1,4] has been explained by a change in the structural factor of the solvent and hence of the contribution II. In the case, however, of a series of solvents such as the dialkyl ethers, or the esters of the aliphatic acids, both chains of formula $(B)_{n-1}B'$ containing two types of segments, a change in the length of the solvent molecule also alters the average force field per segment of the solvent and hence contribution I to ΔH_M. Some heats of mixing of polyisobutylene (PIB) at infinite dilution in dialkyl ethers and the ethyl esters of aliphatic acids have already been reported,[4] and the results were interpreted in terms of the Prigogine cell theory for polymer solutions.

In the present work dealing with heats of mixing of polydimethylsiloxane (PDS) with various homologous series of esters and ethers we use a slightly less refined approximation than that Delmas, Patterson, and Böhme;[4] contribution II is assumed to depend only on the difference in structural factors between polymer and solvent and not on δ or ρ. Furthermore the structural factors of the ester and ether solvents used here are taken to be the same as those of n-alkanes of the same number of segments. This approximation seems to be adequate to explain the results.

EXPERIMENTAL AND RESULTS

The PDS was a commercial sample of DC 200 silicone kindly given by Dow Corning Silicones of Canada, Ltd. and was of 30,000 cstokes viscosity or $\bar{M}_v \simeq 80{,}000$.

The ester solvents corresponded to the general formula $CH_3—(CH_2)_{n-2}—CO—O—(CH_2)_m—CH_3$ and were of four series, the number of atoms in the chain in each case being $n + m + 2$: (*1*) methyl esters of the aliphatic acids ($m = 0$), $n = 3, 4, 6, 8, 10$; (*2*) ethyl esters of the aliphatic acids ($m = 1$), $n = 2, 3, 4, 6, 7, 8, 9, 10, 12$; (*3*) acetic esters derived from normal alcohols ($n = 2$), $m = 1, 2, 3, 4, 5, 9$; (*4*) propionic esters derived from normal alcohols ($n = 3$), $m = 0, 1, 2, 3, 4$. (Three of the solvents appear in more than one series.) The PDS was found to be incompletely soluble in hexadecyl acetate, $m = 15$, and ethyl tetradecanoate, $n = 14$, and hexadecanoate, $n = 16$. The ether solvents were the dialkyl ethers from diethyl to dihexyl and also dimethoxymethane, 1,2-dimethoxyethane, and diethoxymethane. The solvents were of highest purity grade except for two of technical grade. Except for several ethyl esters of aliphatic alcohols ($m = 1$; $n = 6, 7, 8, 10, 12$) and two acetic esters of n-alcohols ($n = 2$;

$m = 5, 9$), the solvents were dried and distilled, the middle fraction being used. No systematic difference, however, could be found between values of the heats of mixing for distilled or undistilled solvents, and finally values obtained with the latter solvents were included.

A Tian-Calvet microcalorimeter was used to obtain the heats of mixing of small quantities of the amorphous polymer with the solvents, the apparatus and experimental technique having been described previously.[1] The concentration of the final solution was 0.5–1%. The heats of mixing observed at this dilution were corrected to infinite dilution by dividing by $(1 - \varphi_A)$, where φ_A is the volume fraction of polymer (see below). This method of correction ignores the lack of homogeneity in the polymer solution at great dilution, but the error so incurred would be negligible. Table I shows average heats of mixing at infinite dilution expressed per mole of repeating units of polymer, —$Si(CH_3)_2$—O—, (mol. wt. 74.2). The solvents are listed by the number of atoms in the chain $= n + m + 2$ for the esters. The table also contains for comparision values found previously[4] for ΔH_M of PDS in n-alkane solvents which are denoted by the number of chain atoms. The standard error and number of determinations for the particular solvent are included in the table. The main source of error is a possible shift of the base-line of the microcalorimeter during the course of an experiment[1] which may take ~1½ hr.

DISCUSSION

Although the heats have been obtained for a dilute final solution, they will be compared with results of the Prigogine theory of polymer solutions which makes no allowance for inhomogeneity of the solution. This is justified since almost all the heat arises from dilution of the polymer solution through the higher concentrations for which "concentrated" solution theory is valid. We interpret the results by assuming that the contribution II to ΔH_m is the same as that for an n-alkane solvent of the same chain length. The difference between the heat found for an ester or ether solvent and for an n-alkane is therefore assumed to be entirely due to a difference in contribution I. It may thus be treated in terms of the difference in contact energies of a repeating unit or segment of the polymer with segments of the ester and alkane liquids as given by the usual lattice theory. The cell model and the concept of a contact requires segments of solvent and of polymer to be of roughly the same size. Since the repeating unit of PDS contains two chain atoms, a similar choice has been made for segments of esters and ethers. Suppose a fraction $(1 - \alpha)$ of the segments of the ester (or ether) to be —CH_2—CH_2— groups (segments of type B) while a fraction α is —CO—O— or —CH_2—O— (segments of type B′). If the ester or ether contains p atoms in the chain, $\alpha = 2/p$. The interchange energies for the formation of contacts between the polymer and the two types of segments are w_{AB} and $w_{AB'}$, while that for a contact between the two types of segment in the solvent is $w_{BB'}$. According to the lattice

TABLE I

No. chain atoms in solvent, p	Heat of mixing at infinite dilution of PDS in homologous solvents, cal./unit						
	Methyl esters	Ethyl esters	Acetates	Propionates	Dialkyl ethers	Other ethers	Alkanes
5	214 ± 7;[a] (7)[b]	225 ± 1; (4)	225 ± 1; (4)	214 ± 7; (7)	−23 ± 3; (5)	Dimethoxymethane 132 ± 2; (4)	−17 ± 1; (4)
6	153 ± 1; (2)	142 ± 6; (3)	152 ± 1; (4)	142 ± 6; (3)		Dimethoxyethane 216 ± 9; (4)	12 ± 1; (4)
7		106 ± 5; (3)	109 ± 4; (6)	99 ± 3; (4)	−21 ± 2; (4)	Diethoxymethane 32 ± 1; (2)	36 ± 2; (2)
8	94 ± 5; (6)		103 ± 2; (5)	86 ± 6; (5)			46 ± 2; (5)
9		76 ± 2; (3)	88 ± 1; (2)	68 ± 4; (4)	11 ± 1; (3)		60 ± 2; (3)
10	88 ± 4; (5)	72 ± 1; (3)					68 (1)
11		68 ± 3; (3)			37 ± 1; (3)		76 ± 1; (3)
12	85 ± 1; (2)	66 ± 4; (4)					79 ± 2; (2)
13		67 ± 2; (4)	80 ± 3; (3)		54 ± 1; (5)		85 ± 3; (2)
14							91 ± 9; (6)
15		68 ± 3; (4)					96 (interpolated)

[a] Standard deviation.

[b] Number of determinations.

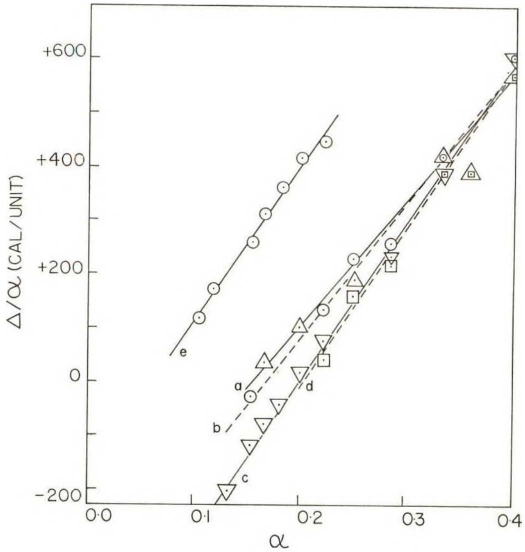

Fig. 1. Test of eq. (3) for PDS and PIB in ester solvents; Δ/α vs. α for: (*a*) PDS–methyl esters; (*b*) PDS–acetates; (*c*) PDS–ethyl esters; (*d*) PDS–propionates; (*e*) PIB–ethyl esters.

theory with random mixing, the heats of mixing of the polymer with an ester or ether solvent and an *n*-alkane are, respectively,

$$\frac{\Delta H_M \text{ (ester)}}{(r_A N_A + r_B N_B)\varphi_A \varphi_B / N} = zN[(1-\alpha)w_{AB} + \alpha w_{AB'} - \alpha(1-\alpha)w_{BB'}] \quad (1)$$

$$\frac{\Delta H_M \text{ (alkane)}}{(r_A N_A + r_B N_B)\varphi_A \varphi_B / N} = zNw_{AB} \quad (2)$$

where z is the lattice coordination number, φ is a volume fraction, r the number of segments and N is Avogadro's number. For dilute solutions,

$$(r_A N_A + r_B N_B)\varphi_A \varphi_B = r_A N_A (1 - \varphi_A)$$

whence the correction to infinite dilution of ΔH_M/mole of repeating unit is made by dividing the observed heat by $(1 - \varphi_A)$. Thus, the corrected heats, eqs. (1) and (2), may be subtracted to yield:

$$\begin{aligned}\Delta &\equiv N[\Delta H_M(\text{ester}) - \Delta H_M(\text{alkane})]/r_A N_A \\ &= zN[\alpha(w_{AB'} - w_{AB} - w_{BB'}) + \alpha^2 w_{BB'}] \quad (3)\end{aligned}$$

The relation (3) has been tested in Figure 1 for the four series of ester solvents by plotting Δ/α against α which should yield a straight line, with intercept and slope being, respectively, $zN(w_{AB'} - w_{AB} - w_{BB'})$ and $zNw_{BB'}$. The points correspond to the mean values listed in Table I, and the lines are drawn to give a least mean square deviation. The values of intercepts and slopes are given in Table II. In a previous study[1] the parameter zNw_{AB} was determined to be 100 cal./unit from heats of mixing of PDS with pure n-alkane solvents. On the basis of this value, for the case of the ethyl ester series, $zNw_{BB'} \simeq 2950 \pm 150$ cal./unit and $zNw_{AB'} \simeq 2470 \pm 200$ cal./unit.

TABLE II

	$zN(w_{AB'} - w_{AB} - w_{BB'})$, cal./unit	$zNw_{BB'}$, cal./unit
Methyl esters	-370 ± 50	2370 ± 150
Ethyl ester	-580 ± 50	2950 ± 150
Acetates	-450 ± 50	2560 ± 150
Propionates	-600 ± 50	2960 ± 200

A generalized Brønsted principle of congruence[5] would predict the heats to be only dependent on the length of the ester molecule and not on the way in which the ester and methylene groups are arranged. It is impossible to differentiate within experimental error between the lines in Figure 1 for the acetate and methyl ester series on the one hand and between the propionate and ethyl ester series on the other. There does, however, seem to be a difference between the two sets of results which might be due to the solvent molecules in one set terminating in a methyl group and in an ethyl in the other set. It is similarly found[6] that the solubility of a solute in the methyl esters and their mixtures is a smooth function of the average length of the solvent molecule but that the solubilities in ethyl esters diverge from this function.

ΔH_M of PIB in Ester Solvents

A test may be made of the validity of this simple approach by using data for the same esters but with another polymer. Heats of mixing of PIB in the ethyl ester series from ethyl pentanoate to ethyl hexadecanoate with the exception of ethyl tridecanoate and pentadecanoate are given elsewhere.[1] These data were treated in the same way as the PDS data, Figure 1 showing the curve of Δ/α against α, which gives an intercept $zN(w_{AB'} - w_{AB} - w_{BB'}) = -180$ cal./unit and slope $zNw_{BB'} \simeq 2940$ cal./unit. The excellent check between the values of $zNw_{BB'}$ found for these esters with PIB and with PDS is no doubt fortuitous but seems to show this simple approach to be adequate for the esters. Using the value $zNw_{AB} = 10$ cal./unit from the previous study, we obtain $zNw_{AB'} \simeq 2770$ cal./unit for PIB.

PDS–Ether Systems

The heats of mixing with the ether solvents may also be discussed in terms of eq. (3). Figure 2 shows the curves of Δ/α versus α for PDS with both the dialkyl ethers and those containing two oxygens. The straight line is drawn ignoring the high value for 1,2-dimethoxyethane. An analogous curve for PIB in the five dialkyl ethers (results of ref. 4) is also drawn. The curvature for PDS with the five dialkyl ethers shows that this simple treatment is not really adequate here, but may still be of interest. On referring to Table I, it is seen that the heats of mixing of PDS with the dialkyl ethers are more exothermic than with the *n*-alkanes. On the other hand, the heats with the ethers containing two oxygens are more positive than with alkanes of corresponding lengths. This may show that steric factors should be taken into account. This is supported by the very large heat with 1,2-dimethoxyethane where the spacing between ether linkages is greater than in the two methane derivatives and where the ether oxygens are in *trans* positions compared with *cis* for the other two ethers. The results for the PIB–dialkyl ether systems seem to be better treated by the theory. Here one finds $zNw_{BB'} \simeq 560$ cal./unit, and the slope gives $zN(w_{AB'} - w_{AB} - w_{BB'}) \simeq -5$ cal./unit so that on the basis of $zNw_{AB} = 10$ cal./unit from the earlier study[4] we find $zNw_{AB'} \simeq 560$ cal./unit. If we treat the straight line for the PDS–ether results in the same way, we find $zNw_{BB'} \simeq 600$ cal./unit and $zNw_{AB'} \simeq 310$ cal./unit. The low values of $zNw_{AB'}$ found here as compared with those found with the esters show the relative ease of forming contacts between the polymers and the —CH$_2$—O— segment as compared with the —CO—O— segment.

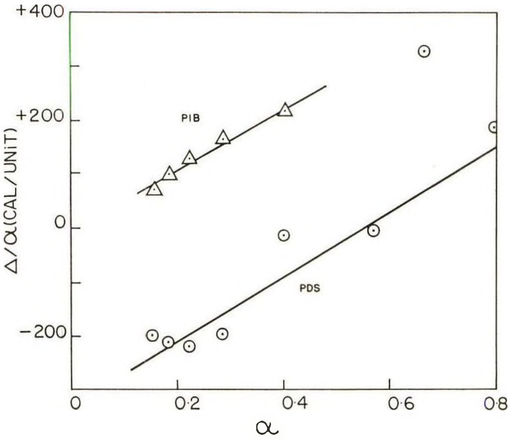

Fig. 2. Test of eq. (3) for PDS and PIB in ether solvents; Δ/α vs. α.

Discussion of the Approximation

The theoretical significance of our present approximation can be assessed by considering the results of the Prigogine theory. Equation (44) of ref. 1 gives ΔH_M as obtained from the average potential theory for a solvent of one type of segment, i.e. $(\mathrm{B})_n$,

$$
\begin{aligned}
\frac{\Delta H_M}{(r_A N_A + r_B N_B)\varphi_A \varphi_B} &= \Delta H^{I} + \Delta H^{II} \\
\Delta H^{I} &= (h_A - Tc_{pA})/r_A[-\delta^2 + 9\rho^2] \\
\Delta H^{II} &= -\frac{T^2}{2r_A}\frac{dc_{pA}}{dT}\left[1 - \delta - \frac{c_B}{r_B}\Big/\frac{c_A}{r_A}\right]^2
\end{aligned} \tag{4}
$$

where h_A and c_{pA} are the molar configurational enthalpy and heat capacity of polymer A. Here the terms ΔH^{I} and ΔH^{II} correspond to contributions I and II of the heat of mixing. Now we consider a solvent with fractions $(1 - \alpha)$ and α of contact points of types B and B′ with different fields of force but the same size of segment in the solvent as in the polymer ($\rho = 0$). It may be shown that if the geometric mean combining rule is accepted as an approximation for the intermolecular contact energies then eq. (4) is still valid provided δ is now considered to be averaged over the two types of segments B and B′:

$$\delta = (1 - \alpha)\delta_{AB} + \alpha\delta_{AB'} \tag{5}$$

(Replacing h_A and c_{pA} by the values given by the smoothed potential cell model gives eq. (10) of ref. 4 used to treat the heats of mixing of PIB with ether and ester solvents in that ref.) Our assumption here is equivalent to ignoring the difference between δ_{AB} and $\delta_{AB'}$ in ΔH^{II} where δ is less important and retaining it in ΔH^{I}. Thus the difference between heats with n-alkane and ester or ether solvents of the same number of chain atoms is:

$$
\begin{aligned}
\frac{\Delta H_M(\text{ester}) - \Delta H_M(\text{alkane})}{(r_A N_A + r_B N_B)\varphi_A\varphi_B} &= -\frac{h_A - Tc_{pA}}{4r_A} \\
&\qquad \left\{[(1 - \alpha)\delta_{AB} + \alpha\delta_{AB'}]^2 - \delta_{AB}{}^2\right\} \\
&= -\frac{h_A - Tc_{pA}}{4r_A}\left\{\alpha[\delta_{AB'}{}^2 - \delta_{AB}]^2 - (\delta_{AB} - \right. \\
&\qquad \left. \delta_{AB}{}')^2] + \alpha^2(\delta_{AB} - \delta_{AB'})^2\right\}
\end{aligned} \tag{6}
$$

which is equivalent to eq. (3).

The competent technical work of Mr. H. Strykowski in carrying out the microcalorimetry is gratefully acknowledged. Financial support was given by the Paint Research Institute and Imperial Oil, Ltd. Thanks are also due to the National Research Council of Canada for their general grant to the physical chemistry section. Finally, a good number of measurements, not however, used here, were made by Mr. C. Ho-Tung and the author would like to thank him for this preliminary work.

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Résumé

On a obtenu les chaleurs de mélange à dilution infinie du polydiméthylsiloxane dans quatre séries de solvants à fonction ester: les esters méthyliques et éthyliques des acides aliphatiques et les esters acétiques et propioniques dérivés des alcools normaux. On a également obtenu les chaleurs de mélange dans certains éthers parmi lequels les dialcoyléthers. On considère les molécules de solvant comme des chaînes formées de segments de deux sortes: —CH_2—CH_2— et —CO—O— ou —CH_2—O—. On émet l'hypothèse que deux facteurs apportent leur contribution à la chaleur de mélange: I une différence dans les champs de force entre les segments de polymère et les molécules de solvant, et II une différence dans les facteurs structurels de ces molécules suivant Prigogine. Cette seconde contribution est sensée être comparable à celle qui proviendrait de solvants alcanes normaux de longueur de chaîne correspondante. En soustrayant les chaleurs trouvées dans les solvants alcanes normaux de celles qui ont été trouvées dans les esters et les éthers, on élimine ce second facteur; le résultat obtenu par différence peut être interprêté sur la base d'un modèle de réseau en admettant un mélange statistique. Cette approximation se révèle valable dans le cas des solvants à fonction ester, mais se trouve quelque peu en défaut dans le cas des éthers où certains écarts à une disposition statistique par suite de facteurs stériques peuvent exister.

Zusammenfassung

Mischungswärmen bei unendlicher Verdünnung wurden für Polydimethylsiloxan in vier Reihen von Ester-Lösungsmitteln erhalten: Methyl- und Äthylester der aliphatischen Säuren und die von den normalen Alkoholen abgeleiteten Essigsäure- und Propionsäureester. Auch in gewissen Äthern, einschliesslich der Dialkyläther wurden Lösungswärmen erhalten. Die Lösungsmittelmolekel wurden als Ketten aus zweierlei Segmenttypen: —CH_2—CH_2— und —CO—O— oder —CH_2—O— betrachtet. Die Mischungswärme wird auf zwei Beiträge zurückgeführt: I., einen Unterschied im Kraftfeld zwischen Polymersegmenten und Lösungsmittelmolekeln und II., einen Unterschied im Molekülstrukturfaktor nach Prigogine. Beitrag II wird als etwa gleich dem bei *n*-Alkan-Lösungsmitteln von entsprechender Kettenlänge betrachtet. II wird durch Subtraktion der bei *n*-Alkanlösungsmitteln gefundenen Wärmen von denjenigen mit Estern oder Äthern eliminiert, und der so erhaltene Unterschied in I kann mit einem Gittermodell unter Annahme einer regellosen Mischung behandelt werden. Dieses Verfahren erweist sich bei Ester-Lösungsmitteln als erfolgreich, etwas waniger hingegen bei Äthern, wo eine Abweichung von der regellosen Mischung auf Grund sterischer Faktoren auftreten kann.

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Electrochemical Transformations of Polymeric Acid Solutions. I. Crossed Koble Synthesis

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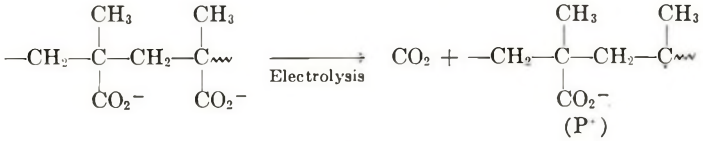
Synopsis

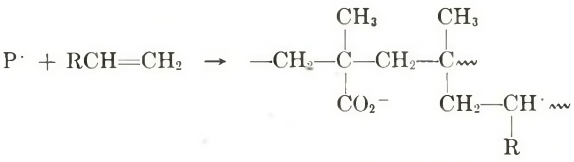
Poly(methacrylic acid) was electrolyzed at 20°C. in 0.2 *M* dry methanol solution in a glass apparatus provided with two polished platinum disk electrodes; the current density was kept constant (300, 800, or 1000 ma.). Before electrolysis the acid was partially neutralized in order to increase the electrical conductivity. The electrolysis was characterized by evolution of carbon dioxide at the anode, while the acid content of the polymer decreased. When the degree of decarboxylation was about 30%, intramolecular lactonization occurred by interaction of unsaturated groups with neighboring acid groups. The changes of chemical composition of the polymer in function of the time were followed by determination of free carboxylic acid groups, of γ-lactones, and unsaturated groups (bromine addition). The amount of methyl ester formed by methanolysis of the lactones was calculated from methoxyl determinations. At the end of electrolysis only 5–6% free carboxylic groups were present, 35–40% lactones, 30% ester groups; the residue was mainly a hydrocarbon fraction (partially unsaturated). The electrolysis was also carried out in the presence of low molecular weight carboxylic acids, acetic, ϵ-acetaminocaproic, and cyanoacetic acids, the ratio of the concentration of these acids to that of polymeric acid being varied over a wide range. With acetic acid the chemical composition of the polymer was only slightly affected through grafting of side methyl groups, as was shown by the use of C^{14} acetic acid. With ϵ-acetaminocaproic and cyanoacetic acids the crossed Kolbe synthesis reactions are much more important, 20–24% side alkyl acetamino groups and 15% cyanomethylene groups being grafted to the main chain by this method. Chain degradation during these experiments can be practically avoided.

I. INTRODUCTION

It was demonstrated previously that the electrolysis of a poly(methacrylic acid) (PMA) solution in methanol produces macroradicals P· with simultaneous evolution of carbon dioxide,[1,2] as shown in eq. (1). In the presence of water, anodic oxidation transforms these radicals, at least partially, into hydroperoxide groups [eq. (3)]. When these macroradicals are used for the initiation of the polymerization of a vinyl monomer present in the solution, graft polymers can be obtained [eq. (2)].



$$-CH_2-\underset{CO_2^-}{\overset{CH_3}{C}}-CH_2-\underset{CO_2^-}{\overset{CH_3}{C}}\sim \xrightarrow[\text{Electrolysis}]{} CO_2 + -CH_2-\underset{\underset{(P\cdot)}{CO_2^-}}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{\dot{C}}\sim \qquad (1)$$



$$P^{\cdot} + RCH{=}CH_2 \rightarrow -CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CO_2^-}{C}}-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2-\underset{\displaystyle R}{CH^{\cdot}}\sim}{C}}\sim \qquad (2)$$

Graft polymer

$$P^{\cdot} + O_2 \rightarrow POO^{\cdot} \xrightarrow[HOH]{} P-O-OH + HO^{\cdot} \qquad (3)$$

This method of electrochemical modification of a high polymeric acid differs from the direct electrolytic polymerization of vinyl monomers where a foreign electrolyte was used as support for the current.[3-5] In the present paper another reaction possibility will be considered: namely, when these macroradicals are produced together with other radicals in the solution, addition may occur with grafting of new side groups; in the case of disproportionation, unsaturated units will be formed. These foreign radicals may originate from an electrolyte present in the solution, e.g., a low molecular weight carboxylic acid; in this case the reaction is called a "crossed Kolbe synthesis." They may also be produced by a chain transfer reaction with compounds having a relatively high transfer constant, such as mercaptans, disulfides, or halomethanes. The reaction we are especially concerned with in the present paper is the reaction between the radicals produced by electrolysis of a polymeric acid (macroradical) ($P^{\cdot}$) and of a low molecular weight carboxylic acid ($R^{\cdot}$). Even if no other radical species are formed, in any case three different reactions must be taken into account [eqs. (4)–(6)]:

$$P^{\cdot} + R^{\cdot} \rightarrow P-R \text{ (crossed Kolbe synthesis)} \qquad (4)$$

$$R^{\cdot} + R^{\cdot} \rightarrow R-R \qquad (5)$$

$$P^{\cdot} + P^{\cdot} \rightarrow \text{crosslinking or disproportionation} \qquad (6)$$

It is well known that radicals formed by electrolysis of branched carboxylic acids essentially disproportionate;[6] insolubilization of the polymer by crosslinking will therefore occur only in concentrated solutions (25% weight); indeed, it was completely prevented by working in dilute systems.

On the other hand, the products of reaction (5) can easily be separated from the modified polyacid produced in reaction (4). Consequently the chemical composition of the crossed Kolbe polymeric acid will give a fairly good picture of the relative importance of the addition/disproportionation reactions between unlike radicals $P^{\cdot}$ and $R^{\cdot}$, as well as with other radicals present in the solution (usually originated from the solvent). In order to determine the conditions which enhance reaction (4) it is of primary importance to know the concentration of the $P^{\cdot}$ radicals and their rate of formation. Therefore this rate has been determined by measuring the carbon dioxide evolved during the electrolysis of the polymer solution. Similarly, the rate of formation of $R^{\cdot}$ was determined from the rate of decarboxylation of the low molecular weight carboxylic acid solution. Thereafter only the mixed systems will be considered.

II. ELECTROLYSIS OF POLY(METHACRYLIC ACID) IN METHANOL SOLUTION

The anodic oxidation of the polymer in solution causes several intrinsic polymeric modifications, namely decarboxylation, lactonization, formation of unsaturated groups, and chain degradation.

A. Decarboxylation

The progress of the electrolysis has been followed by measuring as a function of time the amount of carbon dioxide evolved, the acid and the lactone contents of the polymer, its degree of unsaturation, and its intrinsic

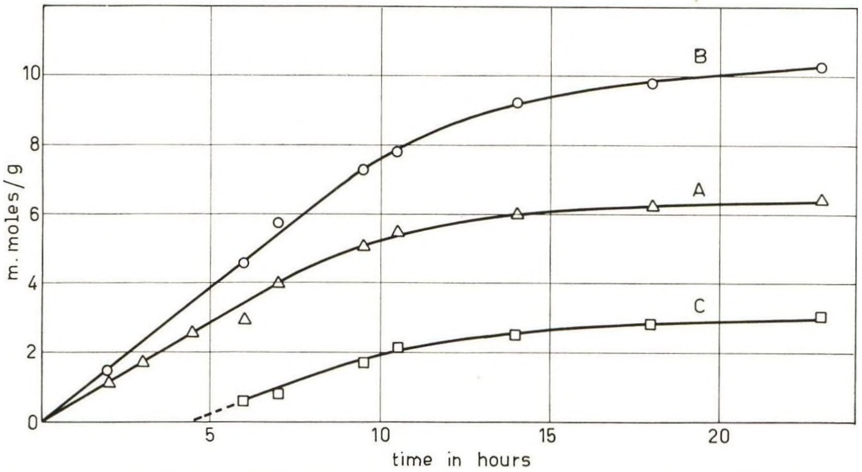


Fig. 1. Electrolysis of poly(methacrylic acid) in methanol solution: (*A*) CO_2 evolved; (*B*) acid content; (*C*) lactone content.

TABLE I

Electrolysis of Poly(methacrylic Acid) in Methanol Solution[a]

Time, hr.	Acid content Wt.-%	Acid content mmole/g.	Lactone content Wt.-%	Lactone content mmole/g.	[η] in MeOH	Acid decomposed, mmole/g. polymer	CO_2 evolved, mmole/g. polymer
0	94.6	11.0	0	0	1.25	0	0
2	83	9.65	0	0	1	1.35	1.2
3	—	—	0	0	—	—	1.75
4.5	73.9	8.6	0	0	0.68	2.4	2.6
6	55.6	6.5	7.5	0.6	—	4.5	2.9
7	45	5.2	10.2	0.8	0.25	5.8	4.0
9.5	32.1	3.7	21.5	1.7	—	7.3	5.1
10.5	28.4	3.2	26.8	2.1	0.12	7.8	5.4
14	15	1.7	31.2	2.5	—	9.3	6.0
18	10.3	1.2	35	2.8	0.06	9.8	6.2
23	6.1	0.7	37.8	3.0	0.05	10.3	6.4

[a] [PMA] = 0.2 mole/l., T = 20°C.

viscosity. The data are summarized in Table I; some of them are shown in Figure 1. It can be seen from the comparison of curves *A* and *B* in Figure 1 that the decrease of acid content is higher than that calculated from the CO_2 evolved. The discrepancy results from an intramolecular reaction with the formation of γ-lactone rings.

B. Lactonization

The presence of γ-lactones was shown by infrared spectrometry ($\gamma = 1775$ cm.$^{-1}$); their content was determined by ring-opening measurements in alkaline medium (see Experimental section). The variation of lactone content as a function of time is given by curve *C* of Figure 1.

In fact, γ-lactone rings can be considered only when the decarboxylation reaction has attained 35% completion; from this point on, it increases progressively with time. This lactone formation must be considered as rather surprising; indeed α-substituted carboxylic acids[6] as well as dibasic acids usually give olefins, e.g., propylene from glutaric acid.[7] Overberger and Kabasakalian,[8] however, observed lactonization during the electrolysis of a methanolic solution of perhydrodiphenic acid, and interpret it by an intramolecular coupling of radicals after rearrangement of one of them.

This interpretation could difficultly be valid in the present case for polymeric acids, where the degree of neutralization is kept low (about 8%) and where lactonization occurs only after appreciable decarboxylation, i.e., when the carboxylic groups are farther separated than initially.

C. Formation of Unsaturated Groups

It is, however, possible to prove the presence of unsaturated groups in the polymer after its isolation; the content of unsaturation was determined by bromine addition. It initially increases with time of reaction, passes through a maximum, and then decreases slowly (Fig. 2).

These double bonds are formed either in a disproportionation reaction with radicals present in the solution or during chain degradation [eq. (7)].

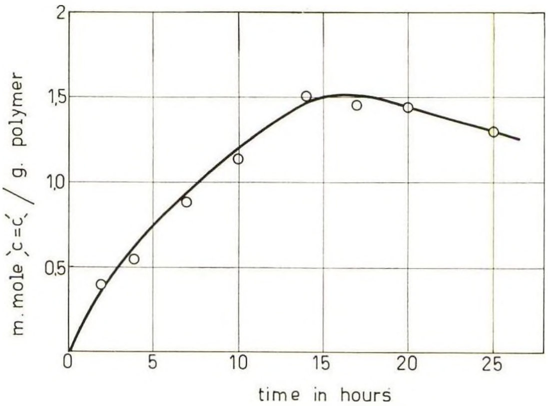
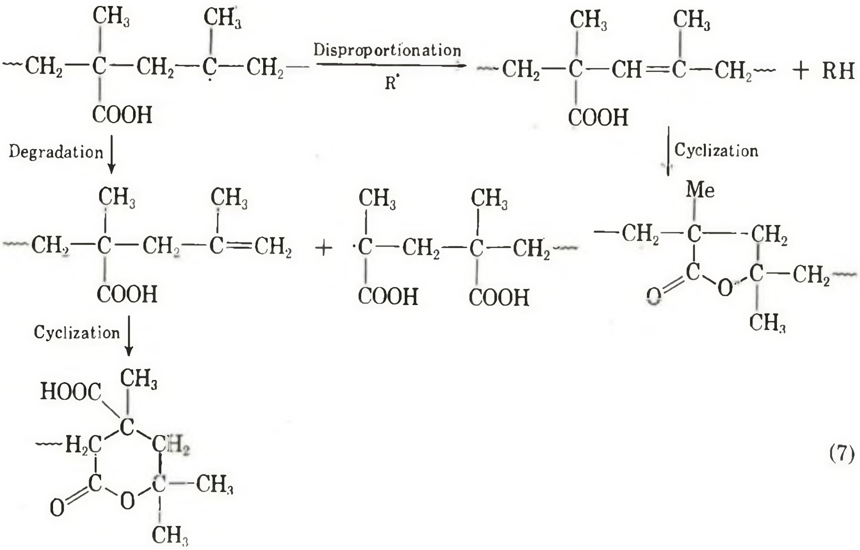


Fig. 2. Degree of unsaturation as a function of time of electrolysis.



(7)

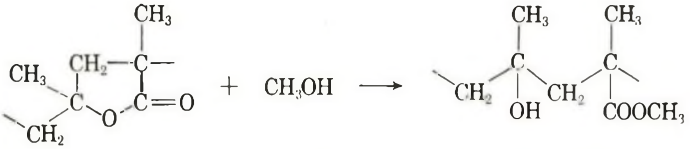
It was therefore considered that β–γ or γ–δ unsaturated carboxylic acid units are formed and undergo further lactonization.[9]

D. Chain Degradation

The formation of macroradicals with a free radical on the main chain explains the occurrence of chain degradation during electrolysis when the overall radical concentration is relatively low (Table I). This effect was shown by intrinsic viscosity determinations; from an initial value of 1.15, $[\eta]$ drops to about 0.05 after 23 hr.

E. Solvent Effects

In addition to these direct polymer modifications some other side reactions occur under the influence of the solvent (in the present experiments, methanol). A first solvent effect consists in the methanolysis of the butyrolactone groups[10] yielding γ-oxymethyl ester units, i.e., an isopropenyl alcohol unit together with a methyl methacrylate unit (infrared absorption of $C{=}O$ ester group at 740 cm.$^{-1}$), as shown in eq. (8).

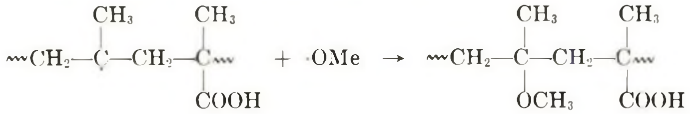


(8)

Indeed it can be seen from Table II that the percentage of ester in the polymer, as evaluated on the basis of methoxyl group determinations, increases with the lactone content and becomes very appreciable.

A second effect of methanol was indicated by infrared analysis showing an ether group absorption at 1075 cm.$^{-1}$. It is well known that the electrolysis of methanol yields oxymethyl radicals, $CH_3O\cdot$, which disproportionate[11] to methanol and formaldehyde (as was shown by the resorcinol test on the solution).

At high degrees of decarboxylation of the polymeric acid the pH of the solution increases and the methoxyl radical concentration becomes appreciable. It must therefore be expected that methyl ether groups are present in electrolyzed polymers at high degree of conversion (Table II, polymer D) and that these are formed as indicated in eq. (9)



$$\sim CH_2-\overset{CH_3}{\dot{C}}-CH_2-\underset{COOH}{\overset{CH_3}{C}}\sim \; + \; \cdot OMe \rightarrow \sim CH_2-\underset{OCH_3}{\overset{CH_3}{C}}-CH_2-\underset{COOH}{\overset{CH_3}{C}}\sim \qquad (9)$$

Table II gives overall compositions of poly(methacrylic acid) samples isolated after different times of electrolysis; it shows the relative importance of the various electrochemical modifications. It can be seen that group interactions resulting in lactone and subsequently ester formation are by far the most important.

III. ELECTROLYSIS OF PMA IN THE PRESENCE OF ACETIC ACID

The rate of decarboxylation of acetic acid in methanol solution is about three to four times as fast as that of PMA; the amount of carbon dioxide evolved during electrolysis, at constant current density, is proportional with time. Only at 80% conversion the rate decreases progressively. During the electrolysis of a mixture of PMA and acetic acid in methanol, the decarboxylation as well as the chemical composition of the polymer will depend on the relative concentration of both acids (Table III). The residual acid content of the polymer (unreacted carboxylic groups) increases with an increasing initial HOAc concentration, while lactone formation and chain degradation decrease.

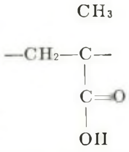
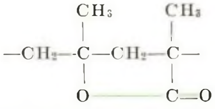
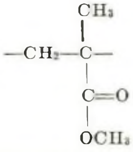
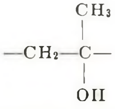
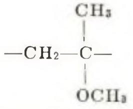
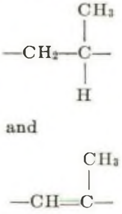
On the other hand, it is known that the anodic oxidation of acetate ions produces essentially methyl radicals, the main product of electrolysis of acetic acid being ethane; only very small amounts of ester (about 2%) are isolated.[6] Thus, the presence of acetic acid will only affect the chemical composition of electrolyzed poly(methacrylic acid) to the extent that the

TABLE III
Electrolysis of Poly(methacrylic Acid) and Acetic Acid in Methanol[a]

		Polymer after electrolysis		
Time, hr.	[HOAc], mole/l.	Acid content, %	Lactone content, %	[η]
12.5	2.6	7.6	19	0.07
"	5.1	21.6	18.3	0.16
"	9.33	49.4	11.2	0.25
20	5.1	2.0	25.2	0.05
"	9.33	34.4	16.6	0.17

[a] [PMA] = 0.2 mole/l., current intensity = 1 amp., T = 20°C.

TABLE II
Polymer Composition after Electrolysis of Poly(methacryclic Acid) in Methanol[a]

Poly-mer	Time, hr.	Polymer composition, wt.-%							C, %		O, %	
		Acid	Lactone	Methoxy	Ester[b]	Alcohol[c]	Ether	Hydrocarbon				
		 $-CH_2-\overset{CH_3}{\underset{\underset{OH}{C=O}}{C}}-$		CH_3O	 $-CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}-$	 $-CH_2-\overset{CH_3}{\underset{OH}{C}}-$	 $-CH_2-\overset{CH_3}{\underset{OCH_3}{C}}-$	 $-CH_2-\overset{CH_3}{\underset{H}{C}}-$ and $-CH=\overset{CH_3}{C}-$	Calc.	Found	Calc.	Found
A	2	83.0	0	1.1	3.5	2.1	—	11.4	60.4	58.5	32.5	33.8
B	9.5	32.0	21.5	6.9	22.2	12.9	—	11.3	62.2	62.7	28.0	29.3
C	10.5	28.4	26.8	6.6	21.3	12.4	—	11.2	63.7	62.8	27.7	29.0
D	23	6.1	37.8	13.3	29.9	17.4	9.3	—	63.4	62.7	28.4	29.25

[a] [PMA] = 0.2 mole/l., T = 20°C., current intensity = 300 ma., degree of neutralization = 5%.

[b] % methoxy × 3.22 = % ester.

[c] % methoxy × 1.87 = % alcohol.

TABLE IV
Electrolysis of PMA and Acetic Acid in Methanol Solution[a]

Polymer	[HOAc], mole/l.	Degree of neutralization, %	Time, hr.	Acid, wt.-%	Lactone, wt.-%	Ester, wt.-%[b]	Alcohol, wt.-%	Hydrocarbon, wt.-%	CH_3, wt.-%[c]	CH_3O, wt.-%	Carbon, %	Oxygen, %
A	1.05	5	8	5.2	29.3	36.4	17	12	2.5	11.3	66.1	25.6
B	4.37	5	10	25.6	19.4	16.5	10	28	2.8	5.1	66	25.7
C	4.37	1.25	10	16.3	20	18.6	12	33	1.2	5.8	69.3	22.3
D	2.1	2.5	10	4.4	29.9	35.1	17	14	2.5	10.9	68.4	25.2
E	1.05 1.05[d]	2.5	10	4.3	20.2	29.3	17	30	0.7	9.1	70	21.1

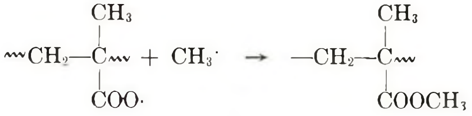
[a] [PMA] = 0.2 mole/l., current intensity 0.8 amp., $T = 20°C$.

[b] Ester content was calculated from % $CH_3O \times 3.22$.

[c] % $CH_3 \times 3.73$ = wt.-% isobutene units; % $CH_3 \times 6.66$ = wt.-% methyl methacrylate units.

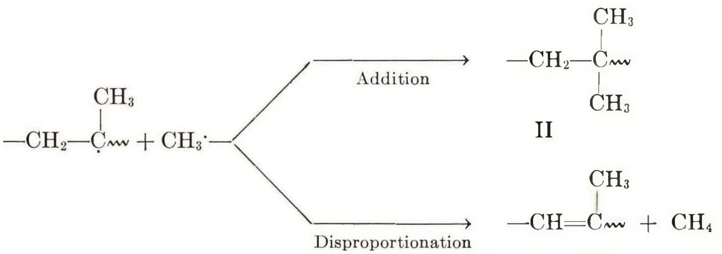
[d] In experiment E, acetic acid was added in two equal quantities at zero time and after 5 hr.

methyl radicals react with polymeric radicals. Three reaction possibilities, shown in eqs. (10–12) must be considered:



$$\sim CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COO\cdot}{C}}\sim + CH_3\cdot \rightarrow -CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}\sim \qquad (10)$$

I



$$-CH_2-\overset{\displaystyle CH_3}{\underset{\cdot}{C}}\sim + CH_3\cdot \xrightarrow[\text{Addition}]{} -CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\sim \qquad (11)$$

II

$$-CH_2-\overset{\displaystyle CH_3}{\underset{\cdot}{C}}\sim + CH_3\cdot \xrightarrow[\text{Disproportionation}]{} -CH=\overset{\displaystyle CH_3}{C}\sim + CH_4 \qquad (12)$$

III

Considering that methyl methacrylate and olefinic units are already formed in the absence of acetic acid, only the isobutene units (II) may be considered as an argument for crossed Kolbe synthesis. Indeed infrared analysis shows an increase of the methyl absorption band at a frequency of 1380 cm.$^{-1}$.

In order to make a quantitative determination possible, radioactive acetic acid $C^{14}H_3COOH$ has been used; whatever the grafted side groups may be ($C^{14}H_3\cdot$ or $C^{14}H_3COO\cdot$) the radioactivity of the polymer will be directly related to the amount of the methyl groups originating from the acetic acid. The reaction conditions as well as the chemical composition of the polymers after electrolysis are summarized in Table IV.

As can be seen from the $C^{14}H_3$ content, the radioactivity of the electrolyzed polymer is relatively low; even if all the labeled methyl is incorporated either as methyl methacrylate or as isobutene units, these crossed-Kolbe units never exceed 19 and 11 wt.-%, respectively. At the same HOAc concentration, the CH_3 grafting is enhanced by a higher degree of neutralization (expts. B,C); conversely, at same degree of neutralization, grafting is favored by a higher concentration of acetic acid (expts. D,E).

By comparing polymers II-D and IV-A of the corresponding tables, which were isolated after about the same number of coulombs (times × amperes), it can be seen that the lactone content is lower and the ester content higher when acetic acid is present during the electrolysis. From these experiments it can be concluded that acetic acid exerts an effect of only secondary importance with respect to the electrochemical modifications of poly(methacrylic acid).

IV. ELECTROLYSIS OF PMA IN THE PRESENCE OF ε-ACETAMINOCAPROIC ACID (ACA)

The rate of decarboxylation of acetaminocaproic acid (ACA) is about twice as rapid as that of PMA; as in the case of acetic acid, the amount of

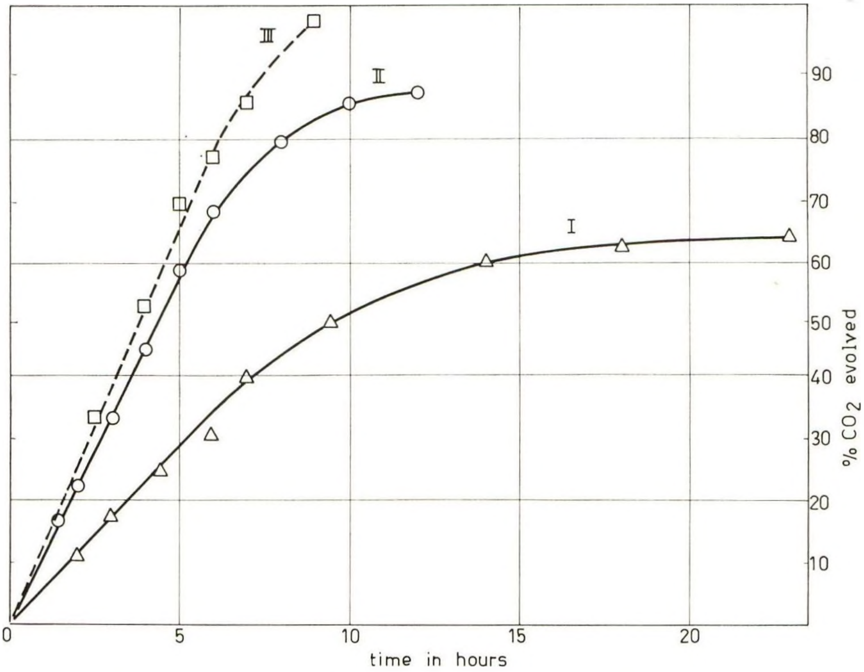


Fig. 3. CO_2 evolved in electrolysis of poly(methacrylic acid) and acetaminocaproic acid in methanol solution: (*I*) [PMA] = 0.2 mole/l.; (*II*) [ACA] = 0.2 mole/l.; (*III*) mixture of both acids, 0.2*M*.

carbon dioxide evolved is proportional to the time up to high conversions (Fig. 3).

Preliminary electrolytic experiments on methanol solutions of both acids at different ratios ACA/PMA have shown that: (*1*) at equimolar concentration (0.2*M*) the grafting of ACA residues attains its final value after 9 hr., further electrolysis being responsible for chain degradation only; (*2*) the amount of ACA incorporated is identical for ACA/PMA ratios varying from 1 to 3.5. High initial concentrations of ACA favor mainly the dimerization reaction, eq. (13):

$$2CH_3CO—NH—(CH_2)_4—CH_2\cdot \rightarrow CH_3CO—NH—(CH_2)_{10}—NH—COCH_3 \quad (13)$$

In order to increase the degree of grafting while preventing dimerization, ACA was added progressively, the rate of decarboxylation of the solution being kept constant. In this way it was possible at ACA/PMA ratios varying from 1 to 4 to increase the content of crossed units from 7.2 to 17.6, respectively (Table V, expts. 4–8). A value higher than 20% is difficult to obtain owing to the decreasing solubility of the polymeric acid; it was only possible in more dilute PMA solution (expt. 8).

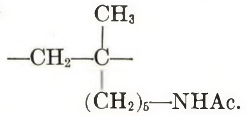
As can be seen from Table V, chain degradation can be avoided by this technique. Moreover the acid content of the polymeric acid remains very high, if one compares it with the results of Table II and Table IV. For experiments 4 and 8 it was calculated that one alkyl acetamino group

TABLE V
Electrolysis of Poly(methacrylic Acid) in the Presence of ε-Acetaminocaproic Acid (ACA)[a]

	Acetaminocaproic acid, mole/l.		Experimental conditions		Polymer after electrolysis				
No.	Initial	Final	Time, hr.	Current, ma.	Acid, %	Nitrogen, %	2-Me-*N*-acetylaminoheptene, wt.-%[b]	Lactone, wt.-%	[η]
1	0.2	—	22	300	28.3	0.55	6.6	14.8	0.23
2	0.2	—	9	300	83.4	0.60	7.2	—	0.85
3	0.56	—	18	400	85.2	0.55	6.6	—	1.25
4	0.2	0.56	18	400	80	1.14	13.7	—	1.35
5	0.2	0.4	18	300	79.6	0.94	11.25	—	1.25
6	0.2	0.8	28	300	69.6	1.46	17.6	—	1.25
7	0.2	1.2	40	300	67.5	1.45	17.4	—	1.25
8[c]	0.1	0.4	18	300	68.8	2.00	24	—	1.25

[a] [PMA] = 0.2 mole/l., T = 20°C.

[b]



$-CH_2-\overset{CH_3}{\underset{(CH_2)_5-NHAc.}{C}}-$

[c] [PMA] = 0.1 mole/l.

was grafted on instead of two or three decarboxylated acid groups; thus the yield, although low in absolute value, is nevertheless appreciable and much better than with acetic acid.

V. ELECTROLYSIS OF PMA IN THE PRESENCE OF CYANOACETIC ACID

Some complementary electrolytic experiments have also been carried out with cyanoacetic acid. It was suggested that the resonance-stabilized cyanomethylene radicals $\cdot CH_2-CN \rightleftharpoons CH_2=C=N\cdot$, formed during the electrolysis[12] would add more easily to the polymeric radicals on account of their polarity differences, as well as of the absence of labile α-hydrogen atoms in the nitrile radical.

On infrared spectrometry, a characteristic C≡N absorption band at 2260 cm.$^{-1}$ has been regularly observed in the polymers isolated after electrolysis. It was found that the amount of 2-methylbutenenitrile $-CH_2-C(CH_3)CH_2CN$ groups incorporated in the polymer increases with the concentration of cyanoacetic acid in the solution; the maximum amount incorporated was 15% (Table VI).

It was estimated that one cyanomethylene group is incorporated per 2.5 decarboxylated acid groups. As in the previous section with ACA, the acid content of the polymers remains high in spite of the duration of the experiments; the polymer degradation is also not very important, the intrinsic viscosity decreasing from 1.25 to 0.6 and 0.85.

TABLE VI

Electrolysis of Poly(methacrylic Acid) in the Presence of Cyanoacetic Acid[a]

	Experimental conditions		Polymer after electrolysis			
Cyanoacetic acid, mole/l.	Current, ma.	Time, hr.	Acid, wt.-%	Nitrogen, %	2-methylbutenenitrile, wt.-%	[η]
0.2	500	4	86	—	—	—
0.2	300	10	71.5	0.35	2	0.62
0.4	300	25	66.4	0.7	4	0.60
2.0	400	20	62.5	2.35	13.6	0.85
4	400	40	58.2	2.67	15.4	0.75

[a] [PMA] = 0.2 mole/l., T = 20°C.

VI. EXPERIMENTAL

A. Electrolysis

Electrolysis Cell. The cell consists of a Pyrex glass cylinder as shown in Figure 4. The two polished platinum disk electrodes used (2.5 cm. diameter) were 1 cm. from each other and were directly connected with two mercury-filled tubes. An iron–hydrogen stabilized power supply

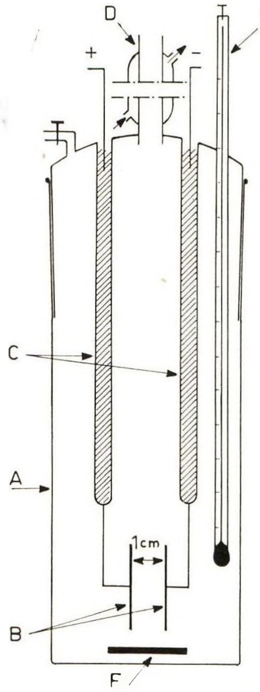


Fig. 4. Electrolysis apparatus: (A) electrolytic cell; (B) platinum electrodes; (C) Hg-filled wire connections; (D) cooling unit; (E) contact thermometer; (F) magnetic stirrer.

provided currents between 100 and 1000 ma., with a stability constant of ±0.002 ma. Continuous stirring of the electrolyte was assured by a magnetic stirrer. The temperature of electrolysis was kept constant with a contact thermometer E connected with a cooling system consisting of a pump and a refrigerating cold acetone–water mixture (−20 to −30°C.); this mixture was allowed to circulate in helical tubing around the electrolytic cell. Carbon dioxide evolved during the electrolysis was absorbed in barium hydroxide solution.

Reaction Conditions. Methanol was used as solvent. The poor conductivity of the methanol solution necessitated, however, a partial neutralization of the poly(methacrylic acid) by addition of a sodium methoxide in methanol solution in order to obtain a degree of neutralization (5–8%). A higher degree of neutralization, however, produces an excessive increase in the viscosity of the solution; the concentration of polymer must be kept below 5% for the same reason.

The experimental conditions of electrolysis were: polymer concentration, 0.2 mole/l., i.e., 17.2 g./l.; degree of neutralization, 5–8%; temperature, 20°C.; current intensity, 300 ma.; voltage, 50–150 v.; electrodes: polished platinum; total volume of the solution, 100 ml.

B. Products

Methacrylic acid a commercial sample, was distilled under reduced nitrogen pressure, b.p. 63°C./15 mm. It was polymerized at 75°C. in 30% benzene solution in the presence of benzoyl peroxide, 1% with respect to the amount of monomer. The polymer precipitated progressively as it formed and was filtered off, washed with dry diethyl ether, and dried *in vacuo* at 50°C. The degree of purity of the poly(methacrylic acid), as determined by acid titration, is 95%. Its viscosity number at 25°C. in methanol is 1.25, denoting a molecular weight of about 100,000.[13]

ε-Acetylaminocaproic acid was prepared from *N*-acetylcaprolactam by the method described by Offe.[14]

ε-Chlorocaproic acid was prepared by treatment of 1,6-hexanediol with hydrochloric acid[15] and oxidation of the resulting 6-chlorohexanol-1 with chromium trioxide.[16]

It should, however, be noted that all the polymers obtained after crossed Kolbe synthesis with ε-chlorocaproic acid are chlorine-free, probably on account of a substitution reaction of the primary aliphatic chlorine by a methoxy group.

The solvent used for electrolysis was methanol dried over iodine-activated magnesium.[17] Water must be avoided in these experiments, because its electrolysis produces oxygen with formation of hydroperoxides.

C. Purification of Polymers after Electrolysis

Poly(methacrylic Acid). The solubility properties of the polyacid vary considerably in the course of the electrolysis, due to the change in the chemical composition of the polymer. When the decarboxylation was less than 30%, the solution was acidified with dilute hydrochloric acid, the polymer precipitated in diethyl ether, filtered off, and dried at 50°C. for 48 hr. At higher degrees of decarboxylation, the polymer was precipitated in water, redissolved in dioxane, and freeze-dried.

Poly(methacrylic Acid) and Acetic Acid. At the end of electrolysis, the solution was acidified with hydrochloric acid and poured into water. The polymer precipitated and was dried *in vacuo* at 50°C.

Poly(methacrylic Acid) and ε-Acetylaminocaproic Acid. After electrolysis the solution was diluted with 400 ml. water. The Kolbe dimerization product of the acetaminocaproic acid [1,10-diacetaminodecane, AcNH-$(CH_2)_{10}$NHAc] precipitated, while the polymer remained soluble. After acidification with hydrochloric acid and addition of 50 ml. diethyl ether, the polymer precipitated; it was redissolved in methanol, reprecipitated in diethyl ether, washed with benzene, and dried *in vacuo*.

Poly(methacrylic Acid) and Cyanoacetic Acid. The polymers were purified by repeated precipitation in diethyl ether.

D. Polymer Analyses

The acid content was determined potentiometrically in an inert atmosphere or directly by titration in the presence of phenolphthalein.

γ-Lactone groups were opened by heating with an excess of 0.1*N* sodium hydroxide for 6 hr. Back-titration was carried out with 0.1*N* hydrochloric acid.

Methoxy groups were determined by microanalysis; their content corresponds to methyl ester units and ether units.

Methoxy ether groups are formed only when the acid content is very low; at this stage, the pH increases and the concentration of methoxy radicals from methanol becomes more appreciable.

The unsaturation of the polymers was determined by bromine addition in aqueous polymer solution. After addition of potassium iodide, the excess of bromine was back-titrated with sodium thiosulfate.[18]

Carbon, hydrogen, and oxygen elements were determined microanalytically (A. Bernhardt, Max Planck Institüt, Mulheim, Germany).

Nitrogen and chlorine determinations were carried out by the Kjeldahl and Schöniger-Volhardt methods, respectively.[19]

Carbon dioxide evolved during electrolysis was absorbed in titrated barium hydroxide.

In some experiments, methyl C^{14}-labeled acetic acid was used (1.1 mc./150 ml. HOAc); standard scintillation detectors were used to determine the C^{14} content by conventional techniques; dioxane was used as solvent for these experiments.

CONCLUSIONS

The electrolysis of methanol solutions of partially neutralized poly(methacrylic acid) causes an anodic decarboxylation, followed by the formation of unsaturated groups, intramolecular lactonization, and chain degradation. On alcoholysis with the solvent of the γ-lactone, alcohol and methyl ester groups are formed; methyl ether groups can also be produced at a high degree of conversion.

In the presence of acetic acid the chemical composition of the electrolyzed polymer is only slightly affected, as was shown with C^{14} acetic acid experiments. With ϵ-acetaminocaproic acid and with cyanoacetic acid the crossed Kolbe synthesis reactions become more important; it permits the grafting on the main chain of alkyl acetamino groups and of cyanomethylene $CNCH_2$ groups, respectively.

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Résumé

L'acide polyméthacrylique a été électrolysé à 20°C. en solution 0.2 molaire dans le méthanol anhydre dans un appareil de verre contenant deux électrodes de platine poli en forme de disques. La densité du courant était maintenue constante (300, 800 ou 1000 mA); avant électrolyse, l'acide était partiellement neutralisé afin d'augmenter la conductivité électrique. L'électrolyse est caractérisée par un dégagement d'anhydride carbonique à l'anode et une diminution du taux d'acide du polymère. Lorsque le degré de décarboxylation atteint environ 30%, il y a lactonisation intramoléculaire par interaction de groupes insaturés avec les groupes acides voisins. Les variations de composition chimique du polymère en fonction du temps ont été étudiées par détermination de groupes carboxyliques libres, des γ-lactones et des groupes insaturés (addition de brome). La quantité d'unités esters méthyliques formés par méthanolyse des lactones a été calculée par détermination des groupes oxyméthylés. À la fin de l'électrolyse il reste uniquement 5 à 6% de groupes carboxyliques, à coté de 35–40% de lactones et 30% de groupes esters; le reste est formé de groupes hydrocarbonés (partiellement insaturés). L'électrolyse a été effectuée en présence d'acides carboxyliques de bas poids moléculaire, acétique, ϵ-acétaminocaproïque et cyanoacétique. Le rapport de la concentration de ces acides par rapport à celle de l'acide polymérique a été varié sur une large échelle. Avec l'acide acétique la composition du polymère n'est que peu affectée et résulte du greffage de groupes méthyles latéraux, ainsi que l'ont démontré des expériences à l'acide acétique marqué au C^{14}. Avec les acides ϵ-acétaminocaproique et cyanoacétique, les réactions de synthèse croisée de Kolbe sont beaucoup plus importantes: 20–24% de groupes alcoyl-acétaminés et 15% de groupes cyanométhyléniques ont ainsi pu être greffés sur la chaîne principale. Au cours de ces expériences, on peut pratiquement éviter la dégradation de la chaîne polymérique.

Zusammenfassung

Polymethacrylsäure wurde bei 20°C in 0,2 molarer trockener Methanollösung in einer mit zwei polierten Platinscheibenelektroden versehenen Glasapparatur elektrolysiert; die Stromdichte wurde konstant gehalten (300, 800 oder 1000 Milliampères). Vor der Elektrolyse wurde die Säure zur Erhöhung der Leitfähigkeit teilweise neutralisiert. Die Elektrolyse wird durch eine Kohlendioxydentwicklung an der Anode charakterisiert, während der Säuregehalt des Polymeren abnimmt. Bei einem Decarboxylierungsgrad von etwa 30% tritt durch Reaktion ungesättigter Gruppen mit benachbarten Säuregruppen intramolekulare Laktonbildung auf. Die Änderung der chemischen Zusammentsetzung des Polymeren wurde in Abhängigkeit von der Zeit durch Bestimmung der freien Carbonsäuregruppen, des γ-Laktons und der ungesättigten Gruppen (Bromaddition) verfolgt. Die Menge der durch Methanolyse des Laktons gebildeten Methylestergruppen wurde aus Methoxylbestimmungen berechnet. Am Ende der Elektrolyse sind nur 5 bis 6% freie Carboxylgruppen vorhanden, 35–40% Lakton und 30% Estergruppen; den Rest bildet in der Hauptsache eine Kohlenwasserstoffreaktion (zum Teil ungesättigt). Die Elektrolyse wurde auch in Gegenwart niedermolekularer Carbonsäuren, Essigsäure, ϵ-Acetaminocapronsäure und Cyanessigsäure ausgeführt. Das Konzentrationsverhältnis dieser Säuren zu dem der polymeren Säure wurde in einem weiten Bereich variiert. Wie durch Anwendung C^{14}-markierter Essigsäure gezeigt wurde, tritt mit Essigsäure nur eine schwache Beeinflussung der chemischen Zusammensetzung der Polymeren durch Aufpfropfung von Methylseitengruppen ein. Mit ϵ-Acetaminocapronsäure und Cyanessigsäure hat die gekreuzte Kolbereaktion eine viel grössere Bedeutung; 20 bis 24% Alkylacetaminoseitengruppen und 15% Cyanmethylengruppen wurden nach dieser Methode auf die Hauptkette aufgepfropft. Bei diesen Versuchen kann Kettenabbau praktisch ausgeschaltet werden.

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Preparation and Structure of Some Carbon Monoxide–Formaldehyde Copolymers

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Synopsis

Polymers obtained by reaction between formaldehyde and carbon monoxide under anhydrous conditions in presence of Lewis acids are described. Mass balance and elemental analysis show that the CO/CH_2O molar ratio in the polymers can reach unity as maximum value. Ammonolysis of the products (A) having a CO/CH_2O molar ratio less than 1 gives glycolamide, diglycolamide, and hexamethylenetetramine. Ammonolysis of the products (B) having a CO/CH_2O molar ratio about 1 gives glycolamide, diglycolamide, and traces of hexamethylenetetramine. These results show that the chain of polymer A contains the structural units: $—CO—CH_2—O—$, $—CO—CH_2—O—CH_2—CO—O—$, and $—CH_2—O—$, while polymer B contains almost exclusively the structural units $—CO—CH_2—O—$ and $—CO—CH_2—O—CH_2—CO—O—$. Infrared spectra of the products are in good agreement with these results and show the presence of ester, ether, and acetal bands in the main chain of the polymers. The polymer structure is described, and a reaction mechanism is proposed.

INTRODUCTION

Carbon monoxide can react by radical or ionic mechanisms. There are few examples of carbon monoxide reacting as a radical; one of these is the free radical-initiated copolymerization of ethylene and carbon monoxide.[1] On the other hand, the ionic character[2] of carbon monoxide and its reactivity toward electrophilic and nucleophilic reagents makes possible many organic syntheses.

Carbon monoxide reacts with aqueous formaldehyde, yielding glycolic acid.[3] It is possible to obtain a polymer either by direct polycondensation[4] of this compound or by heating its cyclic dimer in the presence of catalysts.[5] The polyglycolic acid so obtained is a product with a melting point of about 223°C. which is insoluble in the common solvents and useful for the preparation of films and fibers.

We have already reported some results on the copolymerization of carbon monoxide with anhydrous formaldehyde.[6] In this paper we describe the conditions of this reaction and the structure of the copolymers obtained; a possible mechanism of copolymerization is suggested.

EXPERIMENTAL

Materials

The carbon monoxide used had a purity grade of 99%, the main impurities being O_2 and N_2. Trioxane was purified by crystallization from petroleum ether and dried over $CaCl_2$; the residual moisture was less than 0.01% (by the Fisher method).

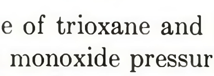
Boron trifluoride (Fluka-purum) was used without further purification; boron trifluoride etherate (Fluka-pract.) was purified by distillation under reduced pressure (20 mm. Hg). The boron trifluoride–methyl formate complex was prepared by bubbling boron trifluoride into a 10% solution of methyl formate in petroleum ether and filtering under nitrogen. Titanium tetrachloride (Fluka-purum), titanium trichloride (Stauffer-HA), tin tetrachloride (BDH, laboratory reagent), iron trichloride (BDH, laboratory reagent), and vanadium trichloride (Fluka-purum) were used without further purification.

All other materials used were reagent grade.

Polymerization

The reaction was carried out in an autoclave under a carbon monoxide pressure of about 200 kg./cm.^{2}; trioxane was used as a source of formaldehyde in the presence of a Lewis acid as catalyst. Boron trifluoride or its complexes with oxygenated compounds (especially diethyl ether and methyl formate) are very active, but $TiCl_4$, $SnCl_4$, $FeCl_3$, VCl_3, and $TiCl_3$ also give good results. The experiments were generally carried out without solvents. Saturated hydrocarbons may be used as reaction media; aromatic hydrocarbons can be sources of side products and polar solvents prevent copolymerization or give lower molecular weights. If the copolymerization is carried out at 110°C., the carbon monoxide adsorption is very fast during the first hour of reaction, but after 3 hr. the pressure drop is quite small. On raising the temperature to 180°C. a further carbon monoxide adsorption is observed.

The product (copolymer A) recovered at 110°C. is a yellow, high viscosity liquid which contains in suspension small amounts of polyoxymethylene. It is soluble in dioxane; when heated at 100°C. in vacuum it loses small quantities of formaldehyde and glycolic acid derivatives like methylene glycolate:



$$\underbrace{\mathrm{CH_2{-}CO{-}O{-}CH_2}}_{\mathrm{O}}$$

For example, with the use of trioxane and boron trifluoride in a molar ratio of 400 under a carbon monoxide pressure of about 300 kg./cm.^{2}, we have obtained a product whose average composition, calculated from the mass balance, was 1.4 moles formaldehyde/mole carbon monoxide.

The product (copolymer B) recovered after further reaction of copolymer A with carbon monoxide at 180°C. is a brown mass containing carbon monoxide and formaldehyde in a molar ratio of about 1. Such a product, after extraction with boiling acetone, leaves a residue (66%) insoluble in common solvents but soluble in dimethylformamide and dimethyl sulfoxide and having a melting point of about 140°C.

ANAL. Calc. for $(C_2H_2O_2)_n$: C, 41.39%; H, 3.47%. Found: C, 41.4%; H, 3.6%.

Infrared Spectra

A Perkin-Elmer 21 double-beam infrared spectrophotometer with rock-salt optics was used to record the spectra as dispersion in pressed KBr pellets or as thin films between NaCl plates. The concentration of the polymers and amides in the 0.5 mm. thick KBr pellets ranged between 0.4 and 0.6%.

X-Ray Diffraction Patterns

X-rays were recorded with a Philips diffraction unit having a Geiger-Muller counter, using Ni-filtered CuKα radiation, 36 kv. and 18 ma., $\omega = 1°/\text{min.}$

Molecular Weight

Product A was purified by precipitation in methanol at −70°C. from a solution in dimethyl sulfoxide. The precipitate was collected and washed with methanol in a Buchner funnel kept cold with Dry Ice; all these operations were carried out in a dry box. The precipitate was dried under high vacuum at −30°C. and then at −10°C.

Product B was purified by precipitation in carbon tetrachloride from a solution in dimethyl sulfoxide decolorized with active charcoal.

Cryoscopic measurements of molecular weight in dioxane for polymer A and in dimethyl sulfoxide for polymer B gave $\bar{M}_n$ values in the range of 500–2000.

Saponification

The product treated with an excess of boiling 1N NaOH for 1 hr. gives a solution which after acidification and concentration under vacuum is extracted with diethyl ether. The product recovered from the ether solution after crystallization from acetone has a melting point of 76–78°C. and an equivalent acidimetric weight of 75.5. (Glycolic acid: m.p. 80°C.; equivalent acidimetric weight 76.)

Ammonolysis

The reaction was carried out with anhydrous liquid ammonia or with an alcoholic solution of ammonia. In the latter case gaseous ammonia was bubbled through a suspension of the polymer in absolute ethyl alcohol at a temperature of 0–10°C. for 8 hr. After this time the mixture was allowed to react for 15 hr. at room temperature, then ethyl alcohol was evaporated under vacuum. The residue was treated twice with boiling chloroform:

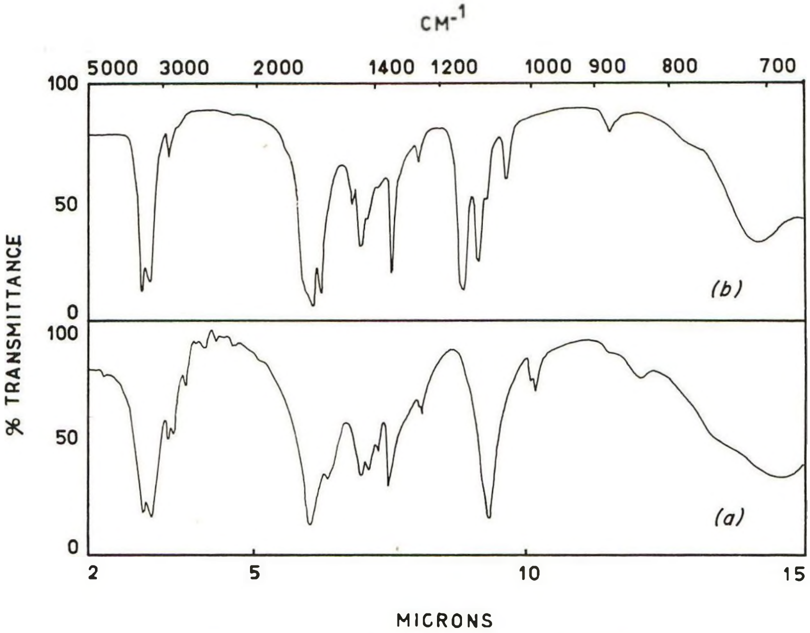


Fig. 1. Infrared spectra of (*a*) glycolamide and (*b*) diglycolamide.

the product from the chloroform extraction, after further recrystallization from absolute ethyl alcohol, decomposed without melting when heated above 200°C. The infrared analysis shows the spectrum of hexamethylenetetramine.

Anal. Calc. for $C_6H_{12}N_4$: C, 51.4%; H, 8.63%; N, 39.97%. Found: C, 51.6%; H, 8.6%; N, 40.2%.

The chloroform-insoluble fraction was treated with boiling ethanol. Two products were obtained by fractional crystallization.

The first one melts at 180°C. (diglycolamide m.p. 180°C.) and shows the same infrared spectrum as a diglycolamide sample prepared by reacting diethyldiglycolate and ammonia in absolute ethyl alcohol. In this spectrum (Fig. 1*b*) amide bands are at 3375, 3205, near 1650, and 1610 cm.$^{-1}$, and the C—O ether band is at 1135 cm.$^{-1}$.

Anal. Calc. for $C_4H_8N_2O_3$: C, 36.35%; H, 6.1%; N, 21.20%. Found: C, 36.1%; H, 5.8%; N, 21.6%.

The second product melts at 115–116°C. (glycolamide m.p. 120°C.) and shows the same infrared spectrum as a glycolamide sample prepared by reacting in absolute ethylalcohol ethylglycolate and ammonia. In this spectrum (Fig. 1*a*) amide bands are at 3370, 3200, near 1665, and 1580 cm.$^{-1}$; the C—OH band is at 1078 cm.$^{-1}$. The stretching frequency of bonded —O—H, near 3300 cm.$^{-1}$, is obscured by the two peaks of amide.

Anal. Calc. for $C_2H_5NO_2$: C, 32.0%; H, 6.71%; N, 18.68%. Found: C, 32.4%; H, 6.9%; N, 18.8%.

RESULTS

Ammonolysis of copolymer A gives hexamethylenetetramine, glycolamide, and diglycolamide. Ammonolysis of copolymer B gives glycolamide, diglycolamide, and traces of hexamethylenetetramine. Relating the compounds obtained by ammonolysis to the functional groups which can be present in the chain of the copolymers indicates that the formation of amides can result only from anhydride or ester groups.

In the infrared spectra of the copolymers[6] (Fig. 2*A* and 2*B*) the 1750 cm.$^{-1}$ band is characteristic of the stretching vibration of C═O ester groups and the broad band at about 1210 cm.$^{-1}$ is characteristic of stretching of C—O ester groups, but no bands characteristic of the anhydride function are evident. The hydroxy groups formed by ammonolysis confirm the presence of ester groups in the chain of the copolymers.

The infrared spectrum of product B is similar to that of polyglycolic acid (Fig. 2*C*), the most important difference being the presence of a weak band at 1140 cm.$^{-1}$, assignable to the stretching vibration of C—O ether group and confirming the presence in the chain of diglycolic units. In the spectrum of product A (Fig. 2*A*) the 1135 cm.$^{-1}$ band is assignable to ν(CO) of diglycolic ether groups. The formation of hexamethylenetetramine by ammonolysis is due to acetal units which give some contribution in the 1080–930 cm.$^{-1}$ region.

To confirm the assignments of the main bands in infrared spectra previously discussed of copolymers A and B, some model compounds have been prepared. Ethyl glycolate and diethyl diglycolate are among the simplest models, resembling in spectral features product B. Ethyl glycolate (Fig. 2*D*) has ester bands at 1740, 1220, and 1024 cm.$^{-1}$ and C—O—H bands at 3435 and 1097 cm.$^{-1}$. The ν(OH) frequency shifts to 3545 cm.$^{-1}$ on dilution of the product in CCl_4 without the appearance of any band due to free —OH in the region 3610 cm.$^{-1}$. This shows the existence of an intramolecular hydrogen bond and accounts for a slight ν(C═O) lowering. Diethyl diglycolate (Fig. 2*E*) has ester bands at 1748, 1212, and 1028 cm.$^{-1}$ and a C—O ether band at 1146 cm.$^{-1}$. Below 1000 cm.$^{-1}$ both products adsorb weakly. These spectra closely support the appearance of ester bands near 1750 and 1210 cm.$^{-1}$ in the copolymers.

We have also studied the infrared spectra of $CH_3COOCH_2OCOCH_3$, (Fig. 2*F*), $CH_3CO(OCH_2)_2OCOCH_3$ (Fig. 2*G*), and $CH_3CO(OCH_2)_3OCOCH_3$ (Fig. 2*H*) prepared according to Tomiska and Spausta,[7] in order to observe spectral feature corresponding to short acetal sequences. $CH_3COOCH_2OCOCH_3$ contains two acyloxy groups bonded to the same carbon; the other two compounds contain adjacent acyloxy and acetal groups. The infrared spectrum of $CH_3COOCH_2OCOCH_3$ (Fig. 2*F*) has ν(C═O) at 1760 cm.$^{-1}$ and other two strong bands at 1199 and 1016 cm.$^{-1}$; these three frequencies correspond to those of an ester but appear largely perturbed if compared to bands of a simple acetate. The first two are quite changed in value, the last one, corresponding to one of two modes ν(C—O—C), is strongly enhanced in intensity. The infrared spectra of the higher

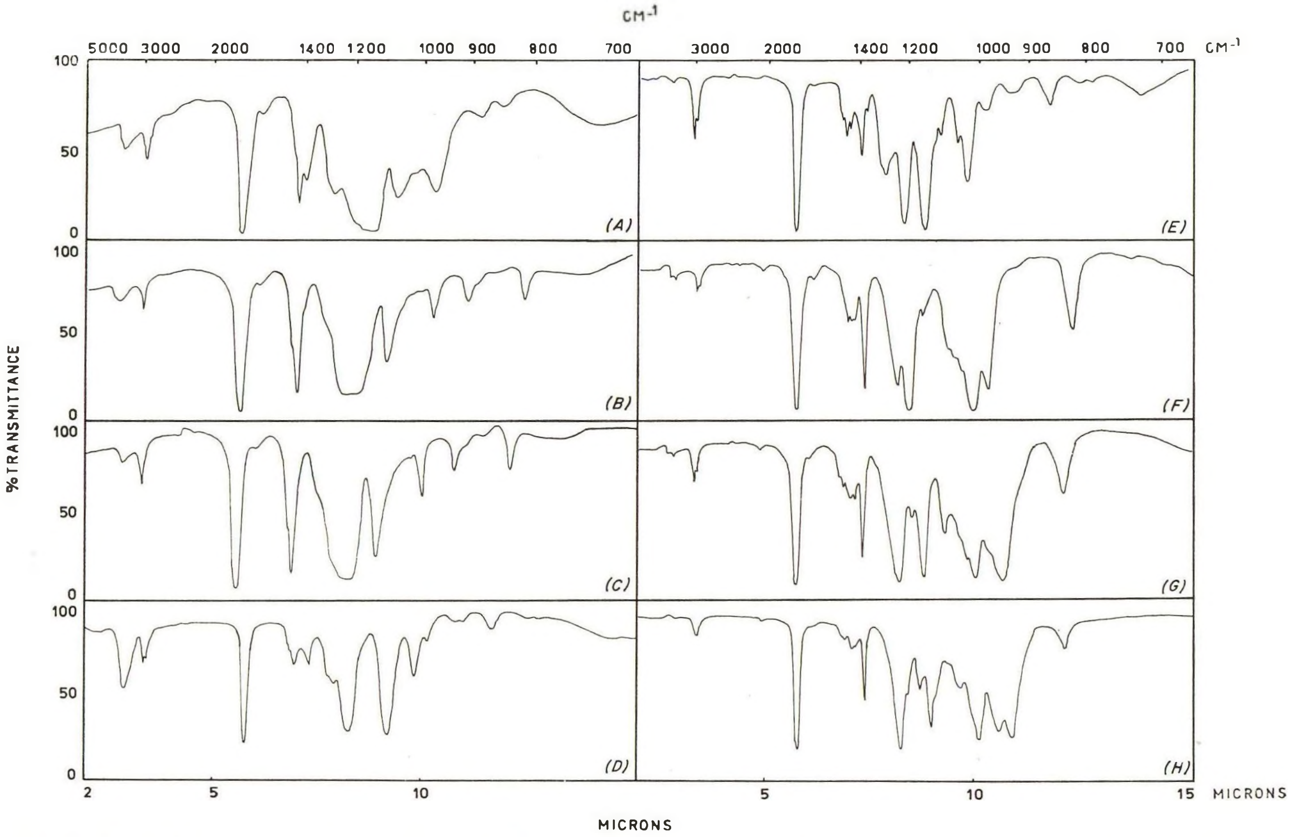


Fig. 2. Infrared spectra of (*A*) a copolymer having a molar ratio CO/CH_2O < 1; (*B*) a copolymer having a molar ratio CO/CH_2O about 1; (*C*) polyglycolic acid; (*D*) ethyl glycolate; (*E*) diethyldiglycolate; and the model compounds: (*F*) CH_3-$COOCH_2OCOCH_3$, (*G*), $CH_3CO(OCH_2)_2OCOCH_3$, and (*H*) $CH_3CO(OCH_2)_3OCOCH_3$.

analogs (Fig. 2*G* and 2*H*) have ester bands at 1754, 1232, 1008 cm.$^{-1}$ and at 1754, 1232, 1005 cm.$^{-1}$, respectively. Strong bands appear in the spectra at 947 cm.$^{-1}$ for $CH_3CO(OCH_2)_2OCOCH_3$ and at 958, 930 cm.$^{-1}$ for $CH_3CO(OCH_2)_3OCOCH_3$. These are assignable to stretching vibration of acetal units. These frequencies are close to those of polyacetal structures rather than to those of simple acetals. A 1148 cm.$^{-1}$ band in the spectrum of $CH_3CO(OCH_2)_2OCOCH_3$ and a 1132 cm.$^{-1}$ band in the spectrum of $CH_3CO(OCH_2)_3OCOCH_3$ may be also assignable to stretching vibration of acetal units, but they are less distinctive.

These results confirm the assignments in the spectra of products A and B. Particularly the presence of diglycolic units is shown by the 1140 cm.$^{-1}$ frequency. The presence of acetal units is shown by the adsorption in 950 cm.$^{-1}$ region, the shape depending on the length and the distribution of acetal chain.

In the chain of the copolymer A are present the structural units: (I) $—CO—CH_2—O—$; (II) $—CO—CH_2—O—CH_2—CO—O—$; (III) $—CH_2—O—$, and in the chain of the copolymer B almost exclusively the structural units I and II. From the ratio of ammonolysis products it is possible to estimate that the contribution of units II to the total number of units present in the copolymer B is about 5%.

The X-ray diffraction patterns of product B (Fig. 3) have lattice parameters and diffraction lines intensity quite similar to those of polyglycolic acid. The two principal diffraction peaks are at $2\theta = 22°.25$ and at $2\theta = 29.10$ corresponding to lattice distance 3.99 and 3.07 A. The maximum of amorphous band is at $2\theta = 21°$.

Although the elemental analysis, the infrared spectra, and x-ray diffraction patterns are quite similar to those of polyglycolic acid prepared from pure glycolic acid, the melting point of product B is about 80°C. lower.

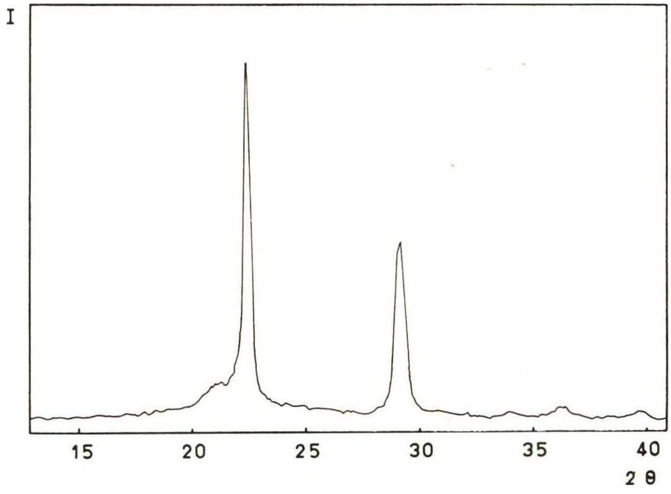


Fig. 3. X-ray diffraction pattern of a copolymer having a molar ratio CO/CH_2O about 1.

DISCUSSION

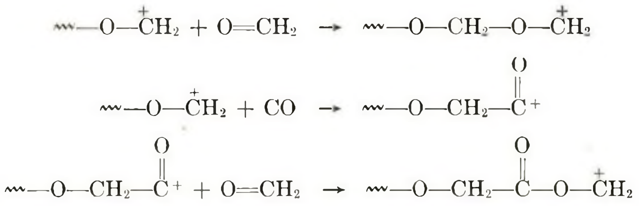
Many authors have studied the polymerization of trioxane and proved that the polyoxymethylene chain formed is in equilibrium with formaldehyde; our experiments were carried out under such conditions that the polyoxymethylene acts mainly as a formaldehyde source so that the latter is the compound that actually reacts with the carbon monoxide.

The reaction between formaldehyde and carbon monoxide in water is well known and industrially employed for the synthesis of glycolic acid.[3] In the absence of a nucleophilic solvent, a chain reaction leading to the formation of a polymer is established.

The characteristics of the initiator and the monomers suggest a cationic mechanism of polymerization.

Carbon monoxide is expected to react with the carbonium ions, in competition with formaldehyde, employing the lone pair of electrons on the carbon atom, since these have largely *p* character and lower ionization potential than the oxygen lone pair which has largely *s* character and is chemically unavailable as those of nitrogen in the N_2 molecule.[2]

The product containing the highest percentage of carbon monoxide we have obtained is copolymer B, in which the carbon monoxide/formaldehyde molar ratio is about 1. Such a result, according to infrared spectra, where no band of α-polycarbonilic sequences is evident, shows that the growing chain, after addition of one carbon monoxide molecule, tends to react with one of formaldehyde:

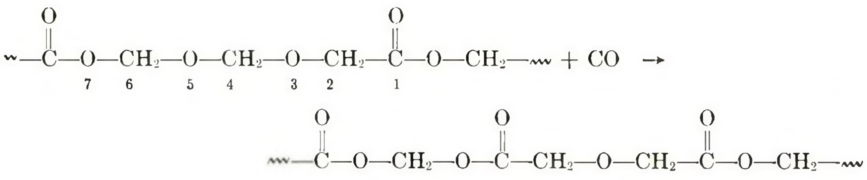


$$\sim O-\overset{+}{C}H_2 + O=CH_2 \rightarrow \sim O-CH_2-O-\overset{+}{C}H_2$$

$$\sim O-\overset{+}{C}H_2 + CO \rightarrow \sim O-CH_2-\overset{\overset{O}{\|}}{C}{}^{+}$$

$$\sim O-CH_2-\overset{\overset{O}{\|}}{C}{}^{+} + O=CH_2 \rightarrow \sim O-CH_2-\overset{\overset{O}{\|}}{C}-O-\overset{+}{C}H_2$$

However, such reactions do not explain the presence on the polymer chains of structure II which might be formed, like dimethyl diglycolate from the methyl ester of (methoxymethoxy)acetic acid in similar conditions,[8] by reaction of insertion



$$\sim\overset{\overset{O}{\|}}{C}-\underset{7}{O}-\underset{6}{CH_2}-\underset{5}{O}-\underset{4}{CH_2}-\underset{3}{O}-\underset{2}{CH_2}-\underset{1}{\overset{\overset{O}{\|}}{C}}-O-CH_2-\sim + CO \rightarrow$$

$$\sim\overset{\overset{O}{\|}}{C}-O-CH_2-O-\overset{\overset{O}{\|}}{C}-CH_2-O-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-\sim$$

The complexation of boron trifluoride with one of the oxygen atoms in the chain results in the relaxation or scission of a carbon-oxygen bond and formation of a carbonium ion that can react with carbon monoxide.

According to this suggested mechanism, diglycolic units are obtained only through catalyst addition on the oxygen atom in position 5 and formation of a cation on position 4 while the other reaction paths lead to the formation of glycolic units or of different kinds of groups that have not been detected by infrared analysis or ammonolysis.

The polymers are easily hydrolyzable, and the determinations of hydroxyl and carboxyl endgroups did not give reproducible results. The total methoxyl groups analysis (according to Zeisel method) carried out on a sample of $\bar{M}_n = 1500$ gave 1 methoxyl group in 6000 g.; this suggests that methoxyl groups are not likely to be the main type of terminal groups.

Polymer B is similar to the polyglycolic acid, but its melting point is about 80°C. lower; we suggest that this may be related to the lower regularity of the structure due to diglycolic units.

The authors are pleased to record their thanks to Mrs. Ornella Santini, to Mr. Carmine Garbuglio, and to Mr. Angelo Mula of this laboratory for their invaluable experimental assistance.

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Résumé

On décrit des polymères obtenus par réaction en milieu anhydre du formaldéhyde et de l'oxyde de carbone en présence des acides de Lewis. Le bilan pondéral et l'analyse élémentaire démontre que le rapport molaire CO/CH_2O dans les polymères peut atteindre l'unité comme valeur maximale. L'ammonolyse des produits possédant un rapport molaire $CO/CH_2O < 1$ (A) donne du polyamide, du diglycolamide, et de l'hexaméthylènetétramine. L'ammonolyse des produits possédant un rapport molaire CO/CH_2O environ égal à 1 (B) donne du glycolamide, du diglycolamide et des traces d'hexaméthylènetétramine. Ces résultats montrent que la chaîne du polymère (A) contient les unités structurelles suivantes: $—CO—CH_2—O—$, $—CO—CH_2—O—CH_2—CH—O—$, $—CH_2—O—$, et que le polymère (B) contient presque exclusivement les unités structurelles $—CO—CH_2—O—$ et $—CO—CH_2—O—CH_2—CO—O—$. Les spectres infrarouges de ces produits sont en bon accord avec ces résultats et montrent la présence de bandes esters, éthers et acétaliques dans la chaîne principale des polymères. La structure du polymère est décrite et on propose un mécanisme de réaction.

Zusammenfassung

Die durch Reaktion von Formaldehyd mit Kohlenmonoxyd unter wasserfreien Bedingungen in Gegenwart von Lewissäuren erhaltenen Polymeren werden beschrieben.

Massenbilanz und Elementaranalyse zeigen, dass das Molverhältnis CO/CH_2O in den Polymeren als Höchstwert 1 erreichen kann. Ammonolyse der Produkte mit einem Molverhältnis $CO/CH_2O < 1$ (A) liefert Glycolamid, Diglycolamid und Hexamethylentetramin. Ammonolyse der Produkte mit einem Molverhältnis CO/CH_2O von etwa 1 (B) liefert Glycolamid, Diglycolamid und Spuren von Hexamethylentetramin. Diese Ergebnisse zeigen, dass die Kette des Polymeren (A) die Strukturelemente: $—CO—CH_2—O—$, $—CO—CH_2—O—CH_2—CO—O—$, $—CH_2—O—$, und das Polymere (B) fast ausschliesslich die Strukturelemente $—CO—CH_2—O—$ und $—CO—CH_2—O—CH_2—CO—O—$ enthält. Die Infrarotspektren der Produkte stimmen mit diesen Ergebnissen gut überein und lassen die Anwesenheit von Ester-, Äther- und Acetalbanden in der Polymerhauptkette erkennen. Die Polymerstruktur wird beschrieben und ein Reaktionsmechanismus vorgeschlagen.

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Kishi Lag Times for O_2 Adsorption onto Irradiated Poly(bisphenol-A Carbonate) and Poly(methyl Methacrylate)

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Synopsis

Re-examination of some data which were originally taken to determine diffusion coefficients and their variation with applied stress in electron irradiated poly(bisphenol-A carbonate) and poly(methyl methacrylate) has verified the existence of Kishi induction periods t_i for the initial stages of O_2 sorption by these polymers. The data conform to the relation $t_i = t_i^0 e^{E/RT} e^{-p/p_1}$. Some new gas sorption data for poly(bisphenol-A carbonate) by Norton are utilized in conjunction with data and equations from our previous paper to estimate initial concentrations of the free radicals associated with the visually sharp diffusion boundary which was the major topic of our previous paper. The value G[oxygen-bleached color-centers/h.e.v.] obtained for these radicals is compared with recent viscometric determinations by Golden and Hazell.

Introduction

In previous papers we have described experiments based on the movement of a visually sharp boundary which occurs when radical-scavenging gases such as O_2 diffuse into polymers previously exposed to high energy irradiation.[1,2] A sharp border occurs when the color center concentration (produced by irradiation) is sufficiently large compared to the normal equilibrium concentration of scavenger molecules in the polymer so that the latter are trapped before they can move very far inward. This results approximately in a step-function distribution of the remaining color centers.

Recently several interesting papers by Kishi[3] which deal with O_2 diffusion in γ-irradiated PMMA and PMMA-AN have come to our attention. Kishi reports that there is a time interval (induction period) between the instant of initial exposure of a sample to O_2 and the moment when the colored boundary first appears. This interval t_i decreases with increasing temperature and/or pressure. Kishi has attributed t_i to an adsorption process and was able to fit his PMMA data with an equation of the form

$$t_i = t_i^0 e^{E/RT} e^{-p/p_1} \tag{1}$$

The values reported for the parameters ($t_i^0 = 9.7 \times 10^{11}$ sec., $E = 9.4$ kcal./mole, and $p_1 = 2.96$ atm.) are of such magnitude as to make the phenomenon not only of considerable academic interest but perhaps of significance in such matters as oxidative degradation, solvent crazing, nuclear fission detection, etc.

In some of our earliest experiments, initial transient effects were observed but these were found to be at least partially due to errors in optical alignment, lack of sufficiently sharp edges on some samples, and temperature lags or overshoots of the sample with respect to that of the observation cell when the gas was admitted. Since the chief interest at that time was the determination of the diffusion coefficient D, the initial complications were usually avoided by choosing an arbitrary reference point from which the rate of penetration of the colored border was measured. In a few cases the data were recorded in such a way that it has been possible to estimate t_i (from the intercepts on penetration distance ξ versus $t^{1/2}$ plots). Although the values thus obtained for t_i leave something to be desired both in accuracy and in the range of variables considered, it is felt that the general importance of the phenomenon outweighs these limitations. As a second purpose, some new calculations of the initial free radical concentration n_0 are reported, based on solubility and diffusion data for O_2 in Lexan resin obtained by Norton[4] since the publication of the earlier paper.[1] [Lexan is the registered trademark of the General Electric Company for its commercial grades of poly(bisphenol-A carbonate).]

Estimation of the Induction Times

Figure 1 shows the results for O_2, at a pressure of 159 Torr, being adsorbed onto PMMA. The presence of the $e^{E/RT}$ term in eq. (1) appears to be borne out, with $E \approx 17$ kcal./mole. This is somewhat higher than the value for Kishi's samples. This makes one suspect that polymer fabrica-

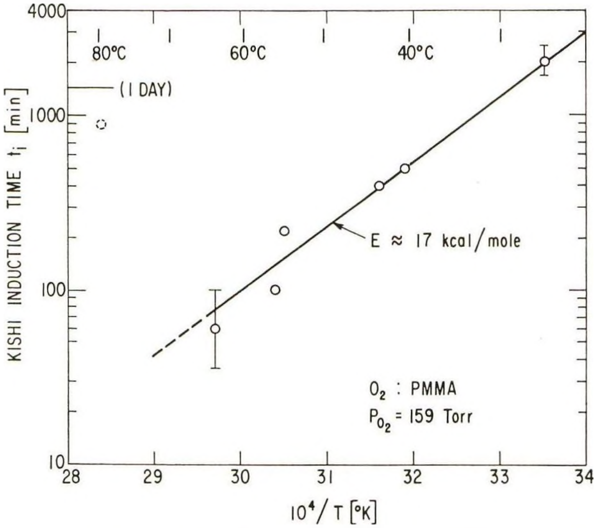


Fig. 1. Kishi induction time for O_2 adsorption onto PMMA vs. reciprocal temperature. The dose was 2.5 Mrad of 1.5 M.e.v. (peak) electrons from a G.E. resonant transformer. The samples were in air, so the partial pressure of O_2 was 159 Torr.

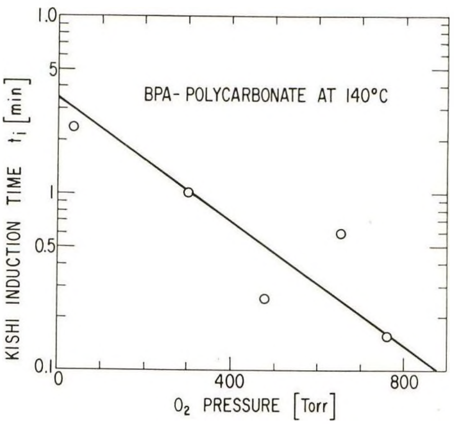


Fig. 2. Kishi time for O_2 adsorption onto 1.5 M.e.v.-irradiated Lexan polycarbonate resin as a function of O_2 pressure. The dose was 17 Mrad.

tion, additives, type of irradiation, etc., might have considerable influence on t_i. One also suspects, from the magnitude of t_i (over a day at room temperature) that something other than simple adsorption is involved. For example, if the polymer surface had a 10 μ thick layer of material with a diffusion coefficient of about 10^{-10} cm.^{2}/sec., then, according to Dayne's[5] "time lag" formula

$$\tau \approx b^2/6D \approx 0.5 \text{ hr.}$$

A layer 30 μ thick would cause a time lag τ of about 5 hr. and thus could account for an appreciable part of the induction period. Since some accumulation of impurities in the surface layer would not be unexpected and since the radiation dose might lead to crosslinking, etc. of this surface material, it seems that a tough surface layer might be possible. Along these same lines of reasoning, the surface layer might have a higher concentration of centers capable of reacting with and retaining oxygen than the interior.

Another line of approach lies in a consideration of the boundary conditions to be imposed on the diffusion equation

$$\partial C/\partial t = D\nabla^2 C + \sum \text{(trapping terms)}.$$

The conventional boundary conditions are $C(0,t) = C_s$ and $C(x,0) = 0$. In the actual problem at hand, $C(0,t)$ is not a constant; it is a function which increases from zero and approaches C_s asymptotically. Also, a finite surface layer ζ may be involved in the initial sorption process. With this sort of model, it appears that t_i is not necessarily a monolayer formation time but might be the time to achieve a concentration approaching C_s in the rather nebulously defined surface zone $\Delta x = \zeta$.

In Figure 2 the results for O_2 adsorption onto Lexan resin at 140°C. are shown. Kishi's hypothesis that $t_i \propto e^{-p/p_0}$ fits, with $p_0 \approx 250$ Torr. It is of interest that t_i has a finite value at $p = 0$. For the polycarbonate data, there were a number of anomalous cases in which negative values of $t_i^{1/2}$

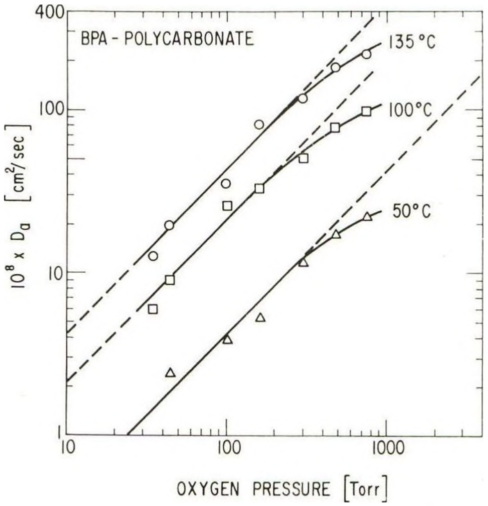


Fig. 3. Apparent diffusion coefficient D_a vs. O_2 pressure for 1.5 M.e.v.-electron irradiated Lexan. Data points are from Barker.[1] Note that the curvature is predicted by Eqs. (3) and (4) due to the presence of ϵ.

were indicated. This may have been the result of brief pre-exposure to oxygen at some time between irradiation and placing these samples in the observation cells.

Discussion of the Color Center Concentration

In eq. (11) of the previous paper,[1] the diffusion coefficient D was shown to be given by

$$D \approx \xi^2 \left[2 \int_0^t (n_0 C_s^{-1} + \epsilon)^{-1} dt \right]^{-1} \qquad (2)$$

where ξ is the penetration of the colored border at time t, n_0 is the concentration of free radicals (color centers) prior to scavenger diffusion, C_s is the surface (or saturation) concentration of scavenger molecules in the polymer and ϵ is a parameter that replaces the value $^1/_2$ which resulted from approximating the area between two C versus x curves by a triangle.[1] Empirically, the value $\epsilon = 0.32$ fits better than $\epsilon = {}^1/_2$. When n_0/C_s is constant, the expression $D \approx D_a\phi$ results, where $D_a = \xi^2/2t$ and $\phi = n_0 C_s^{-1} + \epsilon$. From eq. (2) the general form of the function v (still an approximation, of course) is

$$\phi = t \Big/ \int_0^t (n_0 C_s^{-1} + \epsilon)^{-1} dt \qquad (3)$$

which is obtained by requiring that

$$D = D_a \varphi$$

and

$$D_a = \xi^2/2t \tag{4}$$

Since $C_s = \sigma p$, where σ is the solubility coefficient, eqs. (3) and (4) predict, in the case of constant n_0 (i.e., color centers removed only by scavenger trapping and not by thermal bleaching, crosslinking, etc.), that the slope log D_a versus log p should have a value of unity at low pressures ($p \ll n_0/\sigma\epsilon$) but should decrease at larger p. This behavior was observed and is shown in Figure 3. The approximate effect of thermal bleaching, etc. may be predicted as follows. Assume that ϵ may be neglected and that n_0 of eq. (2) is given by

$$n_0 \approx N_0 e^{-Kt} \tag{5}$$

which corresponds to a random assortment of decay modes. Then the integral of eq. (2) may be written

$$I(t,\epsilon) = \int_0^t (n_0 C_s^{-1} + \epsilon)^{-1} dt \xrightarrow[\epsilon \to 0]{} (C_s/N_0) \int_0^t e^{Kt} dt$$

$$I(t,0) = C_s(e^{Kt} - 1)/N_0 K \tag{6}$$

On expansion of e^{Kt} we obtain

$$I(t,0) \approx (C_s t/N_0)(1 + Kt/2 + \ldots) \tag{7}$$

When eq. (7) is combined with eqs. (3) and (4), we get

$$D_a \approx (DC_s/N_0)(1 + Kt/2 + \ldots) \tag{8}$$

which implies that the apparent diffusion coefficient D_a should increase with time. When $Kt/2 \ll 1$, the change in D_a will be negligible and we can estimate $n_0 \approx N_0$ from the low pressure data (D_a versus p), by using

$$n_0 \approx \sigma p D/D_a \tag{9}$$

TABLE I
Estimate of Free Radical Concentrations in 1.5 M.e.v. Electron-Irradiated Polycarbonate

T, °C.	$\sigma \times 10^{-18}$ mol./cm.^{3} atm.[a]	$D \times 10^{18}$, cm.^{2}/sec.	D_a ($= \xi^2/2t$) $\times 10^{18}$, cm.^{2}/sec.[b]	D/D_a	$C_s(= \sigma p)$ $\times 10^{-18}$, mol./cm.^{3}	$n_0 \times 10^{-18}$, radicals*/cm.^{3} [c,d]
25	13.7	2.1	(1.3)[e]	(1.8)[e]	1.81	(3.3)[e]
50	9.4	5.4	4.5	1.2	1.24	1.5
100	5.6	28	22	1.3	0.74	1.0
135	8.5	70	45	1.5	1.12	1.7

[a] Solubility and diffusion data of Norton[4] for unirradiated polycarbonate.

[b] Data of Barker[1] for irradiated polycarbonate, p = 100 Torr = 0.132 atm.

[c] Computed with eq. (9); only the colored radicals removed by the advancing O_2 are determined.

[d] R = 17 Mrad.

[e] Values in parenthesis are less accurate.

Such estimates are given in Table I. Since the irradiation dose and conditions were the same for all four samples we should obtain the same value of n_0 for them. Neglecting the values in parentheses, which are less accurate, we have $\langle n_0 \rangle = (1.4 \pm 0.3)10^{18}$ radicals*/cm.^{3}. The asterisk (*) is to signify only those radicals which contribute to the color and which are removed by the advancing O_2; however, the presence of other radicals which trap oxygen but do not manifest a noticeable color change would cause a reduction in the observed rate of penetration (i.e., decreased D_a) and act somewhat like an increased solubility σ. In fact there may be a real increase in σ in the irradiated material since increased void space may occur. If so, Norton's values for σ in Table I should be augmented by the quantity

$$\int_0^R (\partial\sigma/\partial R)_T dR$$

where R is the radiation dose. Omission of this sort of correction in the calculation of the last column of Table I may explain the spread of values. It may also help explain why, in the previous study,[1] so little dependence of D_a on R was observed.

The radiation G value corresponding to $\langle n_0 \rangle$ is

$$G \approx 1.4 \times 10^{18} \text{ cm.}^{-3}/(6.2 \times 10^{11} \text{ h.e.v. rad}^{-1} \text{ g.}^{-1} \times 1.2 \text{ g. cm.}^{-3} \times 17 \text{ Mrad})$$

$$= 0.11 \pm 0.02 \text{ h.e.v.}^{-1}$$

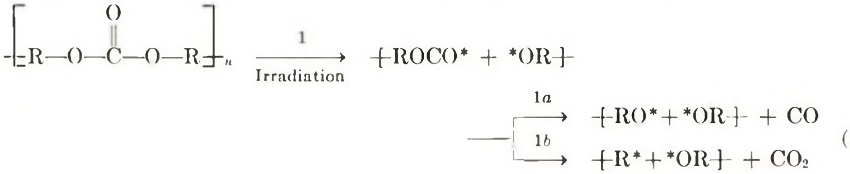
Although this is a reasonable yield for organic materials it is about a factor of 50 below the values we mentioned previously.[1] Miller's[6] value for total gas evolution products was $G = 2.9$ (60% CO, 39% CO_2, 1% H_2) and our ESR estimate was 6 spins-h.e.v.$^{-1}$ (which agrees with the gas products value if there are two residual radicals per liberated gas molecule).[1] The value $G = 0.11$ does, however, agree with recent values for main chain scission (0.09 in vacuum and 0.14 in O_2) determined by solution viscometry of 4 M.e.v. electron-irradiated samples by Golden and Hazell.[7] As implied previously, the large difference in calculated G values is probably due to a combination of factors including increased solubility σ of the irradiated polycarbonate, the presence of several types of free radicals, and an increased diffusion coefficient D due to radiation degradation of the polymer. In support of this idea it may be noted that the estimates of D (Fig. 7 of ref. 1) for the electron-irradiated polymer are about four times Norton's values (Table I) for the unirradiated material.

Conclusion

The functional relations proposed by Kishi for the time lag associated with the appearance of a colored diffusion border in γ-irradiated materials apply to electron irradiated Lexan resin and PMMA. It appears that something more complicated than the deposition of a simple monolayer is associated with the time lag.

The radiation G value of 0.11 h.e.v.$^{-1}$ based on the diffusion and sorption data[1,4] is in accord with the viscometric values obtained by Golden and Hazell[4] but are much smaller than the ESR and gas evolution values.[7] The implication is that the visible diffusion border is associated with only a fraction of the free radicals in the sample.

Some more recent gas evolution studies by Golden[8] indicate a G value which is over six times larger than the viscometric value.[7] This result is in accord with the hypothesis that radical recombination, enhanced by the Franck-Rabinowitch cage effect, is an important factor in reducing G (scission). Our present opinion is that the reactions with the highest probabilities are the following [where R is $C_6H_4—C(CH_3)_2—C_6H_4$]:



$$\left[\text{R—O—}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{—O—R} \right]_n \xrightarrow[\text{Irradiation}]{1} \text{—ROCO}^* + {}^*\text{OR—} \begin{cases} \xrightarrow{1a} \text{—RO}^* + {}^*\text{OR—} + CO \\ \xrightarrow{1b} \text{—R}^* + {}^*\text{OR—} + CO_2 \end{cases} \qquad (1)$$

The low CH_4 yields[8] show that the R group is about fifty times more resistant to electron irradiation than the carbonate linkage and the absence of resolved ESR structure[2] suggests that

$$\text{—RO(CO)OR—}_n \xrightarrow{2} \text{—ROCO}^* + {}^*\text{R—} \qquad (2)$$

is not as likely as reaction (1). The relative CO/CO_2 yields[8] indicate that reaction (1a) is about twice as probable as (1b). Subsequent to reaction of the radicals, one expects the presence of groups such as R—O—R and R—O—O—R. It is also likely that trapped benzene, phenol, and other similar molecules may be present.

The author wishes to thank Mr. C. R. Thomas for assistance with the diffusion measurements and Dr. N. Kishi for his informative correspondence regarding the induction effect.

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Résumé

On a réexaminé certains résultats expérimentaux qui avaient originellement servi à déterminer les coefficients de diffusion ainsi que leur variation avec la tension appliquee dans le cas du polycarbonate de bisphénol-A et du polyméthacrylate de méthyle irradiés par des électrons. On a vérifié l'existence d'une période d'induction dite de Kishi pour la période initiale d'absorption de l'oxygène par ces polymères. Les résultats sont en accord avec la relation $t_i = t_i^0 e^{E/RT} e^{-p/p_1}$. On utilise également des résultats nouveaux de Norton sur l'absorption des gaz par le polycarbonate de bisphénol-A en conjonction avec les résultats et les équations de la référence sus-mentionnée pour estimer la concentration initiale des radicaux libres associés à la zone de diffusion suffisament nette pour être visible à l'oeil et qui était un des points majeurs de la publication précédente. La valeur de G[nombre de centres colorés blanchise par l'oxygène/hev] qui a été obtenue pour ces radicaux, est comparée avec les déterminations viscométriques de Golden et Hazell.

Zusammenfassung

Die Überprüfung einiger Daten, welche ursprünglich zur Bestimmung der Diffusionskoeffizienten und ihrer Abhängigkeit von der angewandten Spannung in elektronenbestrahltem Poly(bisphenol-A-carbonat) und Polymethylmethacrylat herangezogen wurden, hat die Existenz der Induktionsperiode nach Kishi, t_1, für das Anfangsstadium der O_2-Sorption durch diese Polymeren bestätigt. Die Daten entsprechen der Beziehung $t_i = t_i^0 e^{E/RT} e^{-p/p_1}$. Einige neue Gassorptionsdaten für Poly(bisphenol-A-carbonat) von Norton werden zusammen mit Daten und Gleichungen aus der zitierten Arbeit zur Bestimmung der Anfangskonzentration der mit der visuellen scharfen Diffusionsgrenze verknüpften freien Radikale benützt. Diese Diffusionsgrenze bildete den Hauptgegenstand unserer früheren Veröffentlichungen. Der G-Wert [sauerstoffausgebleichte Farbzentren/hev] für diese Radikale wird mit den neuen viskosimetrischen Bestimmungen von Golden und Hazell verglichen.

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Undecoupled and Decoupled High Resolution Nuclear Magnetic Resonance Study of Poly(vinyl Chloride)

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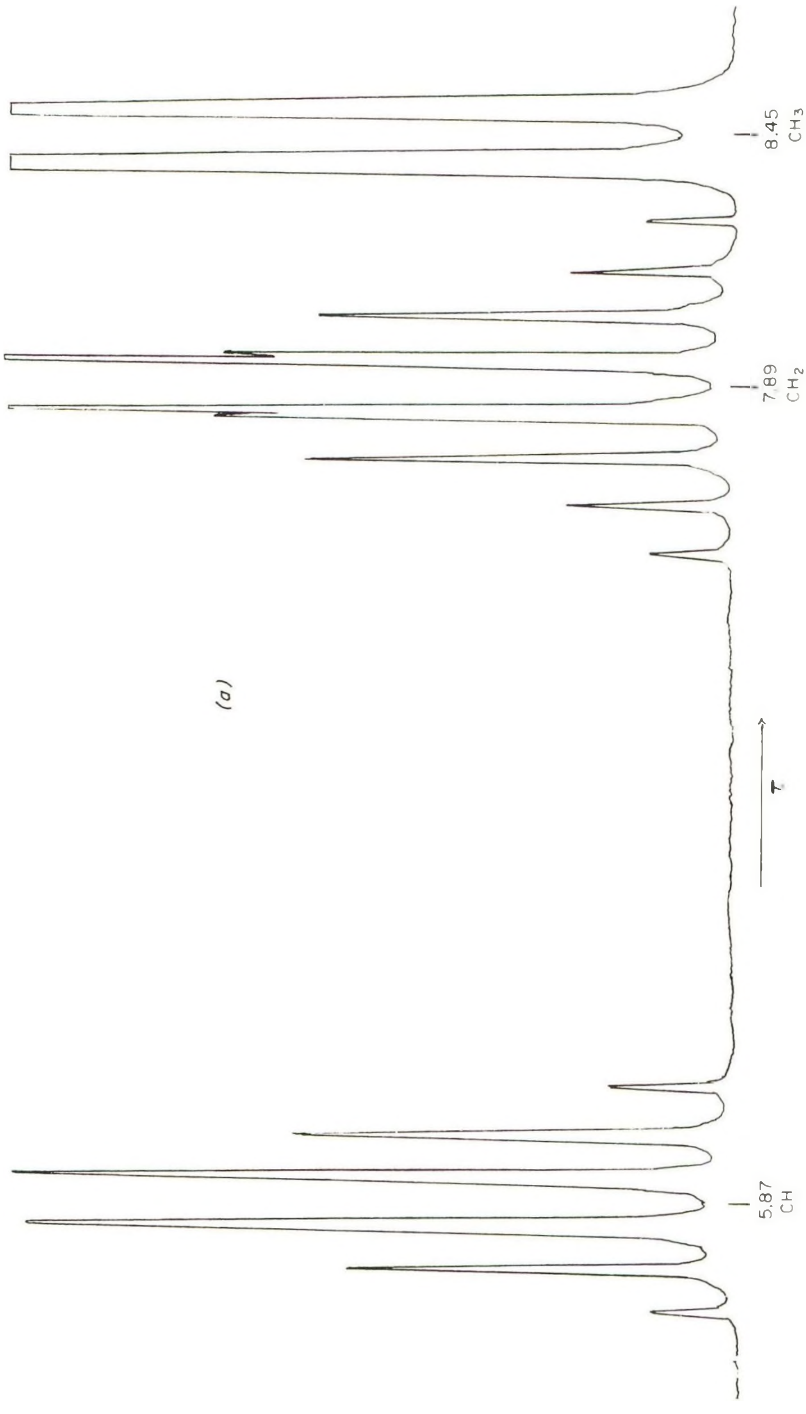
Synopsis

High resolution nuclear magnetic resonance spectra of two kinds of poly(vinyl chloride) and the model compounds, *meso* and *racemic* 2,4-dichloropentane were studied by normal and spin decoupling technique to elucidate the polymer structure. Unlike the methylene resonance of *meso* 2,4-dichloropentane which has been observed as an AB type quartet, only a singlet has been observed as the methylene resonance in isotactic sequences of poly(vinyl chloride) in spin-decoupled spectra. Two peaks of decoupled spectra of the polymer at 7.76 and 7.96 τ are due to methylene protons in isotactic and syndiotactic sequences in the diad, respectively, and the other three peaks at 5.43, 5.53, and 5.69τ correspond, respectively, to syndiotactic, heterotactic, and isotactic units in the triad. By analyzing decoupled spectra of the two kinds of polymer, parameters of local regularity have been determined. A theoretical treatment for the spectrum for four nuclei ABX_2 has been applied to analysis of the methylene resonance of *meso* 2,4-dichloropentane.

INTRODUCTION

High resolution nuclear magnetic resonance studies of poly(vinyl chloride) have been carried out by several authors[1,2,3] to elucidate the microstructure from the point of tacticity. The interpretation of the origin of resonance lines due to methylene protons, however, is not consistent in some respects among them. Assuming that the observed five peaks are composed of two overlapping triplets, Johnsen[1] has assigned the triplet observed at the higher field to methylene protons in syndiotactic sequences of the polymer molecule.

Tincher[2] and Satoh et al.,[3] on the other hand, have assigned the resonance lines due to methylene protons in syndiotactic sequences to a triplet structure, and those due to methylene protons in isotactic sequences to a multiplet other than a triplet considering that these two methylene protons are magnetically not equivalent. It is rather difficult to calculate the transition energies and relative intensities for these protons in explicit analytical form. For this reason, the present author and his co-workers[3] constructed an envelope appropriate for a triplet and used it for the analysis. On the other hand, Tincher[2] has determined the lines due to these protyns by numerical calculation, applying an appropriate mutual spin–spin coupling


(a)
8.45
CH$_3$
7.89
CH$_2$
5.87
CH
τ

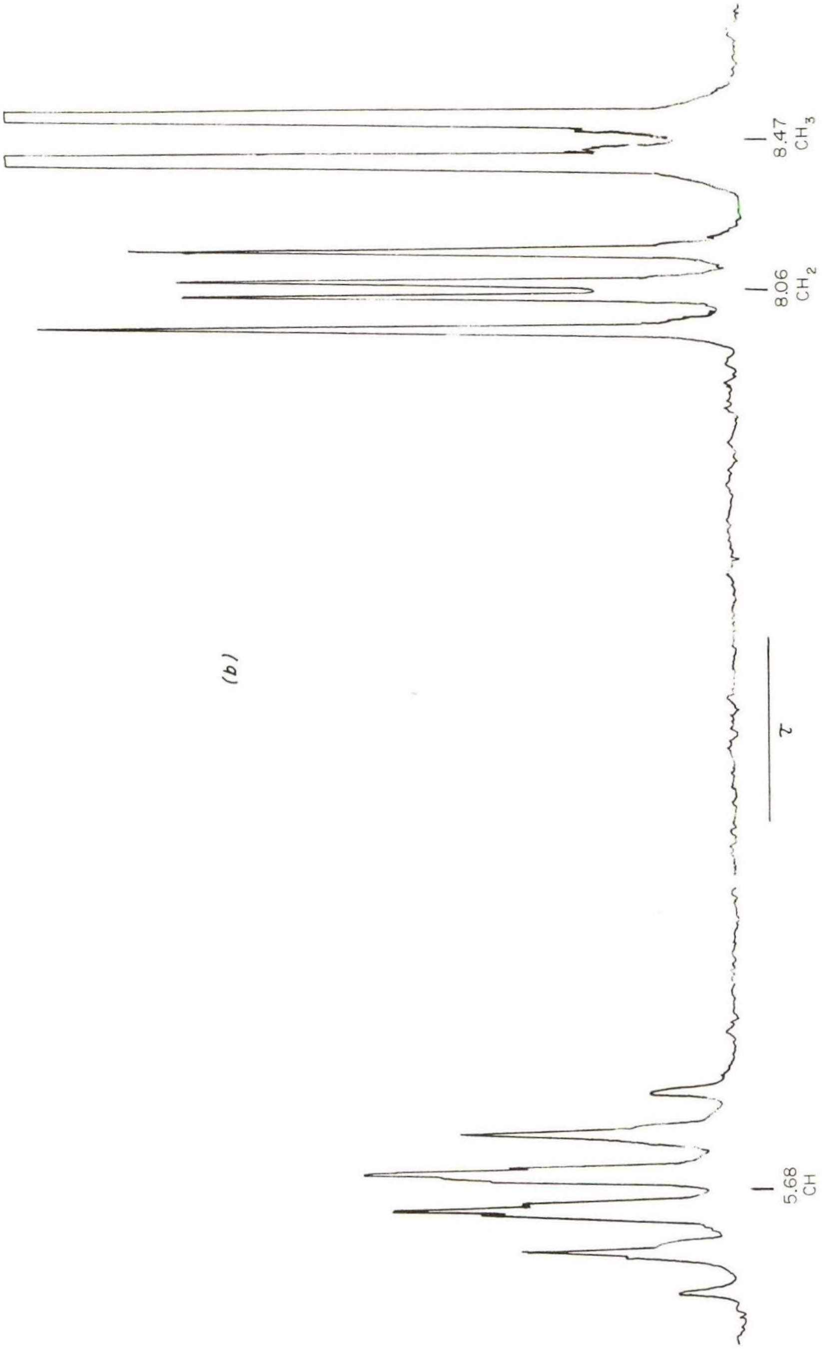


Fig. 1. NMR spectra of (*a*) *meso* 2,4-dichloropentane; (*b*) *racemic* 2,4-dichloropentane.

constant of methylene protons to an ABC_2 proton system (according to the nomenclature proposed by Pople[4]).

Three methods will be used to clarify inherent differences among the analysis of the structures of resonance lines: *(1)* comparisons of model compounds having meso and racemic structures; *(2)* use of polymers such as poly(α-deuterovinyl chloride) as was done by Bovey and Tiers;[5] *(3)* application of a spin decoupling technique.

The success attained by application of the second method is due to the fact that the splitting of methylene resonance by the α-deuteron is small enough to give unresolvable multiplets. The third method is a good procedure to keep methylene resonance free from splitting by α-protons. In other words, the utility of these two methods is based on the idea that the multiplet structure of the spectrum is due to indirect spin-spin interactions between methylene protons and/or between methylene and methyne ones.

The purpose of this paper is to analyze the spectrum of poly(vinyl chloride) by application of the above mentioned methods *(1)* and *(3)* in order to obtain accurate data on the local regularity of this polymer.

EXPERIMENTAL

All samples used were prepared at Kureha Chemical Industry Co., Ltd.

Meso and *racemic* 2,4-dichloropentane were synthesized as follows. A mixture of pentane-2,4-diol obtained by hydrogenation of acetylacetone with Raney nickel and hydrochloric acid was saturated with dry hydrogen chloride at −14°C. in a sealed tube and heated for 4 hr. at 100°C. The upper phase, containing 2,4-dichloropentane was separated from the lower phase and dried over calcium chloride. The separation of the compounds into the two components, *meso* and *racemic* 2,4-dichloropentane was made by using a gas chromatograph designed for preparative purpose. These materials were dissolved in a mixed solvent of *o*-dichlorobenzene and tetrachloroethylene (45:55) in 10% concentration.

Two kinds of poly(vinyl chloride) were used. Sample A was polymerized at 55°C., and sample B at −30°C. The polymers were dissolved in the solvent described above in 10 and 5% concentration, respectively. The latter was less soluble than the former, which would be due to the enhanced tacticity by cold polymerization.

(a) *(b)*

Fig. 2. Spin coupling constants for four nuclei: *(a)* A_2X_2; *(b)* ABX_2.

The instruments used in this work were a Varian Model V-4311 spectrometer operating at 60 Mcycles/sec equipped with temperature control accessory Model V-4340 and Model V-3521 integrator.

The spin decoupling experiment was performed by the side band method[6–8] with a phase-sensitive detector operating at 2 Kcycle/sec.

RESULTS AND DISCUSSION

2,4-Dichloropentane

Nuclear magnetic resonance spectra of solutions of *meso* and *racemic* 2,4-dichloropentane are reproduced in Figures 1*a* and 1*b*, respectively. These spectra changed slightly with temperature.

The methylene resonance in a *racemic* compound has shown to consist of four lines which seem to be expressed by the A part of an A_2X_2 system. This may be due to the fact that the spin coupling constant J between

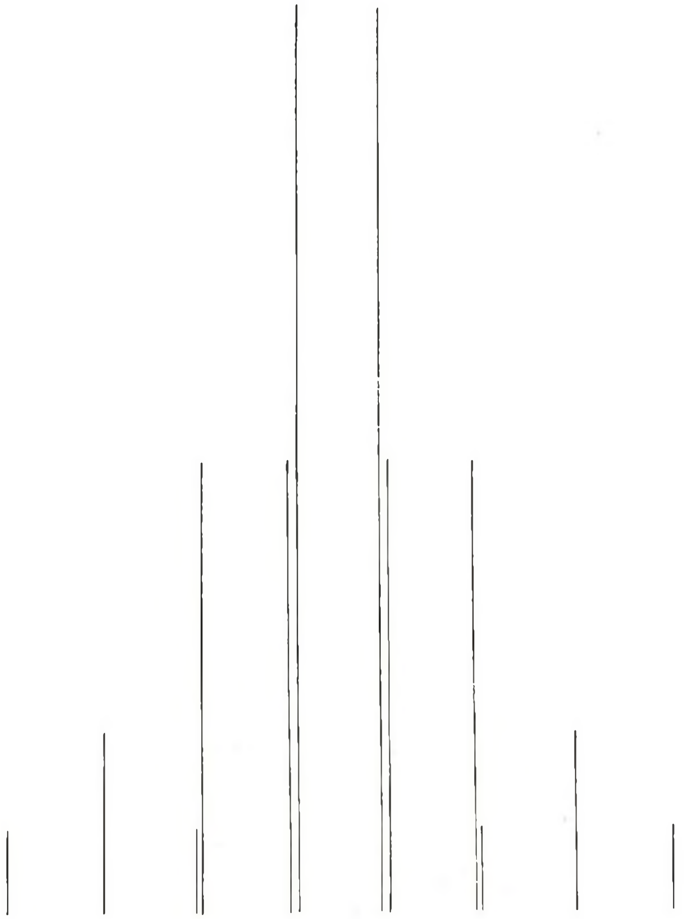


Fig. 3. Calculated methylene resonance of *meso* 2,4-dichloropentane.

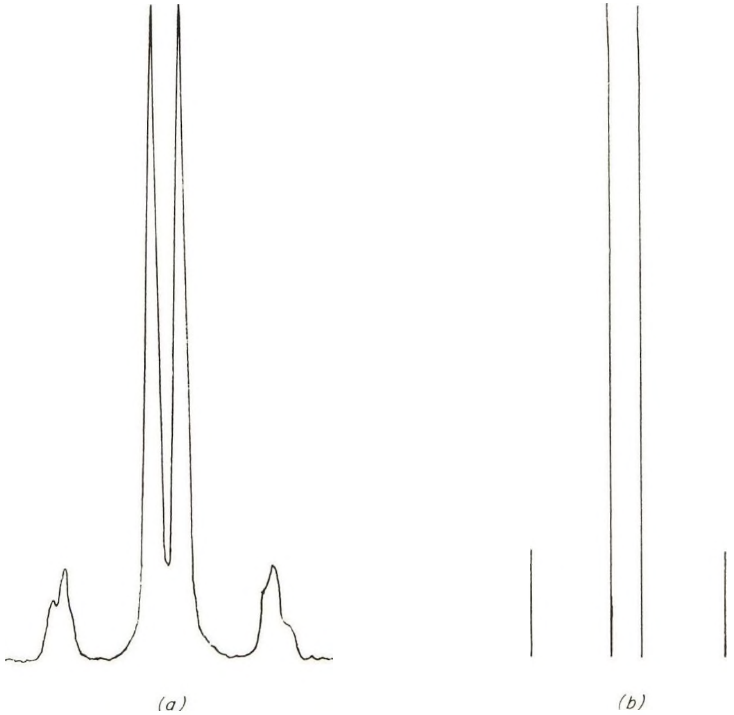


Fig. 4. Decoupled methylene resonance in *meso* 2,4-dichloropentane: (*a*) observed; (*b*) calculated.

A(1) and X(1), is not identical with that J' between A(1) and X(2), as a consequence of the asymmetric α-carbon (Fig. 2). In other words, reorientation of the molecule around the $C(\alpha)$–$C(\beta)$ axis would be insufficient to equalize these coupling constants. The methylene resonance in the *meso* compound consists of more than eight lines which are represented as an AB part of ABX_2 system with $J_1 = J_2 = J_3 = J_4$ (see Appendix). The calculated patterns of the methylene resonance are illustrated in Figure 3. This is again demonstrated by the spin-decoupling experiment. The lines reproduced in Figure 4*a* are observed when spins of methylene protons in the *meso* compound are decoupled from those of α-protons. The methylene resonance of the *meso* compound has been reduced to an AB type quartet, while that of the *racemic* compound to a singlet. Calculated decoupled methylene patterns are also shown in Figure 4*b*. A singlet and an AB type quartet are distinguished from each other in the decoupled spectrum of the mixture of both compounds.

The obtained chemical shifts and coupling constants which were determined at 150°C. are listed in Table I.

There is no significant difference in the chemical shifts of methyl lines in both compounds, but the relative chemical shift between methylene and methyne protons is a little larger in the *racemic* compound. These results support the analysis made by Tincher, in which 14 cycles/sec.

TABLE I
Chemical Shifts and Spin Coupling Constants of *Meso* and *Racemic* 2,4-Dichloropentane

	Chemical shift, τ[a]			Spin coupling constant, cycles/sec.		
	CH_3	CH_2	CH	J_{CH_3-CH}	J_{CH_2}	J_{CH_2-CH}
Meso	8.45	8.02, 7.76	5.87	6.7	14.5	7.1
Racemic	8.47	8.06	5.68	6.7	15.7	3.4, 10.3

[a] τ is defined by $\tau = 10 + (H - H_r)/H_r$, where H_r is the resonance field of tetramethylsilane.

was used as the mutual spin coupling constant of methylene protons in isotactic sequences of poly(vinyl chloride).

Poly(vinyl Chloride)

High resolution nuclear magnetic resonance spectra of poly(vinyl chloride) are reproduced in Figures 5*a* and 5*b*. The group of lines at the higher field corresponds to methylene protons (β-protons) and the group at the lower field is attributed to methyne protons (α-protons). Five peaks are observed clearly in the resonance lines due to methylene protons, while the lines corresponding to methyne protons consist of more than seven peaks instead of a quintet as reported by Johnsen and Tincher. Two possibilities will be considered for the origin of the observed seven methyne lines: (*1*) these lines are composed of more than two overlapping multiplets, or (*2*) these lines cannot be expressed by an A part of AX_4 system.

In contrast to the complicated patterns given by indirect spin-spin interactions between methylene protons and/or between methylene and methyne protons, the spectra obtained by the spin-decoupling technique are much simpler but more reliable for use in analysis of the spectra.

Methylene Resonance Lines. Even when two methylene protons in isotactic units are magnetically not equivalent with each other, the relative chemical shift between these protons may be very small in comparison with that between methylene and methyne protons. This has been shown by Tincher and by the present author for poly(vinyl chloride) and on *meso* 2,4-dichloropentane, respectively. This will exclude the possibility that the mutual spin multiplet due to methylene protons (AB type quartet here) is collapsed into a singlet when spins of methylene protons are decoupled from those of methyne protons.

The spin-decoupling condition (frequency, radio frequency power, etc.) can be so selected that only methylene protons belonging to either sequence are decoupled when there is a moderate difference in the relative chemical shift between these protons and methyne protons in both units. However, when the group of lines at the higher field is decoupled, as in the present case, that at the lower field will be also partially decoupled simultaneously. The resonance lines reproduced in Figure 6*a* are observed

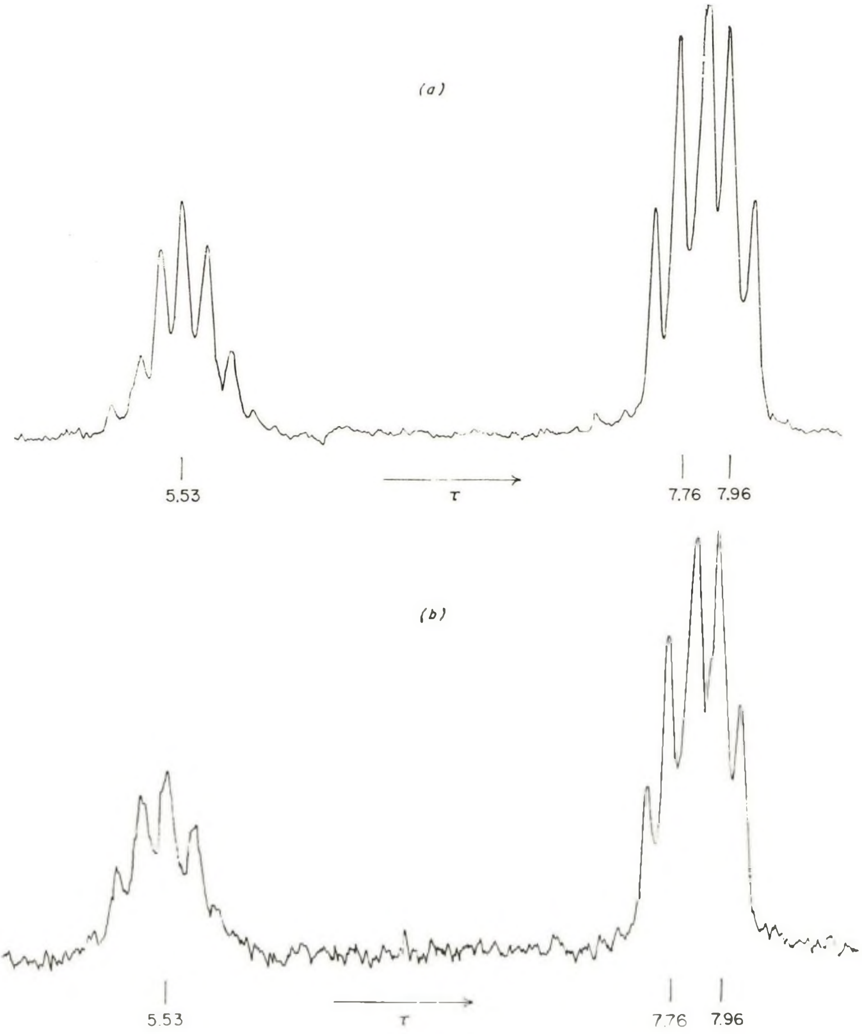


Fig. 5. NMR spectra measured at 150°C.: (*a*) sample A; (*b*) sample B.

under the condition that the group of lines at the lower field is decoupled first; those in Figure 6*b* are obtained under condition that the lines at higher field are decoupled first. The envelope of resonance lines has become sharper with increased power of applied radio frequency and resulted an overlapping singlet with an unresolvable triplet in both conditions. An AB type quartet has not been observed throughout the present study.

Two singlets as reproduced in Figure 7 are obtained when the conditions are so chosen that both groups of lines can be decoupled simultaneously. In order to obtain these conditions, line widths at half intensity were employed as one of measures, assuming both of the longitudinal relaxation time T_1 and the transverse relaxation time T_2 of each line to be identical.

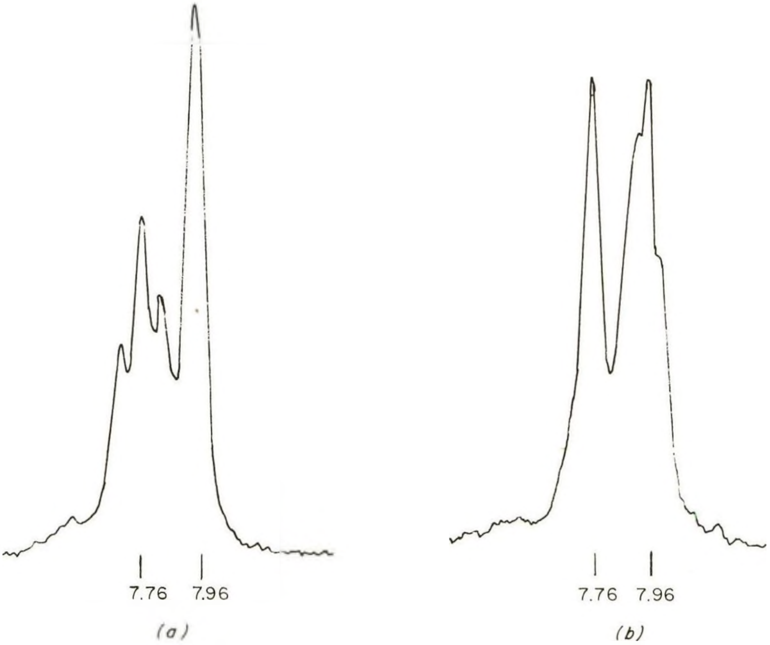


Fig. 6. Partially decoupled methylene resonance of sample A.

The peak positions of these two singlets are 7.76 and 7.96τ, respectively. These values completely coincide with those of two peaks of the five lines in the undecoupled methylene resonance.

Since the peak position of the decoupled line must coincide with that of the center of gravity of undecoupled lines, the above-mentioned result will also exclude the possibility that an AB type quartet may be collapsed into a singlet by erroneous experimental procedures.

These two peaks are due to a difference in their magnetic situation, in other words, in the stereoregularity. A singlet at the higher field is assigned to methylene protons in syndiotactic sequences in the diad.[1]

Methyne Resonance Lines. As described above, when decoupled methylene lines appear at one first side band, spin decoupled methyne resonance can be observed at another first side band. The lines reproduced in Figure 8 are obtained under the same decoupling condition as selected for methylene protons to give the lines reproduced in Figure 7. These three peaks correspond from higher to lower field, respectively, to methyne protons in isotactic, heterotactic, and syndiotactic sequences. This assignment can be proved by the spin-decoupling method described as follows. After the spin-decoupling condition is selected for methylene protons in isotactic sequences at the higher first side band, applied magnetic field is swept till the lower first side band signal is observed. In this case, a sharp singlet at 5.69τ is observed, together with a broad one at lower field side. When the conditions are adjusted at the higher first side band for methylene protons in syndiotactic units, a sharp singlet at

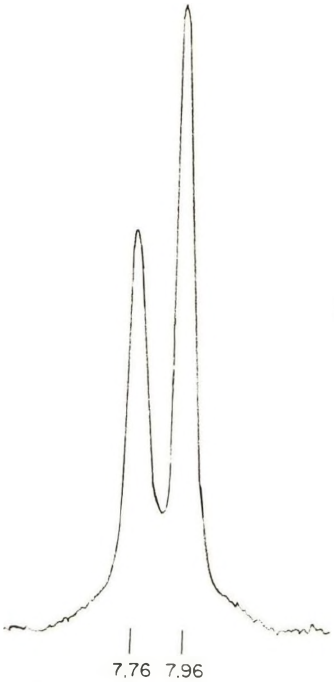


Fig. 7. Spin-decoupled methylene resonance of sample A.

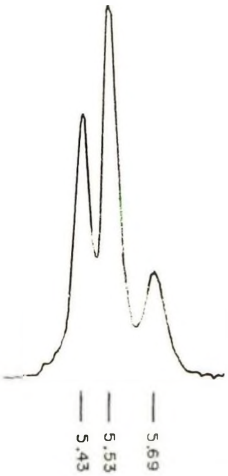


Fig. 8. Decoupled methyne resonance of sample A.

5.43τ and a broad line at higher field side are observed. Since heterotactic units in the triad are to be related to both isotactic and syndiotactic units in the diad, a sharp heterotactic line cannot be observed by the above method.

The envelope of three quintets whose relative intensities and separations of their centers are the same as those found in Figure 8 resembles closely the pattern of methyne resonance obtained by the ordinary nuclear magnetic resonance method. This result suggests that the undecoupled methyne resonance lines are composed of three groups of first-order lines, and that each of these group is expressed by an A part of the AX_4 system. Furthermore, the spin coupling constant between methylene and methyne protons seems to be almost independent of the sequence in which these protons are present.

The obtained chemical shifts and spin coupling constant of this polymer are listed in Table II.

TABLE II

Chemical Shifts and Spin Coupling Constant of Poly(vinyl Chloride)

	Chemical shift, τ		Spin coupling constant J, cycles/sec.
	CH_2 (diad)	CH (triad)	
Isotactic	7.76	5.69	6.5
Heterotactic	—	5.53	
Syndiotactic	7.96	5.43	

Local Regularity

Since the spin-decoupled spectra are simple in their shape, the data given by analyzing these decoupled lines will give more accurate informations on the local regularity of the polymer.

From the analysis of decoupled spectra, the probabilities p_i and p_s of forming isotactic and syndiotactic sequences in the diad (for methylene groups), and P_I, P_H, and P_S of forming isotactic, heterotactic, and syndiotactic units in the triad, respectively, are obtained, where p_i and p_s are the same as the P_m and P_r of Bovey and Tiers.[9] The average persistence lengths $\langle i \rangle$, $\langle s \rangle$, $\langle I \rangle$, $\langle H \rangle$, and $\langle S \rangle$ in number of monomer unit are also determined with the aid of the theory.[10,11] These values are summarized in Table III together with the excess of the activation enthalpy for isotactic placement over that of syndiotactic placement per mole.

When the configuration of growing polymer end is described by a simple Markov process, P_I, P_H, and P_S can be represented in terms of p_i and p_s as follows

$$\begin{aligned} P_I &= p_i^2 \\ P_H &= 2p_ip_s \\ P_S &= p_s^2 \end{aligned}$$

The values calculated from eq. (1) are also listed in Table III. Good agreement is found between these values obtained from decoupled methyne lines and those calculated. This fact seems to suggest that the probability with which a growing polymer chain adds a monomer unit to get

TABLE III
Parameters of Local Regularity for Two Kinds of Poly(vinyl Chloride)

	Sample A	Sample B
Polymerization temp., °K.	328	243
Diad		
Probabilities		
p_i	0.40	0.32
p_s	0.60	0.68
Persistance lengths		
$\langle i \rangle$	1.7	1.5
$\langle s \rangle$	2.5	3.1
ΔE, cal./mole[a]	260	360
Triad		
Probabilities (calc'd.)[b]		
P_I'	0.16	0.10
P_H'	0.48	0.44
P_S'	0.36	0.46
Probabilities		
P_I	0.16	0.09
P_H	0.49	0.44
P_S	0.35	0.47
Persistance lengths		
$\langle \mathrm{I} \rangle$	1.7	1.4
$\langle \mathrm{H} \rangle$	2.0	2.0
$\langle \mathrm{S} \rangle$	2.5	3.3
ΔE, cal./mole[a]	260	400
Persistance ratio ρ	0.96	1.04

[a] Excess in activation enthalpy for isotactic placement over that for syndiotactic placement.

[b] Calculated from eq. (1).

the same configuration as that of the growing end unit depends only on the configuration of this end unit.

Disagreement in the values of the excess of the activation enthalpy for isotactic placement over that of syndiotactic placement for sample B found between the measurements for methylene and for methyne lines will be ascribed to poor signal to noise ratio brought by the poor concentration of the solution.

The persistence ratio ρ which has been proposed by Coleman and Fox[12] as a measure of departure from Bernoulli trial (simple Markov process) is represented in terms of the above probabilities as follows

$$\rho = p_i p_s / (p_s - P_s)$$

Three cases may be distinguished by the value of ρ. The case where ρ is equal to unity corresponds to Bernoulli trial. The other two cases, where ρ is smaller or larger than unity, correspond, respectively, to alternate or to cluster blocks in the polymer[13] with respect to tacticity. The values of ρ are listed in Table III. These results suggest that the polymer prepared at 55°C. is rich in clustered blocks as compared with that prepared at −30°C.

CONCLUSION

The results obtained for the model compounds seem to support the analysis of Tincher, who has assigned the lines due to methylene protons in isotactic sequences to an AB part of the ABC_2 system. On the other hand, the values obtained by Bovey and Tiers from poly(α-deuterovinyl chloride) and by the present spin-decoupling method from poly(vinyl chloride) have confirmed the analysis of Johnsen. Although Tincher has analyzed the methylene resonance in isotactic sequences on the consideration of the geometrical arrangement of groups in the model of polymer chain, the result that an AB type quartet has been observed neither in the spectrum of poly(α-deuterovinyl chloride) nor in the spin-decoupled spectra of poly(vinyl chloride) would indicate that the polymer chain should be considered from some other quantum mechanical point of view for which a concrete expression cannot be given at the present stage. A similar fact would also be involved in the problem of the inconsistency of observed lines between the polymer and its model compound. A study concerned with these problems is now in progress.

APPENDIX

Spectrum for Four Nuclei ABX_2

For a system of four nuclei ABX_2 there are six different coupling constants J_0, J_1, J_2, J_3, J_4, and J_x as illustrated in Figure 2*b*.

TABLE A-I

Basic Functions and Diagonal Matrix Elements

	Function	Diagonal matrix elements
1	$\alpha\alpha\alpha\alpha$	${}^1/_2(\nu_A + \nu_B + 2\nu_X) + {}^1/_4(J_0 + J_1 + J_2 + J_3 + J_4 + J_X)$
2	$\alpha\alpha(\alpha\beta + \beta\alpha)/\sqrt{2}$	${}^1/_2(\nu_A + \nu_B) + {}^1/_4(J_0 + J_X)$
3	$\alpha\beta\alpha\alpha$	${}^1/_2(\nu_A - \nu_B + 2\nu_X) - {}^1/_4(J_0 - J_1 - J_2 - J_3 + J_4 - J_X)$
4	$\beta\alpha\alpha\alpha$	${}^1/_2(\nu_A + \nu_B + 2\nu_X) - {}^1/_4(J_0 + J_1 - J_2 + J_3 - J_4 - J_X)$
5	$\alpha\alpha\beta\beta$	${}^1/_2(\nu_A + \nu_B - 2\nu_X) + {}^1/_4(J_0 - J_1 - J_2 - J_3 - J_4 + J_X)$
6	$\alpha\beta(\alpha\beta + \beta\alpha)/\sqrt{2}$	${}^1/_2(\nu_A - \nu_B) - {}^1/_4(J_0 - J_X)$
7	$\beta\alpha(\alpha\beta + \beta\alpha)/\sqrt{2}$	${}^1/_2(-\nu_A + \nu_B) - {}^1/_4(J_0 - J_X)$
8	$\beta\beta\alpha\alpha$	${}^1/_2(-\nu_A - \nu_B + 2\nu_X) + {}^1/_4(J_0 - J_1 - J_2 - J_3 - J_4 + J_X)$
9	$\alpha\beta\beta\beta$	${}^1/_2(\nu_A - \nu_B - 2\nu_X) - {}^1/_4(J_0 + J_1 - J_2 + J_3 - J_4 - J_X)$
10	$\beta\alpha\beta\beta$	${}^1/_2(-\nu_A + \nu_B - 2\nu_X) - {}^1/_4(J_0 - J_1 + J_2 - J_3 + J_4 - J_X)$
11	$\beta\beta(\alpha\beta + \beta\alpha)/\sqrt{2}$	${}^1/_2(-\nu_A - \nu_B) + {}^1/_4(J_0 + J_X)$
12	$\beta\beta\beta\beta$	${}^1/_2(-\nu_A - \nu_B - 2\nu_X) + {}^1/_4(J_0 + J_1 + J_2 + J_3 + J_4 + J_X)$
13	$\alpha\alpha(\alpha\beta - \beta\alpha)/\sqrt{2}$	${}^1/_2(\nu_A + \nu_B) + {}^1/_3(J_0 - 3J_X)$
14	$\alpha\beta(\alpha\beta - \beta\alpha)/\sqrt{2}$	${}^1/_2(\nu_A - \nu_B) - {}^1/_4(J_0 + 3J_X)$
15	$\beta\alpha(\alpha\beta - \beta\alpha)/\sqrt{2}$	${}^1/_2(-\nu_A + \nu_B) - {}^1/_4(J_0 + 3J_X)$
16	$\beta\beta(\alpha\beta - \beta\alpha)/\sqrt{2}$	${}^1/_2(-\nu_A - \nu_B) + {}^1/_4(J_0 - 3J_X)$

TABLE A-II
Mixed Wave Functions and Energies

	Functions	Energies
1	$\alpha\alpha\alpha\alpha\alpha$	$^1/_2(\nu_A + \nu_B + 2\nu_X) + {}^1/_4(J_0 + J_1 + J_2 + J_3 + J_4)$
2	$\alpha\alpha(\alpha\beta + \beta\alpha)/\sqrt{2}$	$^1/_2(\nu_A + \nu_B) - {}^1/_4J_0$
3′	$\cos\theta\ (\alpha\beta\alpha\alpha) + \sin\theta\ (\beta\alpha\alpha\alpha)$	$\nu_X - {}^1/_4J_0 - D$
4′	$-\sin\theta\ (\alpha\beta\alpha\alpha) + \cos\theta\ (\beta\alpha\alpha\alpha)$	$\nu_X - {}^1/_4J_0 + D$
5	$\alpha\alpha\beta\beta$	$^1/_2(\nu_A + \nu_B - 2\nu_X) - {}^1/_4(J_0 - J_1 - J_2 - J_3 - J_4)$
6′	$\cos\phi\ \{\alpha\beta(\alpha\beta + \beta\alpha)/\sqrt{2}\} + \sin\phi\ \{\beta\alpha(\alpha\beta + \beta\alpha)/\sqrt{2}\}$	$-{}^1/_4J_0 + C$
7′	$-\sin\phi\ \{\alpha\beta(\alpha\beta + \beta\alpha)/\sqrt{2}\} + \cos\phi\ \{\beta\alpha(\alpha\beta + \beta\alpha)/\sqrt{2}\}$	$-{}^1/_4J_0 - C$
8	$\beta\beta\alpha\alpha$	$^1/_2(-\nu_A - \nu_B + 2\nu_X) + {}^1/_4(J_0 - J_1 - J_2 - J_3 - J_4)$
9′	$\cos\theta\ (\alpha\beta\beta\beta) + \sin\theta\ (\beta\alpha\beta\beta)$	$-\nu_X - {}^1/_4J_0 + D$
10′	$-\sin\theta\ (\alpha\beta\beta\beta) + \cos\theta\ (\beta\alpha\beta\beta)$	$-\nu_X - {}^1/_4J_0 - D$
11	$\beta\beta(\alpha\beta + \beta\alpha)/\sqrt{2}$	$^1/_2(-\nu_A - \nu_B) + {}^1/_4J_0$
12	$\beta\beta\beta\beta$	$^1/_2(-\nu_A - \nu_B - 2\nu_X) + {}^1/_4(J_0 + J_1 + J_2 + J_3 + J_4)$
13	$\alpha\alpha(\alpha\beta - \beta\alpha)/\sqrt{2}$	$^1/_2(\nu_A + \nu_B) + {}^1/_4J_0$
14′	$\cos\phi\ \{\alpha\beta(\alpha\beta - \beta\alpha)/\sqrt{2}\} + \sin\phi\ \{\beta\alpha(\alpha\beta - \beta\alpha)/\sqrt{2}$	$-{}^1/_4J_0 + C$
15′	$-\sin\phi\ \{\alpha\beta(\alpha\beta - \beta\alpha)/\sqrt{2}\} + \cos\phi\ \{\beta\alpha(\alpha\beta - \beta\alpha)/\sqrt{2}$	$-{}^1/_4J_0 - C$
16	$\beta\beta(\alpha\beta - \beta\alpha)/\sqrt{2}$	$^1/_2(-\nu_A - \nu_B) + {}^1/_4J_0$

The basic functions and diagonal matrix elements are tabulated in Table A-I, where

$$\begin{aligned} \nu_i &= (\gamma_i/2\pi)H_0(1 - \sigma_i) \\ i &= \mathrm{A, B, X} \end{aligned} \qquad \text{(A-1)}$$

γ_i is the gyromagnetic ratio and σ_i is the shielding constant of nucleus i.

Since the basic functions with different X spins cannot be mixed, only four 2×2 secular equations remain to be solved. The nonvanishing off-diagonal matrix elements are

$$\mathcal{H}_{2,3} = \mathcal{H}_{6,7} = \mathcal{H}_{9,10} = \mathcal{H}_{14,15} = {}^1/_2 J_0 \qquad \text{(A-2)}$$

The final energy levels and wave functions can then be written in explicit analytical form. If we define positive quantities D, C and angles θ and ϕ by

$$\begin{aligned} D \cos 2\theta &= {}^1/_2[\nu_\mathrm{A} - \nu_\mathrm{B} + {}^1/_2(J_1 - J_2 + J_3 - J_4)] \\ D \sin 2\theta &= {}^1/_2 J_0 \\ C \cos 2\phi &= {}^1/_2(\nu_\mathrm{A} - \nu_\mathrm{B}) \\ C \sin 2\phi &= {}^1/_2 J_0 \end{aligned} \qquad \text{(A-3)}$$

so that

$$\begin{aligned} D &= {}^1/_2\{[\nu_\mathrm{A} - \nu_\mathrm{B} + {}^1/_2(J_1 - J_2 + J_3 - J_4)]^2 + J_0^2\}^{1/2} \\ C &= {}^1/_2\{(\nu_\mathrm{A} - \nu_\mathrm{B})^2 + J_0^2\}^{1/2} \end{aligned} \qquad \text{(A-4)}$$

the mixed wave functions can be written in the form given in Table A-II, where two quantities, ${}^1/_4 J_\mathrm{X}$ and ${}^3/_4 J_\mathrm{X}$ are omitted because they have nothing to do with both of the transition energies and relative intensities. Here the case where A and B are of the same species is treated, so $\nu_\mathrm{A} - \nu_\mathrm{B}$ is just the relative chemical shift between A and B. It will be assumed, without loss of generality, that σ_B is greater than σ_A, so that $\nu_\mathrm{A} > \nu_\mathrm{B}$.

We can now write explicit expressions for the energies and relative intensities of the 28 transitions, as summarized in Table A-III.

In order to obtain the spectrum for four nuclei $\mathrm{ABC_2}$, two 3×3 and one 4×4 secular determinants must be solved. The nonvanishing off-diagonal matrix elements are

$$\begin{aligned} \mathcal{H}_{1,2} = \mathcal{H}_{5,6} = \mathcal{H}_{7,8} = \mathcal{H}_{10,11} &= (1/\sqrt{2})(J_2 + J_3) \\ \mathcal{H}_{2,4} = \mathcal{H}_{5,7} = \mathcal{H}_{6,8} = \mathcal{H}_{9,10} &= (1/\sqrt{2})(J_1 + J_5) \end{aligned} \qquad \text{(A-5)}$$

and those given in eqs. (A-2).

The methylene resonance lines in *meso* 2,4-dichloropentane are interpreted as an AB part of $\mathrm{ABX_2}$ system with

$$\begin{aligned} J_1 = J_2 = J_3 &= J_4 \\ &= 7.1 \text{ cycles/sec.} \\ J_0 &= 14.5 \text{ cps} \\ \nu_A - \nu_B &= 0.26\tau \end{aligned} \qquad \text{(A-6)}$$

TABLE A-III
Transition Energies and Relative Intensities for Four Nuclei ABX_2

Transition		Energy	Relative intensity
1	1–3′	$^1/_2(\nu_A + \nu_B) + {}^1/_4(2J_0 + J_1 + J_2 + J_3 + J_4) - D$	$1 + \sin 2\theta$
2	1–4′	$^1/_2(\nu_A + \nu_B) + {}^1/_4(2J_0 + J_1 + J_2 + J_3 + J_4) + D$	$1 - \sin 2\theta$
3	2–6′	$^1/_2(\nu_A + \nu_B) + {}^1/_2J_0 - C$	$1 + \sin 2\phi$
4	2–7′	$^1/_2(\nu_A + \nu_B) + {}^1/_2J_0 + C$	$1 - \sin 2\phi$
5	3′–8	$^1/_2(\nu_A + \nu_B) - {}^1/_4(2J_0 - J_1 - J_2 - J_3 - J_4) + D$	$1 + \sin 2\theta$
6	4′–8	$^1/_2(\nu_A + \nu_B) - {}^1/_4(2J_0 - J_1 - J_2 - J_3 - J_4) - D$	$1 - \sin 2\theta$
7	5–9′	$^1/_2(\nu_A + \nu_B) + {}^1/_4(2J_0 - J_1 - J_2 - J_3 - J_4) - D$	$1 + \sin 2\theta$
8	5–10′	$^1/_2(\nu_A + \nu_B) + {}^1/_4(2J_0 - J_1 - J_2 - J_3 - J_4) + D$	$1 - \sin 2\theta$
9	6′–11	$^1/_2(\nu_A + \nu_B) - {}^1/_2J_0 + C$	$1 + \sin 2\phi$
10	7′–11	$^1/_2(\nu_A + \nu_B) - {}^1/_2J_0 - C$	$1 - \sin 2\phi$
11	9′–12	$^1/_2(\nu_A + \nu_B) - {}^1/_4(2J_0 + J_1 + J_2 + J_3 + J_4) + D$	$1 + \sin 2\theta$
12	10′–12	$^1/_2(\nu_A + \nu_B) - {}^1/_4(2J_0 + J_1 + J_2 + J_3 + J_4) - D$	$1 - \sin 2\theta$
13	13–14′	$^1/_2(\nu_A + \nu_B) + {}^1/_2J_0 - C$	$1 + \sin 2\phi$
14	13–15′	$^1/_2(\nu_A + \nu_B) + {}^1/_2J_0 - C$	$1 - \sin 2\phi$
15	14′–16	$^1/_2(\nu_A + \nu_B) - {}^1/_2J_0 + C$	$1 + \sin 2\phi$
16	15′–16	$^1/_2(\nu_A + \nu_B) - {}^1/_2J_0 - C$	$1 - \sin 2\phi$
17	1–2	$\nu_X + {}^1/_4(J_1 + J_2 + J_3 + J_4)$	2
18	2–5	$\nu_X + {}^1/_4(J_1 + J_2 + J_3 + J_4)$	2
19	3′–6	$\nu_X + D + C$	$2\cos^2(\theta - \phi)$
20	4′–6	$\nu_X - D + C$	$2\sin^2(\theta - \phi)$
21	3′–7	$\nu_X + D + C$	$2\sin^2(\theta - \phi)$
22	4′–7	$\nu_X - D + C$	$2\cos^2(\theta - \phi)$
23	6–9	$\nu_X - D + C$	$2\cos^2(\theta - \phi)$
24	7–9	$\nu_X - D - C$	$2\sin^2(\theta - \phi)$
25	6–10	$\nu_X + D + C$	$2\sin^2(\theta - \phi)$
26	7–10	$\nu_X + D - C$	$2\cos^2(\theta - \phi)$
27	8–11	$\nu_X - {}^1/_4(J_1 + J_2 + J_3 + J_4)$	2
28	11–12	$\nu_X - {}^1/_4(J_1 + J_2 + J_3 + J_4)$	2

as listed in Table I. The AB part of the calculated line spectrum is illustrated in Figure 3.

Under the condition given by eqs. (A-6), an ordinary triplet results for X resonance lines, where peak separations are equal to J_X.

After this work was completed, the author became aware of the paper reported by Bovey and his co-workers[14] in which a similar spin-decoupling technique was applied to polymers to elucidate their structure. We wish to thank Dr. Bovey and his co-workers for the reprints of their work.

The author is much indebted to Professor J. Itoh of Osaka University for valuable discussions on the spin-decoupling experiment. Thanks are also due to Drs. M. Asahina, K. Okuda, and M. Onozuka of Kureha Chemical Industry Co., Ltd. for preparing the samples, to Drs. E. Nagai and R. Chûjô of our Institute for their valuable discussions and comments and for their reading of the manuscript before publication, and to Mr. T. Kuroda for his experimental assistance.

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Résumé

Les spectres de résonance magnétique nucléaire à haute résolution de deux expèces de chlorure de polyvinyle et des composés-modèles, les 2,4-dichloropentanes méso et racémique ont été étudiés par la technique du découplage de spin en vue d'élucider la structure des polymères. Contrairement à la résonance du méthylène dans le 2,4-dichloropentane méso qui apparaît comme un quartet AB, le signal de résonance méthylinique du chlorure de polyvinyle dans une séquence isotactique, apparaît comme un singulet dans le spectre de double résonance. Deux pics dans les spectres découplés du polymère apparaissant à 7.76 et 7.96 τ sont dûs aux protons méthyléniques dans des séquences isotactiques et syndiotactiques (diades) respectivement tandis que les trois pics à 5.43, 5.53 et 5.69 τ correspondent respectivement à des unités syndio- hétéro- et isotactiques en triades. En analysant les spectres découplés des deux types de polymère, on a déterminé les paramètres influençant la régularité locale.

Zusammenfassung

Kernmagnetische Resonanzspektren hoher Auflösung von zwei Arten von Polyvinylchlorid und seinen Modellverbindungen meso- und racemisches Pentan-2,4-dichlorid wurden nach dem normalen und dem Spinentkopplungsverfahren zur Aufklärung der Polymerstruktur untersucht. Im Gegensatz zu der Methylenresonanz von Mesopentan-2,4-dichlorid, die als ein Quartett vom AB-Typ beobachtet wurde, tritt nur ein Singulett als Methylenresonanz in isotaktischen Sequenzen von Polyvinylchlorid in den spinentkoppelten Spektren auf. Zwei Maxima des entkoppelten Spektrums des Polymeren bei 7,76 und 7,96 in τ werden durch Methylenprotonen in isotaktischen bzw. syndiotaktischen Sequenzen in Diaden und die anderen drei Maxima bei 5,43, 5,53 und 5,69 in τ entsprechen syndiotaktischen, heterotaktischen bzw. isotaktischen Einheiten in Triaden. Durch Analyse der entkoppelten Spektren von zwei Arten des Polymeren wurden Parameter für die lokale Regelmässigkeit bestimmt.

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Conformation of Styrene–Maleic Acid Copolymer in Aqueous HCl Solutions*

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Synopsis

The properties of dilute aqueous solutions of styrene–maleic acid copolymer at low degrees of ionization are not compatible with a random coil model. Based upon a study of hydrodynamic and other solution properties of the copolymer, a model is proposed which considers intermolecular and intramolecular interactions of phenyl groups as well as forces of electrostatic repulsion of ionized carboxyl groups. Values of $[\eta]/[\eta]_\theta$ less than unity are better explained by intermolecular aggregation than by a hypercoiled conformation of individual chains. Difficulties previously encountered in copolymer fractionation were resolved.

INTRODUCTION

Aqueous HCl solutions of styrene–maleic acid copolymer (SYMA) exhibit anomalously low intrinsic viscosity when considered from the standpoint of Flory's[1] expansion factor, $\alpha^3 = [\eta]/[\eta]_\theta$, or the more recent development of Kurata, Stockmayer, and Roig[2] in which $\alpha^{2.43} = [\eta]/[\eta]_\theta$. In either case, the lower limit of α should be unity. The experimental measurement of an apparent expansion factor less than unity for SYMA in an aqueous solution, 0.006 and 0.008*M* with reference to HCl and KCl, respectively, led Dannhauser et al.[3] to suggest a hypercoiled chain configuration which was thermodynamically metastable. The present study is concerned with a more detailed investigation of these inconsistencies.

EXPERIMENTAL METHODS

A 1:1 copolymer of styrene and maleic anhydride (Monsanto Research Serial T-1022, supplied through the courtesy of Dr. Robert L. Miller, Plastics Division, Monsanto Chemical Company) was dissolved to a concentration of 0.50% in reagent grade dioxane and fractionated by successive addition of ten portions of cyclohexane. After separating phases

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in the fractionating flask, the subphase was redissolved in excess acetone, reprecipitated by the addition of cold, deionized water, filtered in a sintered glass funnel, and washed thoroughly with cold, deionized water. The precipitate was hydrolyzed at 60°C. in a 50-ml. portion of water, shell-frozen, and dried *in vacuo*. The solution and hydrodynamic properties of these fractions remained constant beyond the 3-month period required to complete the studies described below.

This fractionation procedure was an outgrowth of previous efforts which were unsatisfactory because dry fractions gradually became less soluble in storage. The unstable fractions had been dried *in vacuo* from dioxane solutions. It was presumed that crosslinking had been initiated during freeze-drying (perhaps by peroxides in the dioxane) and that a slow, free-radical polymerization continued in the solvent-free solid phase. Hence a procedure was contrived which avoided freeze-drying from dioxane solutions.

Viscosity measurements were made with Cannon-Ubbelohde dilution viscometers so chosen that kinetic energy corrections (less than 1%) could be neglected. Non-Newtonian flow effects were ignored.[6]

A Brice-Phoenix universal light-scattering photometer was used to measure 436 mμ radiation scattered 45°, 90°, and 135° from the incident beam. Refractive index increments were measured with a Brice-Phoenix differential refractometer. Standard procedures were used to calculate solute molecular weights.

Partial specific volumes were obtained with a 25 ml. pycnometer. A du Nouy tensiometer was used for surface tension measurements.

RESULTS

General Solution Characteristics

Solutions containing 0.5 g. of SYMA/dl. were stable at HCl concentrations up to and including 0.005*M*. These solutions could be heated to their boiling points without inducing precipitation. Metastable SYMA solutions existed in the range of 0.006 to 0.010*M* HCl. They could be maintained at room temperature several days without apparent change, but became turbid when heated to 50°C. This change was irreversible.

The partial specific volume of SYMA in aqueous HCl at 30.0°C. was 0.719 ± 0.005 ml./g. and, within limits of experimental error, was independent of HCl concentration within the range of 0–0.006*M*.

The refractive index increment per unit concentration of copolymer at 25°C. and 436 mμ was 0.180 ± 0.002 g./dl. and likewise was unaffected by added acid within the range of 0–0.006*M* HCl.

SYMA has surface-active properties in aqueous HCl solution inasmuch as the surface tension of the solvent was lowered 25% by the addition of a trace of solute and was unaffected by further increments in solute concentration. The surface tension reduction occurred at lower solute concentrations when fractionated samples of the copolymer were used (Fig. 1). The existence of a critical micelle concentration is suggested.

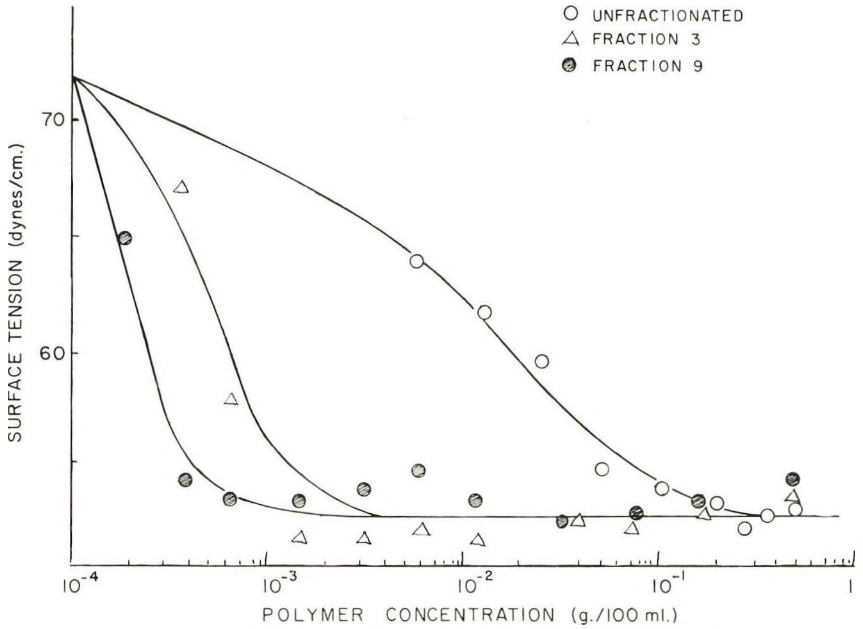

Fig. 1. Surface tension of SYMA solutions in $0.002M$ aqueous HCl at 25°C. as a function of polymer concentration.

Viscosity of SYMA in Aqueous HCl

The upswing of reduced viscosity upon dilution of the copolymer, so characteristic of polyelectrolytes, was repressed by the addition of HCl, and at concentrations of HCl equal to or greater than $0.002M$ meaningful extrapolations of reduced viscosity to obtain intrinsic viscosity were feasible (Fig. 2). Nevertheless, departures from linearity of these plots persisted to the lower ranges of copolymer concentrations, even to the greatest HCl concentration ($0.010M$) at which metastable solutions could be manipulated. The copolymer concentration at which the upswing in reduced viscosity occurs may be associated with a critical micelle concentration.

The intrinsic viscosity of SYMA in $0.010M$ HCl is remarkably near the ultimate limit based upon a model of inpenetrable spheres having the partial specific volume of SYMA quoted above. Furthermore, the reduced viscosity was directly proportional to the degree of ionization of SYMA (Fig. 3) within the copolymer concentration range of 0.500–0.125 g./dl.

Viscosity–Molecular Weight Relationships

Molecular weights of two fractions of SYMA in *sec*-butanol, a theta solvent at 40°C.,[3] were determined by light scattering. As expected, the slope of Hc/τ versus c curves was essentially zero. From measured values of intrinsic viscosity in *sec*-butanol, and from the relationship, $\log [\eta] = a \log M + k$, in which $a = 0.5$ for a theta solvent,[1] the molecular

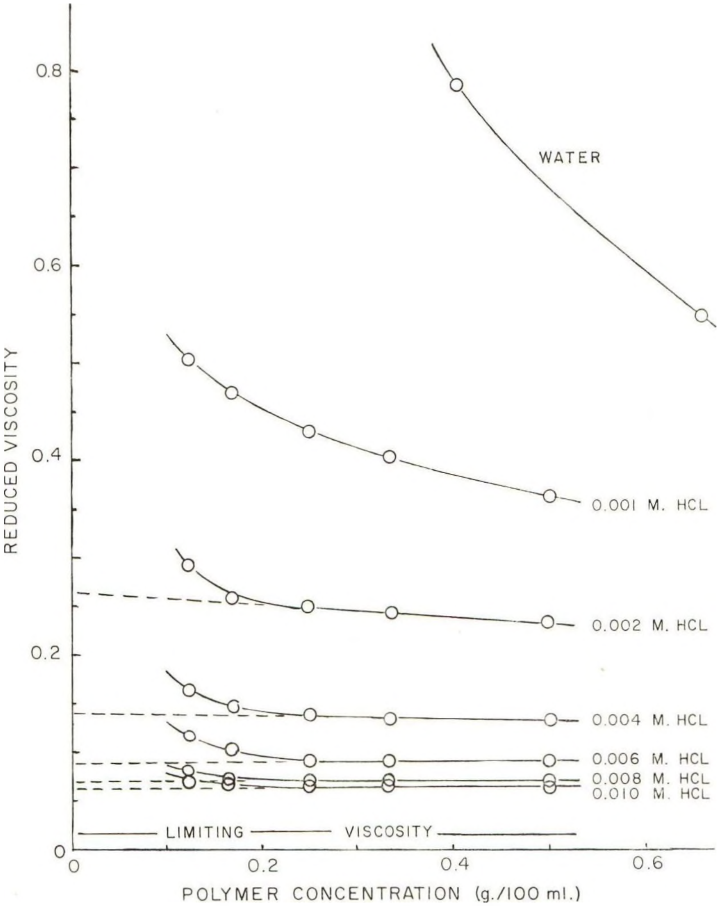

Fig. 2. Reduced viscosity η_{sp}/c vs. concentration of unfractionated SYMA at 30°C. for various levels of added HCl.

TABLE I
Molecular Weights by Light Scattering (M_{LS}) and Intrinsic Viscosities of Styrene–Maleic Acid Copolymer Fractions in *sec*-Butanol and in Aqueous HCl Solutions

	sec-Butanol, 40°C.		0.002*M* HCl, 30°C.		0.005*M* HCl, 30°C.		0.010*M* HCl, 30°C.	
Fraction	[η]	$M_{LS} \times 10^{-4}$	[η]	$M_{LS} \times 10^{-4}$	[η]	$M_{LS} \times 10^{-4}$	[η]	$M_{LS} \times 10^{-4}$
2B			0.516				0.110	
3B	0.631		0.492	27.8		26.6		
4B	0.573	3.60	0.395	23.3	0.155	22.2		
5B	0.480		0.307	17.5	0.140	16.4		
8B	0.398	1.85	0.216		0.104		0.081	
9B	0.318		0.152	9.5	0.083	9.1		
11B					0.070		0.063	

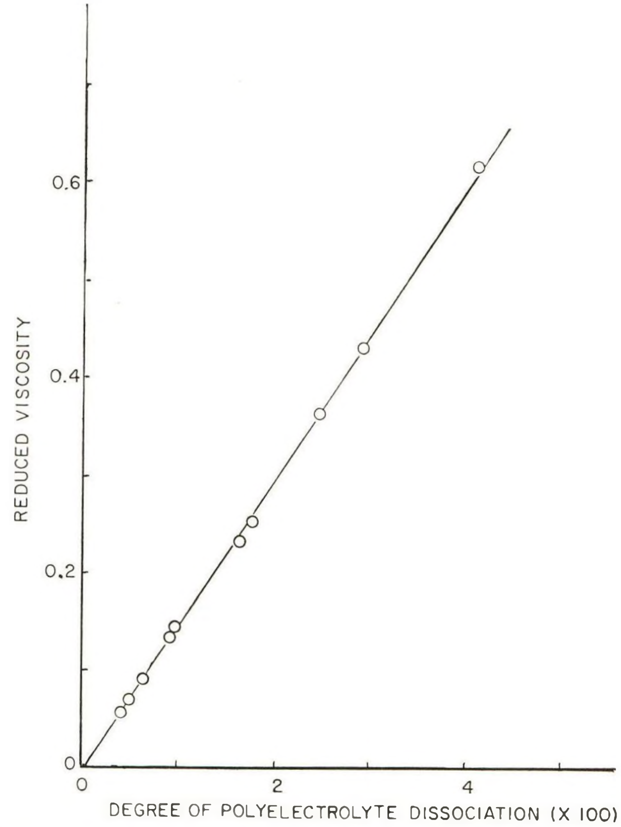

Fig. 3. Reduced viscosity η_{sp}/c (in a range of c of 0.175–0.500 g./dl.) of unfractionated SYMA aqueous HCl solutions at 30°C. vs. degree of polyelectrolyte dissociation. Degree of dissociation calculated by using the equilibrium constant measured by Ferry et al.[6]

weights of a set of five fractions were established (Fig. 4). When these molecular weights were used to calculate a for SYMA in aqueous HCl solutions, values below 0.5 were found in the region of metastability, i.e., at an HCl concentration of $0.010M$. On the other hand, $[\eta]/[\eta]_\theta$ was less than unity when the HCl concentration was greater than $0.002M$. Light scattered by these solutions indicated molecular weights 7 to 9 times greater than the molecular weights of the same fractions in the theta solvent (Table I). It is suggested that this is due to aggregation of solute molecules.

Temperature Effects

In the temperature range of 30–40°C. there was, within limits of experimental error, no influence of temperature upon the specific viscosity of solutions of two different fractions of SYMA in $0.002M$ HCl (Fig. 5). A small reversible decrease in specific viscosity occurred as the temperature was lowered through the range of 30–20°C. This effect may be indicative of an aggregate or micelle transition.

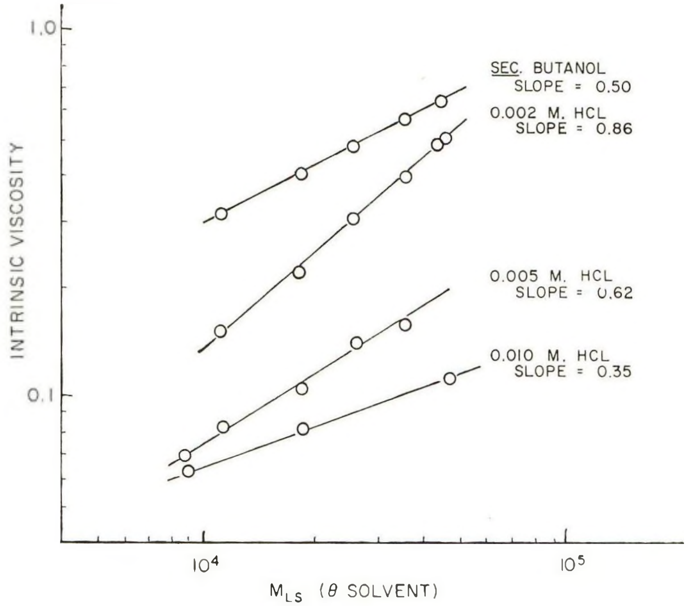

Fig. 4. Intrinsic viscosity [η] vs. molecular weight of SYMA fractions (determined by light scattering in a theta solvent) on a log–log scale.

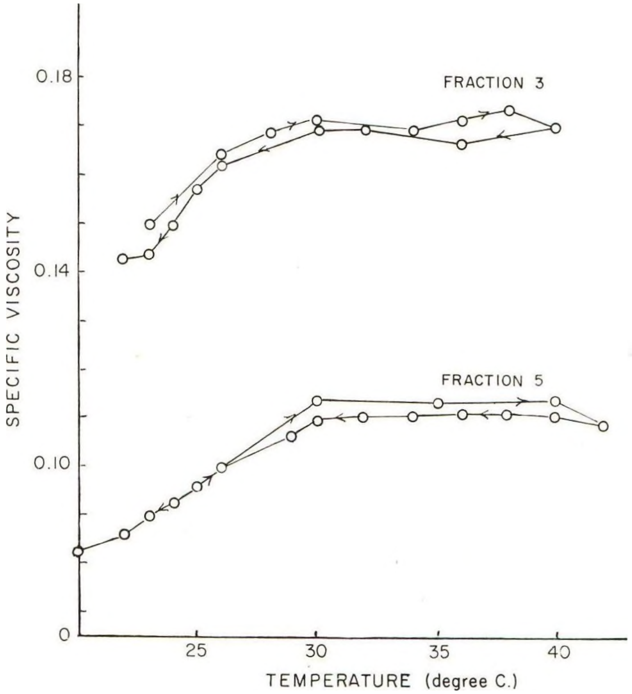

Fig. 5. The effect of temperature changes on the specific viscosity of solutions containing 0.33 g. SYMA/dl. 0.002M aqueous HCl.

DISCUSSION

The polyelectrolyte, SYMA, has an unbranched carbon backbone to which are attached regularly alternating hydrophilic carboxyl groups and hydrophobic phenyl groups.[4] The interaction of carboxyl groups with each other and with the solvent is quite sensitive to changes in the degree of ionization of the copolymer.[6] In aqueous solutions of low ionic strength one can expect strong electrostatic repulsion between ionized carboxyl groups. These forces would be manifested in two ways: (*a*) an extension or uncoiling of molecules, and (*b*) repulsion of neighboring molecules, an effect most pronounced in the more concentrated solutions. Interactions between phenyl groups, whether on the same molecule or neighboring chains have significant magnitudes in solvents of high dielectric constant[6,7] and are to be considered examples of hydrophobic bonding.[5]

That random coils do not exist in aqueous HCl solutions was clearly demonstrated by experimental measurements of $[\eta]/[\eta]_\theta$ values less than unity. A model which explains the properties of SYMA in such solutions requires a consideration, not only of electrostatic repulsion of ionized groups, but also the forces of attraction among phenyl groups. It is possible that aggregates form as a result of the close approach of phenyl groups attached to different chains. A relatively high density of phenyl groups in the interior of an aggregate would displace a proportionate number of carboxyl groups toward the periphery.

The results of the present study are presented as evidence that SYMA forms molecular aggregates as the degree of ionization of the copolymer is reduced in aqueous solutions. The studies of Strauss, et al.[8] on the transition from typical polyelectrolytes to polysoaps also relate to this type of system.

The following model is proposed to explain the properties of SYMA in aqueous HCl solutions. The copolymer in dilute solution is a typical electrolyte when the degree of ionization is appreciably greater than 0.050 because the electrostatic repulsion of ionized carboxyl groups is the dominant force. Aggregation begins to occur near a degree of ionization of 0.050 as shorter-range forces of phenyl group interaction come into play. In the range of 0.006–0.050 degree of ionization, the size of the stable aggregate is determined by a balance of a central contractile force and the electric potential near the periphery of the aggregate. Metastable solutions, in which the degree of ionization of the copolymer is less than 0.006, can be explained by interaggregate repulsion of peripheral charges on aggregates, comparable to metastable suspension of hydrophobic colloids. The existence of a critical micelle concentration is consistent with this model.

The proposed model suggests the possibility of finding a solvent in which aggregates could be inverted, i.e., an aggregate with a predominance of phenyl groups at the periphery and with hydrogen bonded carboxyl groups in the interior of the aggregate. Evidence for this type of inversion in the binary solvent, isopropanol–benzene, recently has been reported.[9]

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Résumé

Les propriétés des solutions aqueuses diluées du copolymère styrène–acide maléique à faibles degrés d'ionisation, ne sont pas compatible avec un modèle où les molécules seraient enroulées au hasard. Sur la base d'une étude hydrodynamique et d'autres propriétés du copolymère en solution, on a proposé un modèle qui tient compte des interactions inter- et intra-moléculaires des groupes phényles ainsi que des forces de répulsion électrostatique des groupes carboxyles-ionisés. Les valeurs $[\eta]/[\eta]_\theta$ inferieures à l'unité trouvent une meilleure explication dans l'aggrégation intermoléculaire que dans une conformation "hyper-enroulée" des chaînes individuelles. On a réussi à éliminer les difficultés rencontrées auparavant dans le fractionnement du copolymère.

Zusammenfassung

Die Eigenschaften verdünnter wässriger Lösungen eines Styrolmaleinsäurecopolymeren bei niedrigem Ionisationsgrad sind nicht mit dem Modell eines statistischen Knäuels vereinbar. Auf Grund einer Untersuchung der hydrodynamischen und anderen Lösungseigenschaften des Copolymeren wird ein Modell vorgeschlagen, das inter- und intramolekulare Wechselwirkung von Phenylgruppen und auch elektrostatische Abstossungskräfte von ionisierten Carboxylgruppen in Betracht zieht. Kleinere Werte von $[\eta]/[\eta]_\theta$ als eins werden besser durch intermolekulare Aggregation als durch eine "Hyperknäuel"-Konformation individueller Ketten erklärt. Frühere Schwierigkeiten bei der Copolymerfraktionierung konnten überwunden werden.

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Polymerization of 2-Nitroolefins

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Synopsis

A series of 2-nitroolefins was synthesized and polymerized, with particular attention given to 2-nitrobutene. Several catalysts were compared, and the sodium cyanide–dimethylformamide system studied in detail. Monomer aging had a pronounced effect on the polymerization of the nitromonomers. The polymerization under ideal conditions is exceedingly fast, and evidence favors chain termination by chain transfer to monomer. Molecular weights, even under optimum conditions, were low, and solvents with high dielectric constants were ordinarily necessary for polymer formation. The effect of chain length on polymer properties was also determined.

In the course of work related to the preparation of polymers applicable as ingredients for solid propellants, a series of 2-nitroolefins was synthesized and polymerized. Although literature exists concerning the preparation and reactions of these compounds,[1–4] their polymerization has been largely ignored except for cursory study of the three lowest members of the group, nitroethylene,[5,6] 1-nitropropene,[7–10] and 2-nitropropene.[11] The monomers are of particular interest because of the strong electronegative character of the nitro group which makes the double bond extremely susceptible to anionic polymerization. Their irritating lachrymatory properties have also discouraged more thorough investigation.

Another unusual aspect of this group of unsaturated compounds is the ability of 1-nitroolefins to polymerize, which is contrary to most other double bonds substituted at the terminal carbon. Greater attention has been applied to the 1-nitroolefins than to the 2-nitroolefins, a class more typical and comparable to other common polymerizable substituted olefins. Our work has been concerned with the 2-nitroolefins in which the appended alkyl group has been lengthened or modified.

An advantage of working with 2-nitroolefins is that in these polymers crosslinking through the active hydrogen of —$CH(NO_2)$ groups (found in the polymers resulting from 1-nitroolefins and nitroethylene) is precluded. Such active hydrogens can act as crosslinking sites by Michael additions to the monomer double bond.[12]

The 2-nitroolefins were prepared by the dehydration of the appropriate nitroalcohol.[3] The nitroalcohols were prepared by the condensation of the

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proper nitroalkane with formaldehyde according to well known methods.[13,14] The required nitroalkanes, when not available commercially, were prepared according to the method of Kornblum.[15] In agreement with Bloomquist,[11] we found that the usual preparative methods used for 1-nitroolefins such as the decomposition of the acetate or benzoate, gave poor yields when applied to the 2-nitroolefins. The product was a low molecular weight, viscous polymeric liquid.

Most of this work was carried out with 2-nitrobutene as a typical member of the group. It is a yellow-green, lachrymatory liquid, which on standing becomes increasingly darker in color. The lachrymatory properties of the group decrease noticeably with increase of alkyl chain length. Simultaneously with the color change, the monomer became more and more difficult to polymerize on standing (Table I).

TABLE I
Effect of Monomer Aging (Closed to Air)[a]

Time, hr.	Conversion, %	Inherent viscosity
0	100	0.113
0.5	100	0.116
1.0	90	0.116
3.0	65	0.098
6.5	50	0.040
18.0	<1	—

[a] Polymerization conditions: 25 ml. solvent (DMF); 2 ml. NaCN-DMF catalyst (0.4 mmoles); 4 ml. monomer; polymerization time, 30 min.

Polymerizability was not restored by passing the monomer through silica gel. Several attempts were made with vapor-phase refractometry to isolate any compounds formed during the monomer aging which could act as polymerization inhibitors. No new compounds could be detected, whether aging was carried out in air or under nitrogen, although other evidence indicated the presence of nitrogen oxides. Long heating, especially during distillation, gave monomer unsuitable for polymerization. The best monomer was obtained from a stainless steel spinning band column. When the monomer was allowed to stand a few hours open to the atmosphere, even at −5°C., no polymer would form with any initiator.

A large number of initiators, mostly basic in character, were tested in various solvents and at a number of temperatures (Table II). 2-Nitrobutene would not polymerize in the presence of aqueous potassium bicarbonate, a very efficient initiator for nitroethylene and the nitropropenes.

This is probably partially due to the decreasing solubility of the olefin in water, and partially to the retarding effect of the alkyl group on nucleophilic attack of the terminal carbon of the double bond. No polymers were obtained from free radical initiators. Of the large number of catalysts screened, none, regardless of solvent, afforded high molecular weight, insoluble polymer, as has been reported for the lower members of the group.

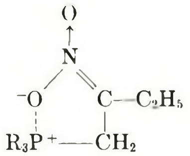
TABLE II
Effect of Catalysts and Solvents on Polymerization[a]

Catalyst	Solvents[b]	Temp., °C.	Conversion, %	Inherent viscosity
Tributylphosphine	Heptane, toluene, THF	−70, 25	0	
Triethylamine	Toluene	25	0	
N-Ethylmorpholine	Toluene	25	0	
$(Ethyl)_2NMgBr$	Heptane, toluene, THF	25, 50	0	
PhenylMgBr	Toluene, THF	50	0	
Lithium dispersion	Heptane, toluene, ether	−70, 25	0	
	DMF	25	60	0.076
	DMSO	25	70	0.115
Butyllithium	Heptane, toluene, ether	−70, 25	0	
	DMSO	25	100	0.067
Lithium aluminum hydride	Toluene	25	48	0.010
Sodium hydride	Toluene	25	0	
	DMSO	25	56	0.061
Sodium naphthalene	Toluene	25	35	0.137
	THF	25	42	0.055
NaCN–DMF	Heptane, toluene, water	25	0	
	CH_2Cl_2	25	20	0.090
	DMF	25	94	0.113

[a] Conditions: 25 ml. solvent; 5 ml. monomer; 0.05 ml. catalyst (as a 10% solution); 20 hr.; except for Na naphthalene, where 0.5 ml. catalyst was required.

[b] THF: tetrahydrofuran; DMF: dimethylformamide; DMSO: dimethyl sulfoxide.

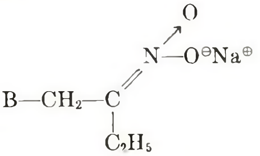
Tertiary amines or phosphines produced no polymer, although reaction occurred as evidenced by color change (to a bright red) and the heating of the solution. In one case in which the monomer was added to a 10% solution of triethylamine in diethyl ether, a violent reaction occurred resulting in spontaneous combustion of the solution. Polymerization with these Lewis bases is probably prevented by the formation of cyclic intermediates (I), which on addition to alcohol to precipitate polymer, are decomposed, reforming the initial reactants.[16]



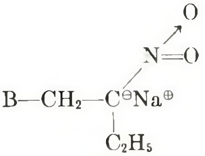
I

Difficulty was experienced in obtaining polymers in solvents of low dielectric constant. Although polymers were obtained with sodium naphthalene in toluene and tetrahydrofuran, and lithium aluminum hydride in toluene, excessively high concentrations of catalyst were required. Only the polymer obtained in the toluene–sodium naphthalene system had a molecular weight comparable to polymers obtained in the highly polar solvents. In this case, the intrinsic viscosity of the polymer increased from 0.055 to 0.137 when the reaction medium was changed from tetrahydrofuran to toluene. This is in agreement with other anionic polymerizations where it has been observed that the molecular weight of the polymer decreases with increasing dielectric constant of the solvent.[17]

Since the initial reaction between the catalyst and the monomer is probably the nucleophilic attack of the terminal carbon of the double bond, the main product to be expected would be the more stable (aci-nitro) ion pair (II). Because of the highly polar nature of this species, it might be expected that only in highly solvating media would separation of the ion pairs be facilitated, allowing formation of III. Product III may then act as an activated donor, adding to another acceptor olefin molecule forming the polymer.



II



III

In solvents such as dimethylformamide and dimethyl sulfoxide (dielectric constants 37.6 and 45, respectively) the ion pairs are probably almost completely dissociated, allowing the polymeric anions to exist in solution. It has been shown that the separation of ions of the $—C^{-}Na^{+}$ pair is much greater than the $—C^{-}Li^{+}$ pair.[18] This fact coupled with the high concentration of catalyst needed to initiate polymerization would account for the polymer obtained with the sodium naphthalene, the catalyst acting partly as an ion separating solvent.

The homogeneous catalyst system sodium cyanide–dimethylformamide was studied in more detail because of its convenience and reproducibility.[19] With 2-nitrobutene, the polymer obtained was a white opaque, amorphous powder melting in the range 95–125°C., depending upon its molecular weight. The polymer was soluble in solvents such as dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, and acetone, but insoluble in alcohols and hydrocarbons. Intrinsic viscosities, as determined in dimethylformamide at 30°C., were in the range of 0.01–0.15. As determined cryoscopically, these viscosities correspond to molecular weights of 1000–5000. Variation in the NaCN catalyst concentration resulted in no apparent change in molecular weight.

The effect of polymerization temperature is shown in Table III. It appears that the optimum temperature for polymerization is approximately 25°C. This is in agreement with observations on other catalysts. None of the polymers showed any crystallinity when observed in a polarizing microscope.

Polymerization with the sodium cyanide catalyst in dimethylformamide is exceedingly fast even at room temperature (Table IV).

TABLE III
Effect of Polymerization Temperature[a]

Temperature, °C.	Conversion, %	Melting range, °C.	Inherent viscosity
−60	30	92–97	0.040
−15	85	105–108	0.053
25	88	122–125	0.113
60	52	90–100	0.071

[a] Polymerization conditions: 25 ml. solvent (DMF); 2 ml. NaCN–DMF catalyst (0.4 mmole); 4 ml. monomer; polymerization time, 30 min.

TABLE IV
Dependence of Conversion of 2-Nitrobutene on Time[a]

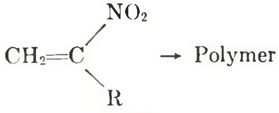
Time, min.	Conversion, %	Inherent viscosity
5	80	0.090
10	100	0.118
20	100	0.115
30	100	0.113

[a] Conditions: 4 ml. monomer; 25 ml. solvent (DMF); 2 ml. NaCN–DMF catalyst; temperature, 25°C.

Lowering the catalyst concentration or changing to a solvent of lower dielectric constant to produce a higher molecular weight polymer proved unsuccessful. Usually, no polymer at all was formed, or, as with methylene chloride, the expected increase in viscosity did not occur.

The data also indicated that the polymerization of 2-nitrobutene with sodium cyanide is independent of monomer concentration from approximately 1.4 to 2.5 moles/l., and independent of catalyst concentration from approximately 6 to 15 mmoles sodium cyanide per liter; this favors a mechanism in which termination occurs by chain transfer to the monomer.[20] Chain transfer of hydrogen from the secondary allylic carbon of the monomer would account for the low molecular weights obtained with these monomers in contrast to nitroethylene and 2-nitropropene.

A series of 2-nitroolefins was prepared in which the alkyl group R was lengthened or varied so that the effect of polymer structure on properties could be determined (IV) (Table V).



$$CH_2{=}C(NO_2)R \rightarrow \text{Polymer}$$

IV

Efforts to synthesize 2-nitrotridecene and 2-nitrobutadiene led to unexpected difficulties. With the former, the reaction of the alkyl bromide

TABLE V
Monomers and Polymers of Nitroolefins

	Monomer		Polymer		
Monomer	Yield, %	B.p., °C./mm. Hg	Conversion, %	Melting range, °C.	η_{inh}
2-Nitrobutene	71	61–62/55[a]	88	122–125	0.113
2-Nitropentene	50	53–54/20	62	90–110	0.053
2-Nitrooctene	58	66–67/4	67	56–64	0.044

[a] Lit.:[2] b.p. 60.5°C./50 mm.

[b] Lit.:[2] b.p. 58°C./20 mm.

with sodium nitrite in dimethyl sulfoxide or ether mixtures gave extremely low yields which were too low to be of use in polymerization studies.

We were unable to synthesize the nitrobutadiene through the diol intermediate; extensive degradation occurred on attempted purification. Purification attempts afforded only dark colored tars from the reaction of 3-nitropropene and formaldehyde.

EXPERIMENTAL

All melting points were determined with a Fisher-Johns melting point apparatus. Boiling points are uncorrected. Viscosity measurements were made in dimethylformamide solutions at 30°C. (0.5 g./100 ml. solvent).

Purification of Materials

All solvents except tetrahydrofuran and methylene chloride were purified by distillation from calcium hydride. Other purifications were carried out by previously described methods.[21] Catalysts were prepared by standard methods.

Preparation of Nitroalkanes

Nitroalkanes which were not available commercially were prepared according to Kornblum by using the corresponding alkyl bromide and dimethylsulfoxide as solvent.[15] Attempts to prepare 1-nitrododecene by this method failed. Yields and boiling points are as follows: 1-nitrobutane: 40% yield, b.p. 70°C./48 mm. (lit.:[22] b.p. 70°C./45 mm.); 1-nitroheptane: 52% yield, b.p. 90°C./10 mm. (lit.:[22] b.p. 64°C./3 mm.).

Preparation of 3-Nitropropene

Attempts to prepare 3-nitropropene by the reaction of sodium nitrite with allyl bromide in dimethyl sulfoxide were unsuccessful.[22] 3-Nitropropene was successfully prepared in 38% yield by the method of Kornblum and Iffland,[23] b.p. 55–57/51 mm. (lit.:[23] b.p. 39–40°C./20 mm.).

Preparation of Nitroalcohols

The following is a typical procedure for the preparation of the nitroalcohols, using 2-nitropentanol as an example. In a three-necked flask equipped with a stirrer, thermometer, and dropping funnel, were placed 149.3 g. (1.45 mole) of nitrobutane and a mixture of 375 ml. of water and 375 ml. of ethanol. The contents of the flask were cooled to 0°C., and 118 g. (1.45 mole) of 37% formalin was added with stirring. Then, 145 ml. of 10*N* potassium hydroxide was added dropwise, the temperature of the mixture being kept between +5 and −5°C. The mixture was further stirred for 1 hr. and then stored at a temperature of −5°C. for 5 days. It was neutralized with dilute hydrochloric acid, keeping the temperature at approximately 0°C., extracted with ether, and the ether extracts dried and distilled. The product had a boiling point of 68–69°C./0.6 mm. and was obtained in 56% yield (lit.:[14] b.p. 117°C./10 mm.). Similarly, 2-nitrooctanol was prepared in 68% yield, b.p. 104°C./0.4 mm. from formaldehyde and 1-nitroheptane.

ANAL. Calcd. for $C_8H_{17}O_3N$: C, 54.83%; H, 9.78%; N, 7.99%. Found: C, 55.01%; H, 9.83%; N, 8.12%.

1-Nitro-2-propanol, an intermediate for the preparation of nitrobutadiene, was prepared as previously described.[9] Attempts to distill this alcohol *in vacuo* resulted in extensive dehydration and polymerization. For this reason the alcohol was used directly for the preparation of the diol, by the reaction with formaldehyde. An attempt to distill the resulting 2-nitro-1,3-butanediol resulted in an explosion. The resulting black tar was water-soluble.[24]

2-Nitro-3-butenol was prepared by the reaction of 3-nitropropene with formaldehyde.[25] The dark viscous liquid, on standing, turned into a black tar. Tars were also obtained on attempted distillations.

Preparation of Nitroolefins

The nitroolefins were prepared from equimolar mixtures of corresponding alcohol and phthalic anhydride.[3] Yields and boiling points are given in Table V.

ANAL. Calcd. for (2-nitrooctene), $C_8H_{15}O_2N$: C, 61.12%; H, 9.62%; N, 8.91%. Found: C, 62.66%; H, 9.83%; N, 7.95%.

Difficulty was experienced in obtaining good analytical results with these monomers. The samples, although sealed under nitrogen in glass vials, decomposed as shown by their color change from green to red-brown. Evolution of nitrogen oxides was also evidenced by low analytical values for nitrogen. A vial containing 2-nitrobutene exploded on standing after the color change occurred.

The infrared spectrum of 2-nitrobutene contained strong absorption at 900 and 950 cm.$^{-1}$ typical of terminal vinyl compounds, in addition to absorption at 1350 and 1540 cm.$^{-1}$ typical of the nitro group, and nitro group conjugated with a double bond, respectively.[26] In addition, a strong absorption was observed at 840 cm.$^{-1}$, shifting to 855 cm.$^{-1}$ in the polymer. The remainder of the spectrum of both the monomer and polymer was consistent with its proposed structure.

Preparation of Polymers

Most polymerizations were carried out by placing freshly distilled monomer and solvent in predried syringe bottles, purging with helium or predried nitrogen, and capping with syringe stoppers. Catalysts were then syringed into the bottles, and placed on a shaker for the duration of polymerization. Polymers were isolated and purified by repeated dissolving in dimethylformamide and precipitating in methanol. Where larger amounts of polymer were desired, the polymerizations were carried out in 100 ml. stirred reactors.

ANAL. Calcd. for $(C_4H_7O_2N)_x$: C, 47.51%; H, 6.98%; N, 13.83%. Found: C, 47.74%; H, 7.14%; N, 13.76%.

Calcd. for $(C_5H_9O_2N)_x$: C, 52.16%; H, 7.88%; N, 12.17%. Found: C, 52.25%; H, 7.80%; N, 12.41%.

Calcd. for $(C_8H_{15}O_2N)_x$: C, 61.12%; H, 9.62%; N, 8.91%. Found: C, 61.42%; H, 9.42%; N, 8.12%.

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Résumé

Une série de 2-nitrooléfines a été synthétisée et polymérisée, avec une attention toute particulière pour le 2-nitrobutène. De nombreux catalyseurs ont été comparés et le système cyanure de sodium-diméthylformamide a été étudié en détail. Le vieilissement du monomère a un effet prononcé sur la polymérisation des monomères nitrés. La polymérisation dans des conditions idéales est excessivement rapide et il semble évident que la terminaison de la chaîne se fait par transfert de chaîne sur monomère. Les poids moléculaires, même dans les meilleures conditions, sont bas et des solvants de constante diélectrique élevée sont ordinairement nécessaires pour la formation du polymère. L'effet de la longueur de la chaîne sur les propriétés des polymères a aussi été déterminé.

Zusammenfassung

Eine Reihe von 2-Nitroolefinen, mit besonderer Beachtung des 2-Nitrobutens, wurde synthetisiert und polymerisiert. Eine grosse Zahl von Katalysatoren wurde verglichen und das Natriumcyanid-Dimethylformamidsystem im Detail untersucht. Die Alterung des Polymeren hatte einen grossen Einfluss auf die Polymerisation der Nitromonomeren. Unter Idealbedingungen verläuft die Polymerisation ausserordentlich rasch, und die Versuche sprechen für einen Abbruch der Ketten durch Kettenübertragung zum Monomeren. Die Molekulargewichte waren auch unter optimalen Bedingungen niedrig, und gewöhnlich wurden zur Polymerbildung Lösungsmittel mit hoher Dielektrizitätskonstante benötigt. Schliesslich wurde der Einfluss der Kettenlänge auf die Polymereigenschaften bestimmt.

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Dependence of the Glass Transition Temperature of Polyacrylonitrile on Molecular Weight

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Synopsis

The glass transition temperature of polyacrylonitrile has been determined for polymer varying in molecular weight from 8×10^3 to 3×10^6. Results could be represented by $T_g = (96.5 \pm 1.0) - (2.8 \pm 0.1) \times 10^5/\bar{M}_n$, giving for the glass temperature of a polymer of infinite chain length, 96.5 ± 1.0°C. Specimens showing coloration gave enhanced glass temperatures attributable to the stiffening effect of conjugated ring structures, and were excluded from consideration of the effect of molecular weight. Determinations of T_g were made on films prepared from solutions of polymer in dimethylacetamide, butyrolactone, and dimethyl sulfoxide in addition to dimethylformamide. Dependence on weight percentage of polymer, w_2, for the range $90 < w_2 < 100$ was given by $T_g = (3.19 \pm 0.03)w_2 - (232 \pm 4)$, no specific solvent effect being observed.

Many measurements of the glass transition temperature of polyacrylonitrile have been made and show a variation from 52 to 130°C. In the majority of cases little additional evidence has been given to characterize the polymers. The more reliable results of Kolb and Izard[1] and Howard[2] for polymer prepared in aqueous emulsion with persulfate–bisulfite initiator gave 87°C. Howard,[2] in addition, reports that different initiators produce polymers with glass temperatures of 92 and 103°C. Krigbaum and Tokita[3] have obtained 104°C., which is substantially in agreement with data previously published,[4] where 100.5 ± 0.5°C. was obtained for the glass temperature of a polymer of infinite chain length.

A limited investigation of the effect of molecular weight has been made by Keavney and Eberlin[5] using polymers varying both in molecular weight and conditions of polymerization from which the glass temperature of polymer of infinite chain length is 79°C. There is clearly a need for clarification of the effect of molecular weight on the glass transition behavior of polyacrylonitrile. Only then will it be possible to explore the effect of different initiating systems on the properties of the polymer.

EXPERIMENTAL

Polymers

Two polymers, W12 and W13, were prepared according to the redox recipe of Schildknecht,[6] details of which are given in Table I. Polymers

TABLE I
Conditions for the Redox Polymerization of Acrylonitrile

	W12	W13
Potassium persulfate, g.	1	
Ammonium persulfate, g.		0.1
Sodium bisulfite, g.	0.3	0.031
Acrylonitrile, ml.	100	100
Water, ml.	1400	1400
Time, hr.	1	3
Temp., °C.	40	40

covering a wide range of molecular weight were also available (see acknowledgments) prepared by conventional free radical initiators. Samples J1–J7, prepared at 60°C. with the use of benzoyl peroxide were of high molecular weight. Polymer of lower molecular weight was prepared by using azobisisobutyronitrile as initiator at 60°C. together with triethylamine (W1–W7) and diethylamine (W8–W11) as transfer agent.

Fractionation

About 20 g. of polymer (W12) in *N*,*N*′-dimethylformamide (DMF) (1% wt./vol.) at 60°C. was fractionated by addition of *n*-heptane.[7,8] Eleven fractions were retained, seven of which were used for glass transition measurements. The remainder of the solution containing 25% polymer was discarded. Fractionation of polyacrylonitrile is complicated by occurrence of aggregation[9] and in many respects is similar to the case of poly(vinyl chloride), which has been investigated by Menčík.[10]

Molecular Weights

Intrinsic viscosities were measured in DMF solution at 25°C. and molecular weights calculated from the relation of Kobayashi[11]

$$[\eta] = 2.78 \times 10^{-4}\bar{M}_n^{0.76}$$

Film Preparation

There is substantial evidence that polyacrylonitrile is partly crystalline, and Krigbaum and Tokita[3] have reported several measurements of the limited crystallization of polymer in DMF solution. In order to minimize the effect of crystallization, all films were prepared under identical conditions as previously described.[4] Solvent removal was carried out in two stages, at 50°C. to give a film containing 8–10% by weight of solvent, and at 100°C. to remove most of the remaining solvent. From the limited data of Krigbaum and Tokita,[3] the relation between crystallization temperature T_c and volume fraction of polymer V_2 is approximately,

$$T_c = 127V_2 + 7$$

Thus during preliminary drying crystallization will occur for $V_2 = 0.35$ but will be small, since the rate of removal of solvent is rapid. During the more prolonged final drying the temperature is well below the crystallization temperature.

Density

The density of polymer films at 25.0 ± 0.01°C. was obtained by using a gradient column prepared from aqueous $CaCl_2$ solutions. Reproducibility was ±0.001 g./ml.[12]

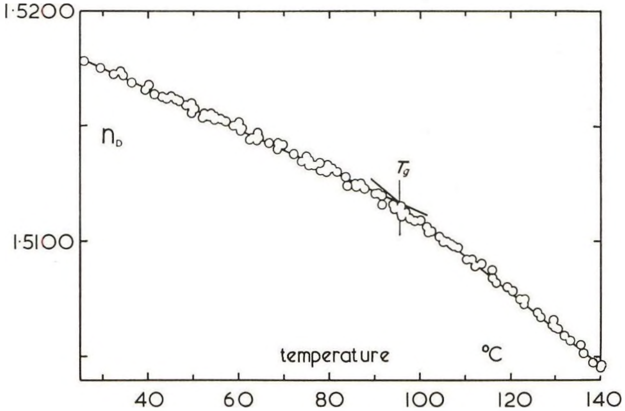


Fig. 1. Dependence on temperature of the isotropic refractive index for polyacrylonitrile (specimen J2, sodium light), with a glass transition at 95.5°C. Repeat observations, heating and cooling runs are not distinguished.

Determination of Glass Transition Temperatures

Glass temperatures T_g were determined refractometrically as described previously.[13] A typical plot of isotropic refractive index (sodium light) against temperature for polyacrylonitrile (sample J2) is given in Figure 1. The data comprise two sets of observations in each case, the temperature being increased and decreased through the glass transition region. In this case the polymer film contained a small amount of DMF and gave a glass transition at 95.5°C. Values of T_g given in Table II were obtained by extrapolation, in all cases over a very small concentration range, of a series of measurements on films containing a decreasing amount of solvent. The thin films used showed two overlapping sets of Herschel fringes in the field of view of the Abbé refractometer which were polarized parallel and perpendicular to the plane of incidence at the critical boundary. An isotropic refractive index for sodium light was calculated for each temperature from $3n_D = (2n_\perp + n_\parallel)$ and used for calculations of the glass-transition data of Table II and the interpolated 25°C. value of the refractive index.

RESULTS

Glass transition data for polyacrylonitrile samples varying in molecular weight from 8×10^3 to 3×10^6 are given in Table II, and the dependence of T_g on molecular weight is shown plotted in Figure 2. Each value of T_g

TABLE II
Properties and Glass Transition Data for Polyacrylonitrile Specimens of Different Molecular Weight

Specimen[a]	$\bar{M}_n \times 10^{-3}$	n_D^{25}	d_4^{25}, g./ml.	$(n_\perp - n_\parallel) \times 10^4$	$(dn/dT)_g \times 10^4$, deg.$^{-1}$	$(dn/dT)_r \times 10^4$, deg.$^{-1}$	T_g, °C.
J6	3260	1.5178	—	33	0.92	1.80	95.5
J4	2460	1.5162	1.201	30	0.88	1.66	95.2
J5	2230	1.5180	1.198	32	1.03	1.86	99.5
J3	1750	1.5174	1.198	32	0.86	1.64	94.5
J1	1120	1.5188	1.204	37	0.93	1.48	100.0
J2	1020	1.5174	1.205	33	0.94	1.80	96.5
W7	877	1.5190	1.197	41	0.92	1.58	101.2
W13	676	1.5174	1.199	49	0.90	1.50	91.2
W12f	254	1.5176	1.200	35	0.99	1.74	95.0
W6	249	1.5192	1.200	31	0.95	1.72	98.0
W12f	179	1.5173	1.207	39	0.91	1.76	95.0
W12	140	1.5203	1.206	35	0.96	1.72	90.2
W12f	103	1.5172	1.200	29	0.92	1.78	85.8
W12f(1y)	100	1.5183	1.197	38	1.00	1.80	92.0
W11(1y)	65.2	1.5230	1.201	14	1.09	1.80	100.6
W12f(1y)	64.6	1.5179	1.204	28	1.04	1.84	93.2
W4	57.9	1.5193	1.195	24	0.90	1.68	98.4
W12f(1y)	42.2	1.5189	1.205	31	1.10	1.84	98.5
W10(1y)	38.9	1.5276	1.208	3	1.02	1.86	102.5
W12f	35.6	1.5172	1.201	33	1.15	1.52	95.0
W3	29.2	1.5185	1.199	22	0.96	1.56	79.5
W2	19.3	1.5172	1.196	21	0.96	1.66	83.3
W9(dy)	12.1	1.5314	1.226	7	1.08	1.60	88.5
W1(y)	8.53	1.5189	1.195	12	1.16	1.74	92.5
W8(y)	8.24	1.5308	1.210	8	0.98	1.63	98.0

[a] f denotes fractionated sample: color is indicated by (ly), light yellow; (y), yellow; (dy), dark yellow.

is the mean of a number of experiments as described and reproducible to ±2.0°C. Several samples, particularly those of low molecular weight,

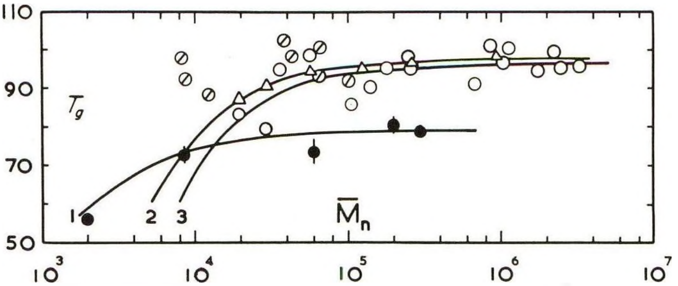


Fig. 2. The dependence of the glass transition temperature, T_g, on number-average molecular weight, $\bar{M}_n$, for polyacrylonitrile. Lines are plotted from the eq., $T_g = T_g^\infty - a/\bar{M}_n$ with (*1*) (●) $T_g^\infty = 78.9$°C., $a = 0.41 \times 10^5$ deg., (data of Keavney and Eberlin;[5] (*2*) (△) $T_g^\infty = 91.7$°C., $a = 2.0 \times 10^5$ deg. (previous data[4]); (*3*) $T_g^\infty = 96.5$°C., $a = 2.8 \times 10^5$ deg., for (○) data from Table II and (⦶) colored samples.

showed some coloration following removal of solvent and have been distinguished in the table by letters indicating qualitatively the extent of coloration. Colored samples are also distinguished among the data of Figure 2.

Accuracy of determination of T_g for polyacrylonitrile is much less than for poly(methyl methacrylate)[13] and other amorphous polymers, since the dependence of refractive index on temperature in the region above the glass temperature is much reduced. Mean values for both regions are, $-(dn/dT)_g \times 10^4 = 0.98 \pm 0.08$ deg.$^{-1}$, $-(dn/dT)_r \times 10^4 = 1.70 \pm 0.11$ deg.$^{-1}$ and compare favorably with previous values,[4] i.e., $-(dn/dT)_g \times 10^4 = 0.88 \pm 0.06$ deg.$^{-1}$, $-(dn/dT)_r \times 10^4 = 1.42 \pm 0.08$ deg.$^{-1}$.

Excluding colored samples, mean values for the refractive index and density are, $n_D^{25} = 1.5180 \pm 0.0010$, $d_4^{25} = 1.200 \pm 0.004$ g./ml., whereas previously[14] (specimen 14), $n_D^{25} = 1.5187$ and $d_4^{25} = 1.213$ g./ml.

DISCUSSION

Effect of Molecular Weight

The dependence of the glass transition temperature of polyacrylonitrile on molecular weight is shown in Figure 2, together with earlier data,[4] the molecular weights in this case being recalculated by the relation of Kobayashi.[11] Keavney and Eberlin made use of the relation of Cleland and Stockmayer,[15] and their molecular weight values have not been recalculated. The results show a greater spread than was found previously[13] for poly(methyl methacrylate) or by Fox and Flory[16] for polystyrene. This partly arises from the much smaller ratio of $(dn/dT)_r$ to $(dn/dT)_g$ for polyacrylonitrile. If the data for colored samples, separately identified in Figure 2, are discounted for reasons which will be discussed below, then the present results clearly reaffirm those given previously and shows the data of Keavney and Eberlin[5] to be incorrect. In this case values of T_g were determined by differential thermal analysis, which may be difficult to interpret in the case of polyacrylonitrile although satisfactory agreement was obtained for several amorphous polymers.

The results have been evaluated by the use of the Fox and Flory[16] relationship:

$$T_g = T_g^{\infty} - a/M$$

where a is a constant, M the molecular weight, and T_g^{∞} the glass transition temperature for a polymer of infinite chain length. From a least-squares analysis of the data the constants for the various sets of results are: (*1*) Keavney and Eberlin,[5] $T_g^{\infty} = 78.9 \pm 2.0$°C., $a = (0.41 \pm 0.1) \times 10^5$ deg.; (*2*) previously,[4] $T_g^{\infty} = 97.7 \pm 1.0$°C., $a = (2.0 \pm 0.1) \times 10^5$ deg.; (*3*) Table II, $T_g^{\infty} = 96.5 \pm 1.0$°C., $a = (2.8 \pm 0.1) \times 10^5$ deg. These data were used to plot curves *1*, *2*, and *3* in Figure 2. The difference between curves *2* and *3* is hardly significant. The value of T_g^{∞} given here (curve *2*) differs from the value previously given[4] of 100.5 ± 0.5°C. which was derived from a statistical mechanical equation of Gibbs and DiMarzio.[13] In view of the greater unreliability of the polyacrylonitrile results as compared with poly(methyl methacrylate) it was not considered worthwhile to repeat these calculations.

Values of T_g for specimens W12 and W13 are low and in better agreement with the measurements of Howard[2] and Kolb and Izard.[1] This may indicate some branching in polymer prepared by redox recipes. There is no evidence, however, of a significant degree of branching in the very high molecular weight polymers, as deduced by Peebles[17] from Zimm plot distortion. This would result in a fall in T_g as shown, for example, by acrylonitrile–acrylamide graft copolymers.[18]

Calculation of $(dV/dT)_g$ and $(dV/dT)_r$, where V is the specific volume of the polymer, from the mean refractometric data given in Table II enables a further check to be made. Assuming the Lorenz–Lorentz relation to hold,[13]

$$[R_{\mathrm{D}}]/M_rV = (n^2 - 1)/(n^2 + 2)$$

where $[R_{\mathrm{D}}]$ is the molar refractivity and M_r the residue molecular weight. Differentiation yields

$$(1/V)(dV/dT) = -[6n/(n^2 + 2)(n^2 - 1)](dn/dT) = \beta$$

Taking mean values for the specific volume, $V = (d_4^{25})^{-1}$, $n = (n_{\mathrm{D}}^{25})_{\mathrm{iso}}$ and the corresponding values of dn/dT gives $(dV/dT)_g = (1.8 \pm 0.3) \times 10^{-4}$ g./ml.-deg., $(dV/dT)_r = (3.3 \pm 0.2) \times 10^{-4}$ g./ml.-deg., and $\beta_g = (1.6 \pm 0.1) \times 10^{-4}$ deg.$^{-1}$, $\beta_r = (2.8 \pm 0.1) \times 10^{-4}$ deg.$^{-1}$. These values compare favorably with those given by Kolb and Izard,[1] (see Table III). The data of Howard[2] have been evaluated assuming the coefficient of cubical expression to be three times the linear expansion.

TABLE III

Coefficient of Cubical Expansion for Polyacrylonitrile

Source	$\beta_g \times 10^4$, deg.$^{-1}$	$\beta_r \times 10^4$, deg.$^{-1}$
Howard[2]	2.3	3.4
Kolb and Izard[1]	1.4	3.0
Present study	1.6 ± 0.1	2.8 ± 0.1

Colored Specimens

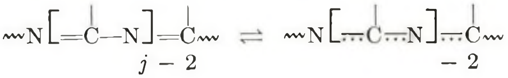
The presence of a color in polyacrylonitrile is evidence of some structural change, the nitrile groups most probably linking to form a conjugated sequence $\left(\mathrm{C{=}N}\right)_n$.[19] This is partly established by the increase in absorption at 1600 cm.$^{-1}$ with increase in coloration. Degree of coloration will depend on the number and planarity of these sequences, and will be affected by the stereoregularity of the chain.[20] The presence of conjugated sequences of C=N groups reduces the flexibility of chain segments, readily demonstrated by space-filling atomic models. The molecular chains are found to pack more closely, and this is affirmed by x-ray examination of colored polymer which shows the intermolecular spacing to decrease from 5.2 to 3.5 A. This will have a direct effect on the glass transition properties and result in an increase in T_g, as shown in Figure 1, by the colored samples. It is reasonable, therefore, to exclude data on colored polymers when considering the molecular weight dependence of the glass temperature.

Further evidence of structural change is given by the low values of $(n_\perp - n_\parallel)$ and the high refractive index of these specimens as given in Table II. Calculation of the molar refractivity shows that in principle the fraction of cyclic imines in the polymer could be estimated. Using mean values of group refractivities given by Vogel, Creswell, Jeffrey, and Leicester,[21] values of $[R_D]$ for polyacrylonitrile and polymer completely conjugated are 13.09 and 12.03, respectively. From the mean values of V_4^{25} and $(n_D^{25})_{iso}$ given above, $[R_D] = 13.4 \pm 0.1$ and was identical, within experimental error, with $[R_D]$ for the most colored specimen, W9, so that the extent of cyclic structures unfortunately remains undetermined but must be less than 10%.

Calculation of the absorption band wavelength λ and its dependence on conjugation may be made using the free-electron theory of Kuhn.[22] For the polyenes this is given by,

$$\lambda = \{(V_0/hc)/1 - (1/N) + (h/8mc)[(N+1)/L^2]\}^{-1}$$

where h is Planck's constant, m the mass of the electron, c the velocity of light, L the length of the conjugated chain, and N the number of π electrons. The periodic potential along the conjugated sequence is of amplitude V_0 and may be taken as approximately equal to 2.0 e.v. For the structure,



$$\sim\!\mathrm{N}\Big[\!=\!\overset{|}{\mathrm{C}}\!-\!\mathrm{N}\Big]_{j-2}\!=\!\overset{|}{\mathrm{C}}\!\sim \;\rightleftharpoons\; \sim\!\mathrm{N}\Big[\!\cdots\overset{|}{\mathrm{C}}\cdots\mathrm{N}\Big]_{-2}\!\cdots\overset{|}{\mathrm{C}}\!\sim$$

containing j elements,

$$N = 2j$$

$$L = (l_1 + l_2)(j + 1/2)$$

where l_1 and l_2 are the bond lengths in the element. Using values of the covalent radii for the partial double bonds given by Pauling,[23] $l_1 = l_2 = 1.33$ A., and we then have,

$$\lambda = 6.20 \times 10^3[1 - (2j)^{-1} + 10.6(2j + 1)^{-1}]^{-1}$$

The observed coloration in the polymer can be accounted for by a small amount of conjugation, $j < 20$. For sample W9 with $M_r = 53.06$, the degree of polymerization is approximately 230, so that only about 10% of the residues are involved, which gives additional weight to the conclusions based on molar refractivity.

Effect of Solvent on T_g

Results given in Table II are derived from measurements made on films prepared from solutions of polymer in DMF. Some uncertainty attaches to the role played by the solvent in deciding the glass temperature of the dry weight polymer, particularly since it can be shown that some solvents are to be preferred in developing crystallinity. A least-squares analysis of the data of Krigbaum and Tokita[3] shows a small effect of solvent, their data for DMF being represented by,

$$T_g = (1.25 \pm 0.11)w_2 - (19.2 \pm 3.6)$$

and for γ-butyrolactone,

$$T_g = (0.80 \pm 0.02)w_2 + (21.3 \pm 4.0)$$

where w_2 is the weight per cent of polymer. This gives for the dry weight polymer $T_g = 106 \pm 7$°C. and $T_g = 101 \pm 6$°C., respectively.

Similar measurements have been made for polymer sample W12 including also solutions in dimethyl sulfoxide and *N,N'*-dimethylacetamide for the concentration range, $90 < w_2 < 100$. The results showed a greater random variation than previously observed[4] for acrylonitrile–methyl methacrylate copolymers, and no specific solvent effect was observed, T_g being given by

$$T_g = (3.19 \pm 0.03)w_2 - (232 \pm 4)$$

This represents the mean of 26 observations and gives for the dry weight polymer, $T_g = 87.0 \pm 4.0$°C., a value not significantly lower than that given in Table II based only on data for DMF.

In addition to the lack of solvent discrimination, dependence on w_2 is much greater than found by Krigbaum and Tokita.[3] The effect of solvents and plasticizers on T_g is usually large, and the effect of solvent has not previously been appreciably different apart from a dependence on copolymer composition.[4] For an acrylonitrile–methyl methacrylate block copolymer (mole fraction MMA = 0.31)

$$T_g = (4.92 \pm 0.02)w_2 - (382 \pm 2)$$

Dilatometric data[24] for an acrylonitrile–methyl acrylate random copolymer (mole fraction MA = 0.10) gave

$$T_g = (3.87 \pm 0.02)w_2 - (319 \pm 2)$$

which was entirely in agreement with refractometric observations on the same polymer.

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Résumé

On a déterminé le point de transition vitreuse du polyacrylonitrile, le poids moléculaire du polymère variant de 8×10^3 à 3×10^6. Les résultats expérimentaux s'expriment par la formule empirique suivante: $T_g = (96.5 \pm 1.0) - (2.8 \pm 0.1) \times 10^5/\overline{M}_n$. Le point de transition vitreuse à poids moléculaire infini est 96.5 ± 1.0°C. Les échantillons colorés ont un point de transition vitreuse plus élevé. Ce phénomène doit être attribué à l'augmentation de rigidité introduite par les cycles conjugués. Ces échantillons ont été exclus des considérations concernant l'influence du poids moléculaire sur le T_g. On a également déterminé le point de transition vitreuse de films de polymère préparés à partir de solutions dans le diméthylacétamide, la butyrolactone et le diméthylsulfoxyde en plus des films préparés à partir de diméthylformamide. La dépendance du T_g de la fraction pondérale en polymère w_2 s'exprime dans la gamme $90 < w_2 < 100$, par la relation empirique: $T_g = (3.19 \pm 0.03)\, w_2 - (232 \pm 4)$. On n'a pas observé d'influence due à la nature du solvant.

Zusammenfassung

Die Glasumwandlungstemperatur von Polyacrylnitril wurde für Polymere im Molekulargewichtsbereich von 8×10^3 bis 3×10^6 bestimmt. Die Ergebnisse können durch $T_g = (96{,}5 \pm 1{,}0) - (2{,}8 \pm 0{,}1) \times 10^5/\overline{M}_n$, dargestellt werden, was für die Glastemperatur eines Polymeren mit unendlicher Kettenlänge 96,5 ± 1,0 °C ergibt. Proben, die Verfärbung zeigten, lieferten eine erhöhte Glastemperatur, was auf den Versteifungseffekt konjugierter Ringstrukturen zurückgeführt werden kann; sie wurden bei der Untersuchung eines Einflusses des Molekulargewichts nicht berücksichtigt. Die Bestimmung von T_g wurde an Filmen aus Polymerlösungen in Dimethylacetamid, Butyrolacton und Dimethylsulfoxyd zusätzlich zu solchen aus Dimethylformamid durchgeführt. Die Abhängigkeit vom prozentuellen Gewichtsanteil an Polymerem, w_2, im Bereich von $90 < w_2 < 100$ ist gegeben durch $T_g = (3{,}19 \pm 0{,}03)w_2 - (232 \pm 4)$. Es wird kein spezifischer Lösungsmitteleffekt beobachtet.

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Interaction Parameters and Heats of Dilution for Ethylene–Propylene Rubber in Various Solvents

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Synopsis

Crosslinked ethylene–propylene rubber gels were swollen in five solvents at 25–100°C. The solvent–polymer interaction parameter μ for each system was determined as a function of temperature and polymer concentration. A thermodynamic criterion of the sign of the heat of dilution, $\Delta\bar{H}_1$, was pointed out. For three of the systems $\Delta\bar{H}_1$ was negative. The entropy contribution to the interaction parameter was found to be smaller than usual for systems having a temperature-dependent heat of dilution. The heats of dilution and the entropy terms may be consistently interpreted in terms of Prigogine's theory of solutions.

Introduction

According to the usual approximations, the free energy of dilution of polymer solutions depends only on properties of the polymer and of the solvent and on the solvent–polymer interaction parameter μ:[1,2]

$$\Delta\bar{F}_1/RT = \ln(1 - v_2) + (1 - \bar{V}_1/\bar{V}_2)v_2 + \mu v_2^2 \qquad (1)$$

Here, v_2 is the volume fraction of polymer in the solution, $\bar{V}_1$ is the molar volume of the solvent, and $\bar{V}_2$ is the molar volume of the polymer. Thus μ provides a measure of the solvent power of a given liquid for a polymer. This parameter was originally conceived to be an interaction energy, but was later recognized to be a free energy. It is, generally, not constant for a particular solvent–polymer system but varies with composition of the solution and with temperature.[3–6] If μ does indeed vary with composition, then eq. (1) is inappropriate and should be replaced by:[7]

$$\Delta\bar{F}_1/RT = \ln(1 - v_2) + (1 + \bar{V}_1/\bar{V}_2)v_2 + \mu v_2^2 - (1 - v_2)\sigma v_2^2 \qquad (2)$$

where $\sigma = (d\mu/dv_2)$. The explicit variation of μ with both temperature and composition has been determined for only a few solvent–polymer systems. This paper describes such an evaluation for several systems of a solvent plus ethylene–propylene rubber (EPR). The heats of dilution are then derived from these data.

A convenient way to measure μ is by equilibrium swelling of crosslinked polymer gels in a solvent, provided that the molecular weight between crosslinks is known:

$$-[\ln(1 - v_2) + v_2 + \mu v_2^2] = (\bar{V}_1\rho_2/M_c)\,(v_2^{1/3} - v_2/2) \qquad (3)$$

Here ρ_2 is the density of the polymer and M_c is the molecular weight between crosslinks. Crespi and Bruzzone[8] measured both the modulus and the degree of swelling for a series of EPR gels swollen in benzene at 25°C. They calculated M_c according to elastic theory:

$$f/RTA_0 = (\rho_2/M_c)v_2^{-1/3}(\alpha - \alpha^{-2}) \tag{4}$$

Here f is the applied force, A_0 is the unswollen cross-sectional area, and α is the relative elongation. These values of M_c were then used to calculate μ by using eq. (3). The formulation of μ as a function of v_2 which resulted was used in the present study to evaluate M_c for a number of EPR gels. Since μ is a function of v_2 for the system EPR–benzene, eq. (3) is inappropriate,[7] as is Crespi and Bruzzone's equation for the concentration dependence of μ. However, the circular process of using their equation for the purpose of calibrating the value of M_c for a series of gels according to eq. (3) still gives the correct M_c. The calibrated gels were then swollen at several temperatures in various solvents. Using χ for the apparent value of μ obtained from eq. (3), χ was then expressed as a function of v_2 and T for each EPR–solvent system. The resulting expressions were then transformed, when necessary, into expressions for μ as a function of v_2 and T. The heat of dilution was obtained by differentiation of eq. (2):

$$\Delta\bar{H}_1 = \partial(\Delta\bar{F}_1/T)/\partial(1/T) = Rv_2^2[\partial\mu/\partial(1/T) - (1 - v_2)\partial\sigma/\partial(1/T)] \tag{5}$$

The entropy of dilution may then be obtained from eqs. (2) and (5). These two quantities are much more rigorous tests of solution theories than is the free energy, since errors in expressions for them often cancel one another to a large extent in the formulation of the free energy.

Experimental

Two samples of EPR were used. EPR-1 was an amorphous rubber containing 55 mole-% of ethylene and having a reduced specific viscosity of 9.7 (in decalin at 135°C.).* It was crosslinked as a 100-mil sheet with the use of 1% of dicumyl peroxide by heating for 1 hr. at 160°C. EPR-2 was Enjay MD 460 of slightly higher ethylene content and a reduced specific viscosity of 2. It was crosslinked as a 35-mil sheet by using 2 and 4% of dicumyl peroxide by heating for 1 hr. at 160°C.

The crosslinked sheets were extracted with boiling benzene for 3 days to remove extraneous products and most of the soluble polymer. The extracted gels were dried overnight at 60°C. in a vacuum oven. Gel densities were determined at 25, 50, and 75°C. by displacement of butanol in a pycnometer. An extrapolated value was used as the gel density at 100°C. since butanol started to swell the polymer at that temperature. The solvent densities were taken from the International Critical Tables and from A.P.I. Project 44. The densities are listed in Table I. All solvents used contained 0.01% of phenyl-β-naphthylamine as a stabilizer.

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* The EPR used by Crespi and Bruzzone had an intrinsic viscosity (in toluene at 30°C.) of 5.4 and contained 55 mole-% of ethylene.

TABLE I
Densities Used in Calculations

Compound	d_4^{25}	d_4^{50}	d_4^{75}	d_4^{100}
EPR-1 gel	0.8567	0.8417	0.8311	0.818
n-Heptane	0.6796	0.6583	0.6351	
Perchloroethylene	1.6070	1.5665	1.5260	1.4855
Chlorobenzene	1.1010	1.0738	1.0462	1.0182
Cyclohexane	0.7743	0.7506	0.7263	
Benzene	0.8737	0.8469	0.8191	

Pieces of the extracted gels weighing 0.5–1 g. were swollen in the various solvents at the temperatures (±0.1°C.) indicated in Table II. Swollen gels were withdrawn, blotted free of surface solvent and quickly transferred to glass-stoppered weighing bottles. Three or four days swelling was sufficient for equilibration. Weight swelling ratios were calculated on the basis of a final dry gel weight, as some additional soluble polymer was leached out over the course of several weeks' swelling. Careful examination of Table II, particularly of the swelling ratios of very similar gels under different swelling conditions, discloses a number of reversals of order of swelling ratios occurring in the second decimal place which corresponds to the fourth decimal place for the value of v_2. The effect of random errors on the calculated values of χ is shown by the standard errors in χ given in Table III. In addition there may be a systematic error resulting from evaporation of solvent from the swollen gels during handling.

When the heats of dilution were calculated from the swelling results, it was concluded that, for the EPR–tetrachloroethylene system, the heat of dilution, and dQ_w/dT should change sign below 25°C. To demonstrate this phenomenon, a loosely crosslinked gel of an EPR containing 48 mole-% of ethylene was first extracted at 70°C. then equilibrated successively at 25, 0, and −17°C. in tetrachloroethylene. The respective values of Q_w were: 31.43, 31.60, and 30.21.

Results

Since Crespi and Bruzzone's data were to be used for calibration, a least-squares fit of their results to $\chi = \alpha + \beta v_2$ was made to determine the precision. The resulting equation* is

$$\chi = 0.483 + 0.28v_2 \tag{6}$$

with a standard error of 0.003 in α and 0.01 in β. This equation and the modified Flory-Rehner equation, eq. (3), were used to calculate M_c from the benzene swelling at 25°C. The resulting values of M_c were used with the additional swelling data for the calculation of χ by eq. (3).

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* Dudek and Bueche[9] found using du Pont ECD-330 containing 53 mole-% ethylene that $\chi = 0.49 + 0.33v_2$ for the benzene system at 25°C.

TABLE IIA
Swelling Data, EPR-1 Gels

Solvent	Benzene at 25°C.		25°C. Swell		50°C. Swell		75°C. Swell		100°C. Swell	
	Q_w	$10^{-4}M_c$	Q_w	χ	Q_w	χ	Q_w	χ	Q_w	χ
n-Heptane	4.941	2.13	6.909	0.360	6.485	0.377	5.938	0.397		
	5.080	2.28	7.081	0.363	6.628	0.386	6.111	0.398		
Tetrachloroethylene	4.687	1.85	17.583	0.343	16.961	0.353	16.331	0.357	15.302	0.375
	4.706	1.87	17.536	0.348	17.107	0.352	16.280	0.362	15.449	0.374
Chlorobenzene	4.836	2.02	8.717	0.457	9.278	0.441	9.552	0.428	9.566	0.425
	4.823	2.01	8.518	0.462	9.142	0.444	9.497	0.429	9.594	0.424
Cyclohexane	4.973	2.17	10.295	0.312	9.773	0.325	9.181	0.339		
	5.120	2.37	10.658	0.313	10.164	0.324	9.615	0.335		
Benzene	5.611	2.94	5.610	0.532	7.619	0.482	8.413	0.460		
	5.361	2.62	5.399	0.537	7.181	0.484	8.173	0.454		

TABLE IIB
Swelling Data, EPR-2 Gels

	Benzene at 25°C.		Benzene at 75°C.			25°C. Swell		75°C. Swell	
Solvent	Q_w	$10^{-4}M_c$	Q_w	χ	$\chi_{\text{calc.}}$	Q_w	χ	Q_w	χ
n-Heptane	5.9196	3.30	9.3912	0.447	0.451	8.6377	0.353	7.5610	0.386
	5.9362	3.46	9.7207	0.444	0.450	8.6936	0.363	7.5730	0.392
	4.4846	1.61	6.3561	0.465	0.465	6.1102	0.356	5.2630	0.395
	4.3709	1.51	5.9974	0.473	0.468	5.8479	0.363	4.9663	0.407
	4.4297	1.57	6.2309	0.468	0.466	5.9592	0.361	5.0950	0.404
Tetrachloro-ethylene	6.2022	3.79	9.7618	0.454	0.450	25.9977	0.343	23.7815	0.363
	5.9362	3.65	9.7485	0.450	0.450	25.1585	0.349	23.8534	0.356
	4.1696	1.31	5.6891	0.472	0.470	14.8134	0.339	13.9151	0.353
	4.0944	1.25	5.4528	0.479	0.472	14.4342	0.340	13.5010	0.354
Chlorobenzene	6.3518	4.08	10.2971	0.445	0.448	12.5355	0.466	14.1388	0.416
	4.2334	1.36	5.7435	0.473	0.470	7.2467	0.462	7.9797	0.428
	4.2070	1.35	5.7104	0.474	0.470	7.3127	0.458	8.1033	0.424
Cyclohexane	6.6975	4.55	10.9602	0.446	0.446	14.9092	0.320	13.5516	0.337
	6.7041	4.67	11.3040	0.441	0.446	15.2082	0.321	13.6687	0.341
	4.2782	1.42	5.8314	0.474	0.469	8.2390	0.314	7.4911	0.335
	4.2692	1.41	5.8462	0.473	0.469	8.1965	0.315	7.2716	0.346
	4.2765	1.42	5.8054	0.475	0.469	8.2150	0.315	7.2503	0.349
Benzene only	8.3946	7.23	14.3979	0.437	0.440				
	7.9665	7.17	14.4669	0.436	0.440				

TABLE III
Coefficient in Equation (8)

Solvent	A	B	C	D	E	F	$\sigma\chi$
Cyclohexane	0.487	0	0	−51	0	0	0.004
n-Heptane	0.360	1.9	0	0	−570	0	0.004
Tetrachloroethylene	1.016	1.3	−7.1	−430	0	64,000	0.003
Chlorobenzene	0.938	0	0	−390	0	74,000	0.005
Benzene	0.912	0.76	0	−450	−143	95,000	0.003

Since EPR-2 had a considerably lower viscosity than EPR-1, and since the gel densities determined for EPR-1 were used with EPR-2 also, it seemed advisable to make certain that the results for the two sets of gels were in agreement. Consequently, an equation of the form $\chi = A + Bv_2 + C/T$ was calculated by multiple correlation analysis of the data of Crespi and Bruzzone at 25°C. pooled with the data for EPR-1 in benzene at 50 and 75°C. The resulting equation was

$$\chi = 0.057 + 0.28v_2 + 126.7/T \tag{7}$$

with a standard error of 0.004 in χ. At 25°C., eq. (7) reduces to $0.482 + 0.28v_2$, similar to eq. (6). The values of χ calculated by using eq. (7) for the EPR-2 gels in benzene at 75°C. are compared in Table IIB with the values of χ derived from the swelling of these gels. The standard deviation between the two sets of values was 0.002. This showed that the two sets of gels did indeed belong to the same population.

The combined data for swelling in benzene were then submitted to computer calculation of the best equation employing any of the terms:

$$\chi = A + Bv_2 + Cv_2^2 + D/T + Ev_2/T + F/T^2 \tag{8}$$

Similar equations were computed for each of the other solvent–EPR systems. The values of the coefficients in eq. (8) and the standard error in χ are listed in Table III for each system.

The solvents are listed in order of increasing χ or decreasing solvent power at 25°C. Examination discloses that the aliphatic solvents get poorer and the aromatic solvents improve with increasing temperature in the range studied. The values of χ for the cyclohexane and chlorobenzene systems were independent of composition over the range studied whereas the values for the other systems depended on both composition and temperature. Consequently, for the heptane, tetrachloroethylene, and benzene systems, eq. (8) was transformed into an expression for μ with the aid of eqs. (1) and (2):

$$\begin{aligned}\mu &= (A + B/2 + 2C/3) + (B/2 + 2C/3)v_2 + (C/3)v_2^2 + (D + E/2)/\\ &\qquad T + Ev_2/2T + F/T^2\\ &= a + bv_2 + cv_2^2 + d/T + ev_2/T + f/T^2 \end{aligned} \tag{9}$$

These coefficients are listed in Table IV.

TABLE IV
Coefficient in Equation (9)

Solvent	a	b	c	d	e	f
n-Heptane	1.31	0.95	0	−285	−285	0
Tetrachloroethylene	−2.9	−3.9	−2.4	−430	0	64,000
Benzene	1.29	0.38	0	−520	−71	95,000

The above results were obtained with crosslinked EPR. However, calculation shows that the slight difference in density between crosslinked network and the uncrosslinked polymer would not detectably affect the results (Table V). Consequently these results should also apply to uncrosslinked EPR.

TABLE V
Effect of Difference in Density

		Swollen in benzene at 25°C.		
Polymer	d_4^{25}	v_2	V_1/M_c	χ
EPR-2 gel	0.8555	0.20000	0.00391	0.538
Gel corresponding to EPR-2 gum	0.8531	0.20045	0.00391	0.539

Discussion

A simple, yet rigorous, thermodynamic relationship applicable to swelling at different temperatures has escaped general emphasis. It applies irrespective of any theory of polymer solutions. For any binary system of two phases in which one component is confined to a solution phase and the other component is also present as a unary phase (which may be vapor, liquid, or solid), the condition for equilibrium is:[10]

$$-(\partial\mu_1/\partial\ln x_1)_{T,P}\, d\ln x_1 + (\bar{V}_1'' - \bar{V}_1')\, dp - L d\ln T = 0$$

where component 1 is present in both phases; μ_1 is the chemical potential of the solvent in the solution phase and L is the enthalpy of transferring one mole of component 1 from an infinite amount of the solution phase to the unary phase. The partial derivative in the first term is always positive. For our system of a swollen gel in a solvent, $L = -\Delta\bar{H}_1$. At constant pressure,

$$d\ln x_1/dT = (\Delta\bar{H}_1/T)(\partial\mu_1/\partial\ln x_1)_{T,p}$$

and for an increase in temperature $\Delta\bar{H}_1$ must be of the same sign and proportional to $d\ln x_1$. Moreover,

$$d\ln x_1 = (x_2{}^2M_2{}^2/x_1M_1)dQ_w$$

so that dQ_w must have the same sign as $\Delta\bar{H}_1$. A similar criterion applies to sorption of solvent vapor. In either case, the measurement of dQ_w is quite easy and sensitive in contrast with the usual difficulty of evaluating $\Delta\bar{H}_1$ for polymer solutions. Quantitative use of this relation would, of course, require evaluation of the partial derivative by some means such as vapor pressure measurements.

Inspection of Table II discloses that dQ_w/dT, and hence $\Delta\bar{H}_1$, is positive for benzene and chlorobenzene and negative for heptane, cyclohexane, and tetrachloroethylene. Substitution of eq. (9) into eq. (5) gives:

$$\Delta\bar{H}_1 = Rv_2^2(D + Ev_2 + 2F/T) \tag{10}$$

The heats of dilution given by eq. (10) are listed in Table VI. Each agrees in sign, in the range studied, with the thermodynamic dQ_w/dT criterion.

TABLE VI

Solvent	$\Delta\bar{H}_1/Rv_2^2$	$-\Delta\bar{S}_1$ noncomb$/RV_2^2$
Cyclohexane	-51	0.487
n-Heptane	$-570v_2$	$1.31 + 0.95v_2$
Tetrachloroethylene	$-430 + 128{,}000/T$	$-2.9 - 3.9\,v_2 - 2.4v_2^2 - 64{,}000/T^2$
Chlorobenzene	$-390 + 148{,}000/T$	$0.938 - 74{,}000/T^2$
Benzene	$-450 - 143v_2 + 190{,}000/T$	$1.29 + 0.38v_2 - 95{,}000/T^2$

The concombinatorial entropy of dilution may be obtained from eqs. (2), (5), and (9):

$$-\Delta\bar{S}_1,\ \text{noncomb}/Rv_2^2 = a + bv_2 + cv_2^2 - f/T^2 \tag{11}$$

Values of this function are also given in Table VI. It is noteworthy that the values are 0.5 or larger for the systems with temperature-independent heats of dilution and much smaller for the systems with temperature-dependent heats of dilution.

These thermodynamic results may be interpreted in terms of the molecular theory of solutions developed by Prigogine and collaborators.[11] The theory indicates that the heat of dilution of a polymer solution might be positive or negative, depending upon the relative importance of the structural effect and the energetical effect. The structural contribution is a function of temperature, the temperature derivative of the heat capacity of the solvent at constant pressure, the stiffness of the polymer chain, and the site fraction of polymer. This contribution is negative. The energetical contribution arises from differences between solvent and polymer segments in size and in shape of interaction field and also from deviation of the solvent–polymer interaction energy from the arithmetic mean of like interactions. This contribution is generally positive, but might become negative if there is a specific solvent–polymer interaction. Using this theory, one would account for the positive heats of dilution with the aromatic solvents (and the smallness of the negative value with tetrachloroethylene) as arising from a positive energetical contribution.

Such an interpretation carries with it implications regarding the entropy of dilution. This entropy arises from three effects. The geometrical or combinatorial contribution depends on the chain length but not on the specific structures of polymer and solvent. This contribution is positive. The structural contribution to the entropy resembles the contribution to the enthalpy except for a dependence on the heat capacity of the solvent. This contribution to the entropy is negative, and for solutions of flexible polymers it makes a considerable reduction in the net positive entropy. The energetical contribution to the entropy tends to become positive due to differences in segment size and negative due to differences in interaction energy. The observed small noncombinatorial entropies for the benzene, chlorobenzene, and tetrachloroethylene systems might thus be attributed to sizable positive energetical contributions due to differences in segment size. This interpretation would be consistent with that for the heats of dilution.

The results reported here for heats of dilution are qualitatively similar to those obtained calorimetrically by Delmas, Patterson, and Somcynsky[12] for systems of polyisobutylene in various solvents. It is interesting, also, to note that the proportionality they observed between the heat and the solubility parameter difference in the series of normal alkanes did not extend to branched alkanes, cycloalkanes, aromatic solvents, or ether. The breakdown of this proportionality may well be due to a change in segment size for the solvent such as was adduced to account for the thermodynamics of the EPR systems.

It has been pointed out that there should be a temperature of maximum solvent power for a solvent–polymer system.[13] If there is a region of miscibility, this will lie between the upper and the lower critical solution temperatures. For a crosslinked gel, this maximum swelling temperature will occur where $dQ_w/dT = 0$ and also by the thermodynamic criterion $\Delta\bar{H}_1 = 0$. By eq. (10), this temperature is:

$$T = -2F/(D + Ev_2) \tag{12}$$

For tetrachloroethylene, $\Delta\bar{H}_1$ was negative from 25 to 100°C. Equation (12) predicts that below 25°C. it should become positive. The low temperature swelling experiments showed that at 0–25°C. dQ_w/dT was nearly zero and at -17 to 0°C. it was positive. Thus the change in the sign of dQ_w/dT (and also of the heat of dilution) was observed to occur near the predicted temperature.

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Résumé

Des gels de caoutchouc ponté d'éthylène–propylène ont été mis à gonfler dans cinq solvants à des températures de 25 à 100°C. Le paramètre d'interaction solvant–polymère, μ, de chaque système a été déterminé en fonction de la température et de la concentration en polymère. Un critère thermodynamique pour déterminer le signe de la chaleur de dilution, $\Delta\bar{H}_1$, a été mis en évidence. Pour trois des systèmes $\Delta\bar{H}_1$ est négatif. La contribution de l'entropie au paramètre d'interaction est plus faible que normalement pour des systèmes possédant une chaleur de dilution dépendante de la température. Les chaleurs de dilution et les facteurs d'entropie peuvent être interprêtés par conséquent suivant la théorie des solutions de Prigogine.

Zusammenfassung

Vernetzte Äthylen-Propylenkautschukgele wurden in fünf verschiedenen Lösungsmitteln bei 25 bis 100°C zur Quellung gebracht. Der Lösungsmittel–Polymerwechselwirkungsparameter μ wurde für jedes System in Abhängigkeit von Temperatur und Polymerkonzentration bestimmt. Ein thermodynamisches Kriterium für das Vorzeichen der Verdünnungswärme $\Delta\bar{H}_1$ wurde angegeben. Für drei Systeme war $\Delta\bar{H}_1$ negativ. Der Entropiebeitrag zum Wechselwirkungsparameter war kleiner, als gewöhnlich bei Systemen mit einer temperaturabhängigen Verdünnungswärme gefunden wird. Die Verdünnungswärme und der Entropieterm können widerspruchsfrei auf Grundlage der Lösungstheorie von Prigogine interpretiert werden.

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Copolymerization of Nonconjugated Diolefins: General Composition Relationships

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Synopsis

The copolymerization of nonconjugated diolefins with vinyl monomers involves departures from conventional vinyl copolymerization kinetics and the standard forms of the binary or ternary copolymerization composition equations are inadequate. These departures include intramolecular cyclization reactions and generally the formation of some pendent double-bonds. A general treatment of the copolymerization of symmetrical nonconjugated diolefins with vinyl monomers gives closed form relationships which take such reactions and their consequences into account. The general relationships may be approximated by a new series of composition equations which take into account the formation of both cyclized and noncyclized units in the chain and are simple enough for experimental use. The latter expressions are:

$$dm_1 : dM_3 : dm_4 : :$$

$$[\mathrm{M}_1]\,([\mathrm{M}_1] + \alpha_c + \alpha_4[\mathrm{M}_4]):$$

$$-[\mathrm{M}_1]([\mathrm{M}_1] + \alpha_4[\mathrm{M}_4]):$$

$$[\mathrm{M}_4]([\mathrm{M}_1] + [\mathrm{M}_4]/\delta_1)\,\{\alpha_4 + \alpha_c/([\mathrm{M}_1]/\beta_4 + [\mathrm{M}_4])\}$$

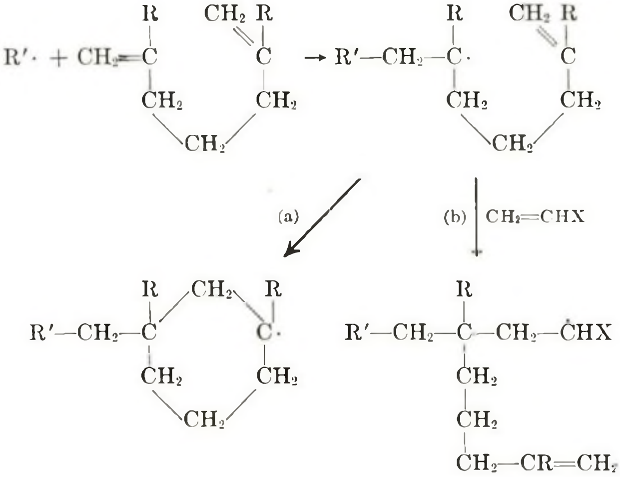
where: $\alpha_c = k_c/k_{11}$, $\alpha_4 = k_{14}/k_{11}$, $\delta_1 = k_{41}/k_{44}$, and $\beta_4 = k_{24}/k_{41}$, and $[\mathrm{M}_1]$, $[\mathrm{M}_3]$, and $[\mathrm{M}_4]$ refer to the concentrations of diolefin double bonds, pendent double bonds, and comonomer, respectively.

Introduction

In continuation of our earlier work[1-3] on the mechanism of alternating inter-intramolecular propagation,[4] we have more recently been concerned with the copolymerization of nonconjugated diolefins in an effort to determine the reactivities of the diolefinic monomers and their radicals in comparison with monovinyl monomers and their radicals. Previously, work in this area has been hampered by the lack of suitable general copolymer composition equations. In this paper we wish to present general composition equations for the copolymerization of symmetrical nonconjugated diolefins with monovinyl monomers.

The differential or integral forms of the standard binary or ternary copolymer equations as derived from vinyl copolymerization kinetics do not describe the situation here correctly and are not satisfactory. Wiley and co-workers[5–8] have found that a modified binary equation appears to describe adequately the copolymerization of divinylbenzene with styrene and ethylene glycol dimethacrylate with methyl methacrylate, and have calculated relative reactivity ratios for these systems. Hwa and Miller[9] have used a similar modification, although derived on a different basis, in an attempt to determine copolymerization parameters for certain methacrylic anhydride–monovinyl monomer systems.

The basic difference between the usual binary and ternary copolymerization schemes and that for systems involving nonconjugated diolefins stems from two facts. First, the nonconjugated diolefins have two reactive functional groups, both of which are available for reaction with an active radical. This leads to the conclusion that the effective concentration of diolefinic monomer double bonds is twice the diolefin concentration. Second, the initial radical formed from the diolefin may undergo an intramolecular cyclization reaction (a), as well as the more conventional intermolecular propagation reaction (b):



Thus, not only does the nature of the growing radical change in the usual way, by reaction with the comonomer, it can also change as the result of this intramolecular cyclization. Further, when the initial diolefin radical does not cyclize, but reacts intermolecularly, another reactive species, the pendent double bond, is created in the system. This type of copolymerization, therefore, has some aspects of a binary system: it initially consists of only two types of monomers, the nonconjugated diolefin and the monovinyl comonomer; it has some aspects of a ternary system: at any point following the start of reaction there are present, generally, three types of reactive double bonds (the double bonds of the two monomers and the pendent double bonds); it has some aspects of systems of higher functionality: at any point following the start of reaction there are present at least four types of active radicals (the initial radical formed from the diolefin, the radical formed from attack on the pendent double-bond, the cyclized radicals, and the radical formed from the monovinyl comonomers); and it has some features not common to any standard copolymerization scheme: the number of types of radicals does not correspond to the number of different monomers, and the mechanism of changing a growing radical from one type to another can involve an intramolecular cyclization reaction, in addition to the usual bimolecular reactions.

The modified binary equations used by Wiley and co-workers[5–8] and by Hwa and Miller[9] represent limiting cases where certain of the processes listed above are assumed to have a negligible effect on copolymer composition. In the former case, the copolymerization of divinylbenzene and ethylene glycol dimethacrylate with monovinyl monomers, it is assumed that no cyclization occurs and that the pendent unsaturated groups formed do not undergo subsequent reaction. Therefore, the propagating radicals are the initial radical from the diolefin and the comonomer radical. The only reactive double bonds are assumed to be those of the initial monomers. In the latter case, the copolymerization of methacrylic anhydride, there is assumed to be complete cyclization with no formation of pendent unsaturation. Therefore, the propagating radicals are only the cyclized radical and the comonomer radical. The reactive monomers here are also those charged initially.

With the exception of those diolefinic monomers, such as perhaps the *m*- and *p*-divinylbenzene, where cyclization can be completely restrained due to steric effects, most diolefins show some significant degree of cyclization during polymerization. The cyclization is particularly pronounced for those monomers which can form five-, six-, or seven-membered rings, but has been observed for cases where the number of ring atoms has been twenty or more.[13,14]

However, even those diolefins, such as methacrylic anhydride[1,14] which tend to cyclize almost quantitatively during homopolymerization, generally form copolymers containing significant numbers of noncyclized diolefin units.[9,16] The most common situation arising from the copolymerization of diolefinic monomers with olefinic monomers, then, is the formation of copolymers containing both cyclized and noncyclized diolefinic residues in the chain.

The need for a relationship to better describe these types of copolymerizations has prompted us to consider the development of a general copolymer composition equation which takes into account all of the various processes listed above. The general relationship found is somewhat more complex than is generally desirable for experimental use. Additional work has also been done in an effort to derive better approximate relations for the cases where the extent of cyclization is relatively high although definitely not quantitative. This equation reduces to that of Hwa and Miller if one assumes cyclization to be quantitative. The development of composition relationships for cases where the degree of cyclization is low or zero, and where the proportion of pendent unsaturated groups varies during the polymerization, has been obtained directly from the approach presented here. However, these latter relationships have been published separately[17] and will not be discussed here.

Following completion of the work reported here an article by Roovers and Smets[18] appeared in which the derivative of an approximate solution closely resembling eqs. (18) and (20) of the present paper are given. However, they did not consider the general derivation presented here.

General Composition Equations

The general kinetics of polymerization of nonconjugated diolefin has recently been discussed.[3] The mechanism of copolymerization involving such monomers may be obtained by the additional consideration of those reactions involving the monovinyl comonomer and its radical. That part of the general mechanism of interest here may be given as follows, where M_1 = either double bond of a previously unreacted, symmetrical nonconjugated diolefin; $M_1\cdot$ = the initial radical formed from the diolefin; $M_2\cdot$ = the radical formed by cyclization of $M_1\cdot$; M_3 = the pendent double bond formed when $M_1\cdot$ does not cyclize; $M_3\cdot$ = the radical from M_3; M_4 = the monovinyl comonomer; $M_4\cdot$ = the radical from M_4.

Chain Propagation:

$$M_1\cdot \xrightarrow{k_c} M_2\cdot$$

$$M_1\cdot + M_1 \xrightarrow{k_{11}} M_1\cdot$$

$$M_1\cdot + M_4 \xrightarrow{k_{14}} M_4\cdot$$

$$M_2\cdot + M_1 \xrightarrow{k_{21}} M_1\cdot$$

$$M_2\cdot + M_4 \xrightarrow{k_{24}} M_4\cdot$$

$$M_3\cdot + M_1 \xrightarrow{k_{31}} M_1\cdot$$

$$M_3\cdot + M_4 \xrightarrow{k_{34}} M_4\cdot$$

$$M_4\cdot + M_1 \xrightarrow{k_{41}} M_1\cdot$$

$$M_4\cdot + M_4 \xrightarrow{k_{44}} M_4\cdot$$

Crosslinking:

$$M_1\cdot + M_3 \xrightarrow{k_{13}} M_3\cdot$$

$$M_2\cdot + M_3 \xrightarrow{k_{23}} M_3\cdot$$

$$M_3\cdot + M_3 \xrightarrow{k_{33}} M_3\cdot$$

$$M_4\cdot + M_3 \xrightarrow{k_{43}} M_3\cdot$$

From the above equations the rate of change of each monomer concentration is:

$$-d[M_1]/dt = 2\,(k_{11}[M_1\cdot] + k_{21}[M_2\cdot] + k_{31}[M_3\cdot] + k_{41}[M_4\cdot])\,[M_1] \quad (1)$$

$$-d[\mathrm{M}_3]/dt = (k_{23}[\mathrm{M}_2\cdot] + k_{33}[\mathrm{M}_3\cdot] + k_{43}[\mathrm{M}_4\cdot])\,[\mathrm{M}_3] \\ -(k_{11}[\mathrm{M}_1] + k_{14}[\mathrm{M}_4])\,[\mathrm{M}_1] \quad (2)$$

$$-d[\mathrm{M}_4]/dt = (k_{14}[\mathrm{M}_1\cdot] + k_{24}[\mathrm{M}_2\cdot] + k_{34}[\mathrm{M}_3\cdot] + k_{44}[\mathrm{M}_4\cdot])\,[\mathrm{M}_4] \quad (3)$$

The coefficient, 2, in eq. (1) arises from the fact that the reaction of one of the diolefin double bonds removes two monomer double bonds from the system—the second unreacted double bond becoming the site for an intramolecular cyclization reaction or a pendent double-bond depending upon the fate of the $\mathrm{M}_1\cdot$ radical.

The rate of change of each radical concentration is given by:

$$d[\mathrm{M}_1\cdot]/dt = (k_{11}[\mathrm{M}_1\cdot] + k_{21}[\mathrm{M}_2\cdot] + k_{31}[\mathrm{M}_3\cdot] + k_{41}[\mathrm{M}_4\cdot])\,[\mathrm{M}_1] \\ -(k_c + k_{11}[\mathrm{M}_1] + k_{13}[\mathrm{M}_3] + k_{14}[\mathrm{M}_4])\,[\mathrm{M}_1\cdot] \quad (4)$$

$$d[\mathrm{M}_2\cdot]/dt = k_c[\mathrm{M}_1\cdot] - (k_{21}[\mathrm{M}_1] + k_{23}[\mathrm{M}_3] + k_{24}[\mathrm{M}_4])\,[\mathrm{M}_2\cdot] \quad (5)$$

$$d[\mathrm{M}_3]/dt = (k_{13}[\mathrm{M}_1\cdot] + k_{23}[\mathrm{M}_2\cdot] + k_{33}[\mathrm{M}_3\cdot] + k_{43}[\mathrm{M}_4\cdot])\,[\mathrm{M}_3] \\ -(k_{31}[\mathrm{M}_1] + k_{33}[\mathrm{M}_3] + k_{34}[\mathrm{M}_4])\,[\mathrm{M}_3\cdot] \quad (6)$$

$$d[\mathrm{M}_4\cdot]/dt = (k_{14}[\mathrm{M}_1\cdot] + k_{24}[\mathrm{M}_2\cdot] + k_{34}[\mathrm{M}_3\cdot] + k_{44}[\mathrm{M}_4\cdot])\,[\mathrm{M}_4] \\ -(k_{41}[\mathrm{M}_1] + k_{43}[\mathrm{M}_3] + k_{44}[\mathrm{M}_4])\,[\mathrm{M}_4\cdot] \quad (7)$$

Invoking the usual steady-state assumption, that the rate of change of a given radical concentration is very small compared with either its rate of formation or rate of disappearance, eqs. (4)–(7) may be taken approximately equal to zero. On collecting like terms, eqs. (4)–(7) may then be written as:

$$-(k_c + k_{13}[\mathrm{M}_3] + k_{14}[\mathrm{M}_4])\,[\mathrm{M}_1\cdot] + k_{21}[\mathrm{M}_2\cdot]\,[\mathrm{M}_1] \\ + k_{31}[\mathrm{M}_3\cdot][\mathrm{M}_1] = -k_{41}[\mathrm{M}_4\cdot][\mathrm{M}_1] \quad (4a)$$

$$k_c[\mathrm{M}_1] - (k_{21}[\mathrm{M}_1] + k_{23}[\mathrm{M}_3] + k_{24}[\mathrm{M}_4])\,[\mathrm{M}_2\cdot] = 0 \quad (5a)$$

$$k_{13}[\mathrm{M}_1\cdot][\mathrm{M}_3] + k_{23}[\mathrm{M}_2\cdot][\mathrm{M}_3] - (k_{31}[\mathrm{M}_1] + k_{34}[\mathrm{M}_4])\,[\mathrm{M}_3\cdot] \\ = -k_{43}[\mathrm{M}_4\cdot][\mathrm{M}_3] \quad (6a)$$

$$k_{14}[\mathrm{M}_1\cdot][\mathrm{M}_4] + k_{24}[\mathrm{M}_2\cdot][\mathrm{M}_4] + k_{34}[\mathrm{M}_3\cdot][\mathrm{M}_4] \\ = (k_{41}[\mathrm{M}_1] + k_{43}[\mathrm{M}_3])\,[\mathrm{M}_4\cdot] \quad (7a)$$

These four equations represent a set of linear, dependent, homogeneous equations in four unknowns: the respective radical concentrations. The solutions of these expressions in terms of any one of the unknowns has been treated by Walling and Briggs.[19] It will be sufficient for our purposes here to obtain solutions for three of the radical concentrations in terms of the fourth since the relative rates of disappearance of the monomers, or the relative rates of formation of the structural units in the copolymer, can be obtained independent of the absolute values of the radical concentrations. If eq. (4a) is solved for the right-hand side of eq. (1) we have:

$$(k_{11}[\mathrm{M}_1\cdot] + k_{21}[\mathrm{M}_2\cdot] + k_{31}[\mathrm{M}_3\cdot] + k_{41}[\mathrm{M}_4\cdot])\ [\mathrm{M}_1] = (k_c + k_{11}[\mathrm{M}_1] + k_{13}[\mathrm{M}_3] + k_{14}[\mathrm{M}_4])\ [\mathrm{M}_1\cdot]$$

If this is then substituted for the right-hand side of eq. (1) we have:

$$-d[\mathrm{M}_1]/dt = 2(k_c + k_{11}[\mathrm{M}_1] + k_{13}[\mathrm{M}_3] + k_{14}[\mathrm{M}_4])\ [\mathrm{M}_1\cdot] \tag{1a}$$

Similarly eqs. (2) and (6a) and (3) and (7a) yield eqs. (2a) and (3a):

$$-d[\mathrm{M}_3]/dt = (k_{31}[\mathrm{M}_1] + k_{33}[\mathrm{M}_3] + k_{34}[\mathrm{M}_4])\ [\mathrm{M}_3\cdot] - (k_{11}[\mathrm{M}_1] + k_{13}[\mathrm{M}_3] + k_{14}[\mathrm{M}_4])\ [\mathrm{M}_1\cdot] \tag{2a}$$

$$-d[\mathrm{M}_4]/dt = (k_{41}[\mathrm{M}_1] + k_{43}[\mathrm{M}_3] + k_{44}[\mathrm{M}_4])\ [\mathrm{M}_4\cdot] \tag{3a}$$

The relative rate of change of $[\mathrm{M}_1]$ and $[\mathrm{M}_3]$ and $[\mathrm{M}_1]$ and $[\mathrm{M}_4]$ in the system is given by:

$$\frac{d[\mathrm{M}_1]}{d[\mathrm{M}_3]} = \frac{2\ (k_c + k_{11}[\mathrm{M}_1] + k_{13}[\mathrm{M}_3] + k_{14}[\mathrm{M}_4])\ [\mathrm{M}_1\cdot]}{(k_{31}[\mathrm{M}_1] + k_{33}[\mathrm{M}_3] + k_{34}[\mathrm{M}_4])\ [\mathrm{M}_3\cdot] - (k_{11}[\mathrm{M}_1] + k_{13}[\mathrm{M}_3] + k_{14}[\mathrm{M}_4])\ [\mathrm{M}_1\cdot]} \tag{8}$$

$$\frac{d[\mathrm{M}_1]}{d[\mathrm{M}_4]} = \frac{2(k_c + k_{11}\ [\mathrm{M}_1] + k_{13}[\mathrm{M}_3] + k_{14}[\mathrm{M}_4])\ [\mathrm{M}_1\cdot]}{(k_{41}[\mathrm{M}_1] + k_{43}[\mathrm{M}_3] + k_{44}[\mathrm{M}_4])\ [\mathrm{M}_4\cdot]} \tag{9}$$

These equations as written describe the loss of M_1 double bonds compared with the loss of M_3 double bonds and M_4 monomer in the system. These expressions may be modified to reflect the relative rate of formation of M_1, M_3, and M_4 type structures in the copolymer. For this purpose the coefficient, 2, must be dropped from these equations, since the reaction of one M_1 double bond results in the incorporation of an entire diolefin residue into the chain. This M_1 type unit (diolefin residue) may be cyclized or noncyclized. Lower case symbols will be used to identify monomer units incorporated into the chain, except that M_3 will still be used to denote the pendent double bond.

The next step will be to obtain expressions for $\mathrm{M}_1\cdot$ and $\mathrm{M}_3\cdot$ in terms of $\mathrm{M}_4\cdot$ so the radical concentrations can be canceled from the above equations. Walling and Briggs[19] have used determinants to accomplish a similar end for the treatment of the n-component vinyl copolymerization system, and this method will also be used here. The determinant expressions for $\mathrm{M}_1\cdot$ and $\mathrm{M}_3\cdot$ in terms of $\mathrm{M}_4\cdot$ based on eqs. (4a), (5a), and (6a) are:

$$[\mathrm{M}_1\cdot] = \frac{\begin{vmatrix} -k_{41}[\mathrm{M}_4\cdot][\mathrm{M}_1] & k_{21}[\mathrm{M}_1] & k_{31}[\mathrm{M}_1] \\ 0 & -(k_{21}[\mathrm{M}_1] + k_{23}[\mathrm{M}_3] + k_{24}[\mathrm{M}_4]) & 0 \\ -k_{43}[\mathrm{M}_4\cdot][\mathrm{M}_3] & k_{23}[\mathrm{M}_3] & -(k_{31}[\mathrm{M}_1] + k_{34}[\mathrm{M}_4]) \end{vmatrix}}{\begin{vmatrix} -(k_c + k_{13}[\mathrm{M}_3] + k_{14}[\mathrm{M}_4]) & k_{21}[\mathrm{M}_1] & k_{32}[\mathrm{M}_1] \\ k_c & -(k_{21}[\mathrm{M}_1] + k_{23}[\mathrm{M}_3] + k_{24}[\mathrm{M}_4]) & 0 \\ k_{13}[\mathrm{M}_3] & k_{23}[\mathrm{M}_3] & -(k_{31}[\mathrm{M}_1] + k_{34}[\mathrm{M}_4]) \end{vmatrix}} \tag{10}$$

$$[\mathrm{M}_3\cdot] = \frac{\begin{vmatrix} -(k_c + k_{13}[\mathrm{M}_3] + k_{14}[\mathrm{M}_4]) & k_{21}[\mathrm{M}_1] & -k_{41}[\mathrm{M}_4\cdot][\mathrm{M}_1] \\ k_c & -(k_{21}[\mathrm{M}_1] + k_{23}[\mathrm{M}_3] + k_{24}[\mathrm{M}_4]) & 0 \\ k_{13}[\mathrm{M}_3] & k_{23}[\mathrm{M}_3] & -k_{43}[\mathrm{M}_4\cdot][\mathrm{M}_3] \end{vmatrix}}{D_4} \tag{11}$$

where D_4 is the denominator of the M_1. expression.

It is convenient at this point to introduce the relative reactivity ratios. Since the comparisons to be used here are the rate constants for the homopolymerization reactions, i.e., k_{11}, k_{33}, and k_{44}, and the comparison for the cyclized ($\mathrm{M}_2\cdot$) radical reactions will be k_{21}, the numerator and denominator of the determinant will be divided by the product of these parameters.[20] Making this change and solving the determinant expression for $\mathrm{M}_1\cdot$ yields:

$$[\mathrm{M}_1\cdot] = \frac{k_{44}[\mathrm{M}_1][\mathrm{M}_4\cdot]}{D_4k_{11}} (\gamma_1\delta_1[\mathrm{M}_1] + \gamma_1\delta_3[\mathrm{M}_3] + \gamma_4\delta_1[\mathrm{M}_4]) ([\mathrm{M}_1] + \beta_3[\mathrm{M}_3] + \beta_4[\mathrm{M}_4]) \tag{12}$$

where:

$$\alpha_c = k_c/k_{11}$$

$$\alpha_3 = k_{13}/k_{11}$$

$$\alpha_4 = k_{14}/k_{11}$$

$$\beta_3 = k_{23}/k_{21}$$

$$\beta_4 = k_{24}/k_{21}$$

$$\gamma_1 = k_{31}/k_{33}$$

$$\delta_1 = k_{41}/k_{44}$$

and

$$\delta_3 = k_{43}/k_{44}$$

In a similar manner the expression for $\mathrm{M}_3\cdot$ may be shown to be:

$$[\mathrm{M}_3\cdot] = \frac{-k_{44}[\mathrm{M}_3][\mathrm{M}_4\cdot]}{D_4k_{33}} \{\alpha_c(\beta_3\delta_1[\mathrm{M}_1] + \beta_3\delta_3[\mathrm{M}_3] + \beta_4\delta_3[\mathrm{M}_4]) + ([\mathrm{M}_1] + \beta_3[\mathrm{M}_3] + \beta_4[\mathrm{M}_4]) (\alpha_3\delta_1[\mathrm{M}_1] + \alpha_3\delta_3[\mathrm{M}_3] + \alpha_4\delta_3[\mathrm{M}_4])\} \tag{13}$$

D_4', the denominator of the $M_1\cdot$ and $M_3\cdot$ determinants divided by the product of the rate constants, is given by:

$$D_4' = [M_4]\,(\alpha_4\gamma_1[M_1] + \alpha_3\gamma_4[M_3] + \alpha_4\gamma_4[M_4])$$
$$([M_1] + \beta_3[M_3] + \beta_4\,[M_4]) + \alpha_c(\beta_4\gamma_1[M_1] + \beta_3\gamma_4[M_3] + \beta_4\gamma_4[M_4]) \quad (14)$$

Substituting eq. (14) in eqs. (12) and (13) and substituting the resulting expressions for $M_1\cdot$ and $M_3\cdot$ in eqs. (8) and (9), respectively, carrying out the indicated divisions by k_{11}, k_{33}, and k_{44} leads to the desired relationships. These may be summarized as follows:

$$dm_1 : dM_3 : dm_4 :: \quad (15)$$

$$[M_1](\alpha_c + [M_1] + \alpha_3[M_3] + \alpha_4[M_4])A\cdot B:$$
$$-[M_3](\gamma_1[M_1] + [M_3] + \gamma_4[M_4])\,\{\alpha_c(\beta_3\delta_1[M_1] + \beta_3\delta_3[M_3]$$
$$+ \beta_4\delta_3\,[M_4]) + BC\} - [M_1]([M_1] + \alpha_3[M_3] + \alpha_4[M_4])A\cdot B: \quad (16)$$
$$[M_4](\gamma_1[M_1] + \delta_3[M_3] + [M_4])\,\{(\alpha_4\gamma_1[M_1] + \alpha_3\gamma_4[M_3] + \alpha_4\gamma_4[M_4])\cdot B$$
$$+ \alpha_c(\beta_4\gamma_1[M_1] + \beta_3\gamma_4[M_3] + \beta_4\gamma_4[M_4])\} \quad (17)$$

where

$$A = (\gamma_1\delta_1[M_1] + \gamma_1\delta_3[M_3] + \gamma_4\delta_1[M_4])$$
$$B = ([M_1] + \beta_3[M_3] + \beta_4[M_4])$$
$$C = (\alpha_3\delta_1[M_1] + \alpha_3\delta_3[M_3] + \alpha_4\delta_3[M_4])$$

These expressions represent the general composition relationships for the copolymerization of symmetrical nonconjugated diolefins with vinyl monomers. They quantitatively account for the formation of cyclized and noncyclized diolefin units and take into account the reactions of pendent double bonds with growing radicals. While these expressions are given as the differential form they may be used, as are the usual differential binary and ternary copolymerization expressions, to reflect the composition of relatively low conversion copolymer, i.e., polymer formed under conditions where compositional changes in the system are small and usually may be neglected.

Approximations to the General Solution

In cases where the copolymerization gives evidence for significant, but less than complete cyclization an approximation of the general relationship can be obtained if it may be assumed that the concentration of pendent unsaturation is not measureably depleted by crosslinking reactions. This would seem a very fair approximation for most real systems providing the extent of conversion of monomer to polymer is low. Applying the restriction that the rates of reaction of radicals with M_3 are very slow in comparison with the rates of reaction of radicals with monomer due to the low concentration of M_3, a new set of equations may be written:

$$-d[M_1]/dt = 2(k_{11}[M_1\cdot] + k_{21}[M_2\cdot][M_1] + k_{41}[M_4\cdot][M_1])$$

$$+d[M_3]/dt = k_{11}[M_1\cdot][M_1] + k_{14}[M_1\cdot][M_4]$$

$$-d[M_4]/dt = k_{14}[M_1\cdot][M_4] + k_{24}[M_2\cdot][M_4] + k_{44}[M_4\cdot][M_4]$$

$$d[M_1\cdot]/dt = k_{21}[M_2\cdot][M_1] + k_{41}[M_4\cdot][M_1] - k_c[M_1\cdot] - k_{14}[M_1\cdot][M_4]$$

$$d[M_2\cdot]/dt = k_c[M_1\cdot] - k_{21}[M_2\cdot][M_1] - k_{24}[M_2\cdot][M_4]$$

$$d[M_4\cdot]/dt = k_{14}[M_1\cdot][M_4] + k_{24}[M_2\cdot][M_4] - k_{41}[M_4\cdot][M_1]$$

Following standard procedures, the expressions for copolymer composition are found to be:

$$dm_1 : dM_3 : dm : \tag{18}$$

$$[M_1]([M_1] + \alpha_c + \alpha_4[M_4]) : - [M_1]([M_1] + \alpha_4[M_4]) : \tag{19}$$

$$[M_4]([M_1] + [M_4]/\delta_1)\ \{\alpha_4 + \alpha_c/([M_1]/\beta_4 + [M_4])\} \tag{20}$$

where the notation is the same as before.

Equations representing eqs. (18)–(20) here have been developed in a somewhat different form by Roovers and Smets.[18] These workers preferred to consider the composition relations in terms of k_c/k_{14} rather than the k_c/k_{11} used here. Both forms are useful.

These approximate equations are significantly less complex than those more general equations derived earlier. Since they are simple enough to use experimentally and do take into account the formation of cyclized and noncyclized units in the chain, they should be more appropriate relationships than those which have been used formerly.

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Résumé

La copolymérisation des dioléfines non conjuguées avec des monomères vinyliques manifeste des déviations vis-à-vis des cinétiques habituelles de la copolymérisation vinylique et les formes habituelles des équations de composition pour la copolymérisation binaire ou ternaire sont inadéquates. Ces déviations proviennent de réactions de cyclisation intramoléculaire et généralement de la formation de certaines liaisons doubles pendantes. Un examen général de la copolymérisation des dioléfines non conjuguées symétriques avec des monomères vinyliques fournit des relations qui tiennent compte de telles réactions et de leurs conséquences. Les relations générales peuvent être obtenues au moyen d'une nouvelle série d'équations de composition qui tiennent compte de la formation d'unités cyclisées et non cyclisées dans la chaîne et sont suffisamment simples pour être utilisées expérimentalement. Ces expressions sont:

$$dm_1 : dM_3 : dm_4 : :$$

$$[M_1]\ ([M_1] + \alpha_c + \alpha_4[M_4]):$$

$$-[M_1]\ ([M_1] + \alpha_4[M_4]):$$

$$[M_4]\ ([M_1] + [M_4]/\delta_1\ \{\alpha_4 + \alpha_c/([M_1]/\beta_4 + [M_4])\}$$

où $\alpha_c = k_c/k_{11}$, $\alpha_4 = k_{14}/k_{11}$, $\delta_1 = k_{41}/k_{44}$ et $\beta_4 = k_{24}/k_{21}$, et $[M_1]$, $[M_3]$ et $[M_4]$ sont les concentrations en doubles liaisons dioléfiniques, en doubles liaisons pendantes et en comonomère respectivement.

Zusammenfassung

Bei der Copolymerisation von nichtkonjugierten Diolefinen mit Vinylmonomeren treten Abweichungen von der konventionellen Vinylcopolymerisationskinetik auf, une die Standardformen für die Zusammensetzungsgleichung für die binäre oder ternäre Copolymerisation treffen nicht mehr zu. Zu diesen Abweichungen gehören intramolekulare Zyklisierungsreaktionen und im allgemeinen die Bildung einiger anhängender Doppelbindungen. Eine allgemeine Behandlung der Copolymerisation symmetrischer nichtkonjugierter Diolefine mit Vinylmonomeren liefert Beziehungen in geschlossener Form, welche solchen Reaktionen und ihren Konsequenzen Rechnung tragen. Die allgemeinen Beziehungen können durch eine Reihe von Zusammensetzungsgleichungen angenähert werden, welche die Bildung sowohl zyklisierter als auch nichtzyklisierter Einheiten in der Kette in Betracht ziehen und einfach genug für den experimentellen Gebrauch sind. Diese Ausdrücke lauten:

$$dm_1 : dM_3 : dm_4 : :$$

$$[M_1]\ ([M_1] + \alpha_c + \alpha_4[M_4]):$$

$$-[M_1]([M_1] + \alpha_4[M_4]):$$

$$[M_4]\ ([M_1] + [M_4]/\delta_1)\ \{\alpha_4 + \alpha_c/([M_1]/\beta_4 + [M_4])\}$$

wo $\alpha_c = k_c/k_{11}$, $\alpha_4 = k_{14}/k_{11}$, $\delta_1 = k_{41}/k_{44}$ und $\beta_4 = k_{24}/k_{21}$, und $[M_1]$, $[M_3]$ und $[M_4]$ sich auf die Konzentration der Diolefindoppelbindungen, der anhängenden Doppelbindendungen und des Comonomeren beziehen.

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Polyelectrolytes in Salt Solutions

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Synopsis

It is shown that the exceptionally low expansion values expected by Kimball, Cutler, and Samuelson's theory result from their interpretation of the Gaussian distribution function for polymer chain segments rather than a statistical mechanical additivity problem.

Introduction

Several theories concerning the behavior of flexible polyelectrolyte molecules in salt solutions have been developed. It is well known that the increase of the dimensions of these molecules with increasing charge density or decreasing ionic strength is overestimated by all theories except one.[1]

The extremely low value calculated by Kimball, Cutler, and Samuelson[1] has been the subject of some discussion. The authors hold the low electrostatic potential, calculated with the use of the Donnan approximation, responsible for their result. Flory[2] remarks that Kimball et al. assume that the segments of the random chain representing the polymer molecule may be treated as statistically independent particles. Lifson[3] compared the theories of Kimball et al. and Hermans and Overbeek.[4] He concludes that the origin of the low expansion calculated by Kimball et al. is not the Donnan approximation but the assumed additivity of potentials in contrast to the assumption of the additivity of free energies used by Hermans and Overbeek. As it is clear that such an essential difference resulting from similar additivity assumptions would be a serious obstacle for polyelectrolyte theory, it may be useful to reinvestigate this problem.

The Segment Distribution

In the theory of Kimball et al.[1] the approximate equation, eq. (1), for the distribution of the segments of the random chain relative to its center of mass is interpreted as the distribution of particles in a central force field with a potential $V(r) = 3kTr^2/2R_0^2$.

$$C_0(r) = A \exp\{-3r^2/2R_0^2\} \tag{1}$$

Here, $C_0(r)$ is the segment concentration at a distance r from the molecular center of mass and R_0 is the root mean square distance of the segments from this center. Now, Kimball et al. interpreted $V(r)$ as a potential function for the spatial distribution of independent segments.

It should be noted, however, that there has been given no derivation for eq. (1), although it has been shown[5,6] that it approximates numerically the real distribution function. This function is proportional, at each value of r, to the sum of all the molecular configurations contributing segments at a distance r from the center of mass, each configuration multiplied with the number of segments it contributes.

The fact that eq. (1) is just an approximate mathematical representation of the real distribution function makes any physical interpretation of $V(r)$ rather difficult. Instead of treating the polymer molecule as a cloud of independent segments, eq. (1) may be connected with the random coil model for polymers.

Consider the distribution function $W(h)$ for the end-to-end distance h of the random chain model of the polymer molecule:

$$\begin{aligned} W(h)dh &= A' \exp\{-3h^2/2h_0^2\}4\pi\, h^2dh \qquad (2) \\ &= A' \exp\{-h^2/4R_0^2\}4\pi h^2dh \end{aligned}$$

It is useful to compare this expression with the function giving the number of segments between r and $r + dr$:

$$C_0(r)4\pi\, r^2\, dr = A \exp\{-3r^2/2R_0^2\}4\pi r^2dr \qquad (3)$$

From eqs. (2) and (3) it may be seen that the number of segments between r and $r + dr$ as given by eq. (1) is directly proportional, for any value of r, to the probability of the occurrence of an end-to-end distance $h = 6^{1/2}r$. Thus it is reasonable to conclude that $C_0(r)$, just like $W(h)$, has the physical meaning of a distribution function for the molecular configurations of the random chain. Consequently, if the "potential" $V(r)$ is introduced, it should be interpreted as an energy relating to the whole molecule, all configurations characterized by the same end-to-end distance having the same value for $V(r)$.

Starting from these considerations it may be of interest to examine the consequences of this interpretation of eq. (1) and $V(r)$ if it is introduced in the theory of Kimball et al.

Polyelectrolyte Expansion

Consider the polyelectrolyte model of Kimball et al., consisting of a spherical segment distribution in a solution of a (1–1) electrolyte. The distribution of the segments will be perturbed by the interaction of the fixed charges along the molecular chain. To account for this effect Kimball et al. multiply eq. (1) with a Boltzmann factor exp. $\{-\epsilon\psi/kT\}$, where ψ is the electrostatic potential within the polyelectrolyte region. In this way, however, $C_0(r)$ is only lowered by the electrostatic factor relating to one segment. If eq. (1) is interpreted as discussed above, the electrostatic terms for all of the fixed charges of the molecule should be used here. Now, following the procedure of Kimball et al. in which all electrostatic interactions are replaced by a central electrostatic potential ψ in which the charges are situated, the potential energy term for the whole molecule becomes $\sum_i^z \epsilon_i\psi_i$, where ψ_i is the potential near the charge ϵ_i.

Introducing a mean value

$$\epsilon\psi(r) = (1/z)\Sigma\epsilon_i\psi_i$$

for a configuration with $h = 6^{1/2}r$, the electrostatic term reduces to $z\epsilon\psi$. The electrostatic free energy for a permeable polyelectrolyte molecule in salt solution is given by $F_e = {}^1/_2\, z\epsilon\psi$.[4] Thus it is seen that, judged by the electrostatic terms, the macromolecular expansion will in fact be larger by the method of Kimball et al.

Using F_e in the electrostatic exponential term, eq. (1) may be replaced by eq. (4).

$$C(r) = Be^{-3r^2/2R_0^2}\, e^{-z\epsilon\Psi/2kT} \tag{4}$$

From eq. (4) it is possible to calculate the polyelectrolyte expansion as a function of ionic strength. By using the Donnan approximation, Kimball et al. derive an expression for Ψ:

$$\Psi = (kT/\epsilon)\sinh^{-1}[\alpha C(r)/2M] \tag{5}$$

Here α is the degree of ionization of the polyelectrolyte and M is the concentration of the neutral salt present. With eqs. (4) and (5) it is possible to find r_p, the most probable value of r, with

$$[d(r^2C)/dr]_{r=r_p} = 0$$

The resulting equation for r_p is:

$$\frac{3\,r_p^2}{2R_0^2} = 1 + \frac{z\alpha C(r_p)/4M}{[1 + \alpha^2C^2(r_p)/4M^2]^{1/2}} \tag{6}$$

Assuming that the segment distribution keeps its Gaussian form after expansion, it follows that $r_p^2 = {}^2/_3\, R^2$, where the meaning of R is analogous to that of R_0 for the uncharged molecule. Therefore eq. (6) may be written:

$$\frac{R^2}{R_0^2} = 1 + \frac{z\alpha C(r_p)/4M}{[1 + \alpha^2C^2(r_p)/4M^2]^{1/2}} \tag{7}$$

Thus, for infinite ionic strength $R^2 = R_0^2$ and for $M \rightarrow 0$, $R^2 = R_0^2\,(1 + Z/2)$ (note however that for $M \rightarrow 0$ the Donnan approximation is invalid). In the region $0 < \alpha C(r_p)/2M < 1$, eq. (7) may be approximated by

$$\beta^2 = R^2/R_0^2 = 1 + z\alpha C(r_p)/4M \tag{8}$$

The assumption of the continued Gaussian distribution leads to eq. (9) for $C(r_p)$:

$$C(r_p) = D\exp\left\{-3r_p^2/2R^2\right\} = D/e \tag{9}$$

Replacing $C(r_p)$ in eq. (8) by eq. (9) gives eq. (10):

$$\beta^2 = 1 + (Z\ \alpha D)/4Me = 1 + [(3/2\pi)^{3/2} z\alpha N/4eMR^3] \qquad (10)$$

Here the value of the normalization factor D has been introduced, and N is the number of segments of the polymer chain. Multiplication of eq. (10) by $R^3/R_0{}^3$ and rearrangement of terms gives eq. (11)

$$\beta^5 - \beta^3 = (9Z^2)/(8e\pi^{1/2}MV_0) \qquad (11)$$

Here, $V_0 = \pi 6^{1/2} R_0{}^3 = (\pi/6)h_0{}^3$, and h_0 is the root mean square end-to-end distance of the uncharged molecule.

This expression for the expansion of a polyelectrolyte is essentially equal to Flory's result.[2] It is easily seen that the use of the electrostatic potential energy term increases the right-hand side of eq. (11) by a factor of two. This means that the assumption of additive potentials increases the expected expansion somewhat, in contrast to the result of Kimball et al. Thus it may be concluded that the small expansion values of Kimball et al. did not arise from additivity problem (the additivity of potentials versus the additivity of free energies) but rather from the use of a model which did not account for the fact that the polymer segments are bound to each other to form a macromolecular chain.

I would like to thank Prof. M. Mandel for the many discussions we had on this subject.

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Résumé

On montre que les valeurs d'expansion extrêmement basses, prévues par la théorie de Kimball, Gutler et Samuelson, sont dues à leur interprétation de la fonction de distribution gaussienne pour les segments de chaînes des polymères et non à un problème de statistique mécanique.

Zusammenfassung

Es wird gezeigt, dass die nach der Theorie von Kimball, Cutler und Samuelson zu erwartenden ausserordentlich niedrigen Expansionswerte durch ihre Interpretation der Gauss-Verteilungsfunktion für Polymerkettensegmente bedingt sind und nichte ein statistisch-mechanisches Additivitätsproblem vorliegt.

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Polymerization of Conjugated Trienes*

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Synopsis

The polymerization of 1,3,5-hexatriene, 1,3,5-heptatriene, and 2,4,6-octatriene with a variety of catalysts established the trienes as a distinct class of monomers which lead to unique unsaturated polyolefins. Soluble, high molecular weight polymers with predominantly 1,6-enchainment were prepared with a soluble coordination catalyst system; this mode of polymerization resulted in 1,3-dienyl groups in the polymer backbone. A stereospecific 1,6-polyhexatriene, with a novel type of crystallinity based on *trans, trans*-1,3-diene repeat units, was prepared by low temperature polymerization with a vanadyl trichloride–triisobutylaluminum catalyst.

INTRODUCTION

A detailed evaluation of conjugated triolefins as a separate class of monomers has not been reported, despite the potential of such unsaturates as vinylogs of the conjugated dienes, which have been thoroughly studied by numerous polymerization techniques. Alloöcimene, a tetramethyl derivative of hexatriene, has been polymerized to a polymer of somewhat complex structure.[1] Dimers, trimers, and tetramers of hexatriene were reported to result from internal Diels-Alder reactions of hexatriene.[2]

This investigation of three simple trienes: 1,3,5-hexatriene (I), 1,3,5-heptatriene (II), and 2,4,6-octatriene (III) has established the conjugated triolefins as a distinct class of monomers. A variety of polymerization catalysts were used to prepare a series of unique polyolefins containing a high degree of unsaturation as conjugated 1,3-dienyl groups within the polymer backbone.

DISCUSSION

A number of polymer structures are theoretically possible from the polymerization of conjugated trienes, each of which should have two residual carbon-carbon double bonds, disregarding any secondary reactions on the unsaturated polymer, such as crosslinking and cyclization. Three directions of polymerization could be expected from hexatriene (I) and octa-

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TABLE I

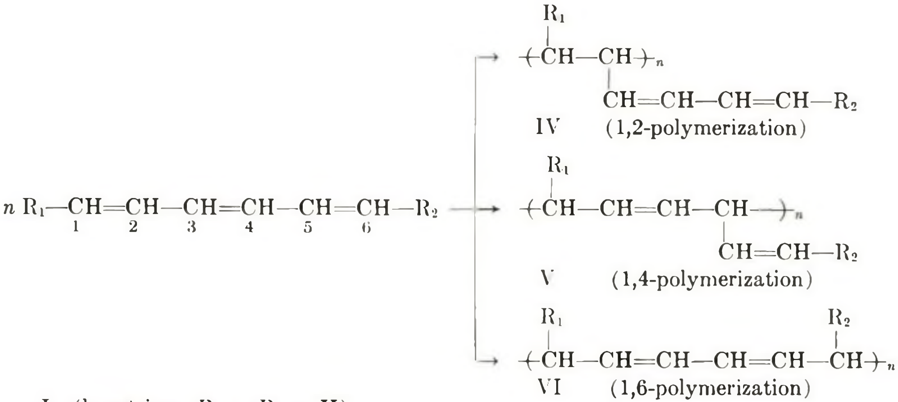
Summary of Conjugated Triene Polymers

Monomer	Solvent	Catalyst (mmole ratio)	Time, hr.	Temp., °C.	η_{inh}	Modes of polymerization
1,3,5-Hexatriene	C_6H_5Cl	2:1:15 $Ti(OC_6H_5)_4$:$VOCl_3$:($Et_2AlCl\cdot$Anisole)	24	−25	0.61[a]	1,6-(*trans*, *trans* and *cis*,*trans*)
1,3,5-Hexatriene	C_6H_5Cl	1:4 $VOCl_3$:(*i*-Bu)$_3$Al	2.5	−30	—	1,6-*trans*,*trans*
1,3,5-Hexatriene	*n*-C_7H_{16}	1:3 Ti(*i*-OC_3H_7)$_4$:Et_3Al	48	0	0.51[a]	1,4-; 1,6-(*trans*, *trans* and *cis*,*trans*)
1,3,5-Hexatriene	H_2O	$K_2S_2O_8$	48	25	—	1,6-*cis*,*trans*
1,3,5-Hexatriene	THF	*n*-BuLi	0.5	0	1.15[b]	1,2-; 1,4-; 1,6-.
1,3,5-Heptatriene	C_6H_5Cl	1:4 $VOCl_3$:(*i*-Bu)$_3$Al	24	−30	0.73[a]	1,6-(*trans*,*trans* and *cis*,*trans*)
2,4,6-Octatriene	C_6H_5Cl	1:6 $VOCl_3$($Et_2AlCl\cdot$Anisole)[3]	1	−35	0.99[a]	1,6-(*trans*,*trans* and *cis*,*trans*)
1,3,5-Heptatriene	THF	*n*-BuLi	1	0	0.13[b]	1,2-; 1,4-; 1,6-
2,4,6-Octatriene	THF	*n*-BuLi	1	0	0.09[b]	1,2-; 1,4;; 1,6-

[a] 0.5% in benzene at 30°C.

[b] 0.5% in tetrahydrofuran at 30°C.

triene (III): 1,2-, 1,4-, and 1,6-enchainment. For heptatriene, two additional structures are also possible, those resulting from 3,6- and 5,6-polymerization.



I (hexatriene, $R_1 = R_2 = H$)
II (heptatriene, $R_1 = H$; $R_2 = CH_3$)
III (octatriene, $R_1 = R_2 = CH_3$)

In addition to the structurally isomeric polymers, numerous other possibilities exist when *cis* and *trans* variations are considered. It was anticipated that certain specific structures might be favored by the proper choice of catalyst, in the same way that nearly exclusive 1,2-, 1,4-*cis*, and 1,4-*trans* polymers of butadiene have been obtained.[3] A major objective of this work was the synthesis of 1,2- and 1,6-polytrienes, which would result in residual conjugated diene groups (structures IV and VI) in the polymers for post-reaction studies.[4]

Monomer Synthesis

The three triene monomers were synthesized by dehydration of the appropriate dienic alcohols over alumina. Inasmuch as the dehydration led to a preponderance of *trans* isomers, it is possible that the use of all-*trans* monomers may have simplified the elucidation of the resulting polymer structures.

A high degree of monomer purity was achieved by low temperature fractional crystallization of the crude monomers prior to distillation. For example, *trans*-hexatriene was separated from the *cis* isomer and cyclohexadiene by recrystallization from methanol at −50 to −25°C., followed by water extraction and distillation from calcium hydride which resulted in better than 99.8% purity as determined by vapor-phase chromatography. Whereas hexatriene could be stored satisfactorily for several months as a solid (−12°C.), heptatriene and octatriene required Dry Ice storage since they were subject to polymerization as solids.

Coordination Polymerization of Trienes

The major share of the polymerization work was performed with coordination catalysts since the conjugated diolefins have been found to respond

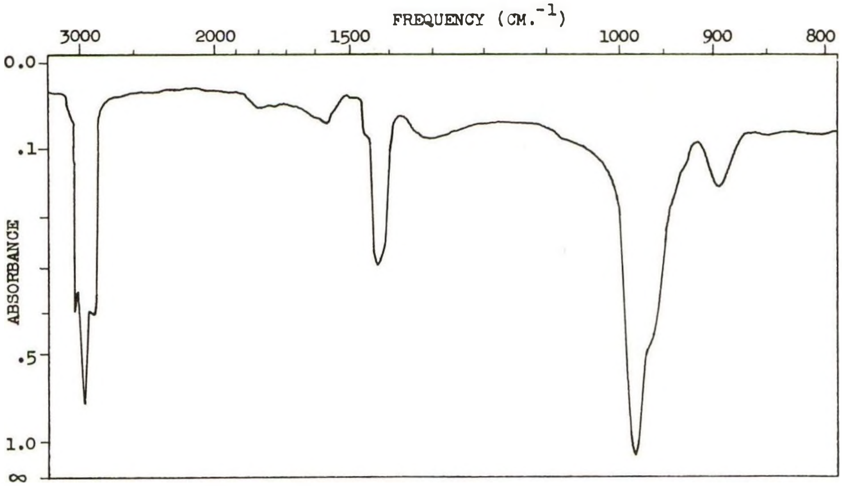


Fig. 1. Infrared spectrum of amorphous 1,6-polyhexatriene.

quite selectively to such catalyst combinations. It was anticipated that the use of less reactive catalyst systems, i.e., those which have been modified with Lewis bases, might be imperative to minimize secondary reactions on the polymeric diene groups; this was found to be the case.

Amorphous 1,6-Poly(1,3,5-hexatriene). The most favored direction of hexatriene polymerization with coordination catalysts appeared to be through the 1,6-conjugated triene system. The resulting polymer (VI $R_1 = R_2 = H$) contained residual conjugated diene groups within the polymer backbone. The preferred catalyst systems which led to the soluble, predominantly 1,6-structures were those which included a transition metal ester, such as tetraphenyl titanate, to moderate the Lewis acid nature of vanadyl trichloride or titanium tetrachloride. Triisobutylaluminum or diethylaluminum chloride reducing agents were usually satisfactory. Polymerization at 0–30°C. in benzene solvent resulted in soluble, high molecular weight polymer. Clear, tough, flexible films which were quite stiff, in contrast to the elastomeric 1,4-polyhexatriene films, were obtained from benzene solutions of the polymer.

The infrared spectrum (Fig. 1) of the polymer showed an intense *trans*, *trans*-dienic absorption band at 985 cm.$^{-1}$, with a less intense shoulder at 970 cm.$^{-1}$. Absorption attributed to vinyl structures (915–900 cm.$^{-1}$) were minor, compared to the amount found for the 1,4-polyhexatriene and the anionic polymer. Amorphous patterns only were observed by x-ray.

Crystalline 1,6-Polyhexatriene. Extensively crosslinked hexatriene polymers invariably resulted when "strong" coordination catalysts, such as vanadyl trichloride–triisobutylaluminum were used at room temperature. However, when the catalyst components were premixed at low temperatures (−30°C.), a catalyst system was formed which polymerized hexatriene to an insoluble, high molecular weight polymer. The polymer displayed a high order of crystallinity, estimated at 75%, and gave two sharp peaks at 21.6° and 23.3° (2θ) on the x-ray goniometer trace. A crystalline melting point of 250°C. was observed; subsequent cooling of the molten polymer did not redevelop the crystallinity. This was suggestive of an internal crosslinking reaction.

The crystalline polymer could be melt-pressed at 110°C. to tough, opaque films. The infrared spectrum (Fig. 2) indicated nearly exclusive *trans,-trans*-diene in-chain groups, as shown by a single, intense absorption band at 985 cm.$^{-1}$ The polymer insolubility was attributed to the crystalline structure, inasmuch as the polymer did not swell with hydrocarbon solvents, as was the case for crosslinked polytrienes.

1,4-Polyhexatriene. When hexatriene was polymerized with a titanium tetraisopropoxide–triethylaluminum catalyst which had been used by Natta[5] to prepare 1,2-polybutadiene, an elastomeric polyhexatriene was obtained which was readily soluble in benzene. The infrared spectrum (Fig. 3) revealed, in addition to a large amount of *trans,trans*- and *cis,-trans*-diene absorption from 1,6-polymerization, a strong vinyl band at 910 cm.$^{-1}$ This was thought to be conjugated vinyl absorption which would have resulted from the expected polymerization in a 1,2-fashion. However, the failure of the 910 cm.$^{-1}$ band to disappear upon reaction of the polymer with dienophiles, together with the subsequent finding of a 900 cm.$^{-1}$ vinylic band in anionic polyhexatriene which was eliminated in Diels-Alder post-reactions, suggested that the polymer was formed in a combined 1,6 and 1,4 manner. The isolated *trans* band was thought to be hidden by the intense 985–970 cm.$^{-1}$ region of absorption. However, a low intensity absorption band at 945 cm.$^{-1}$ could have been isolated *trans*, although the amount of absorption was quite small compared to the amount of vinyl absorption at 910 cm.$^{-1}$

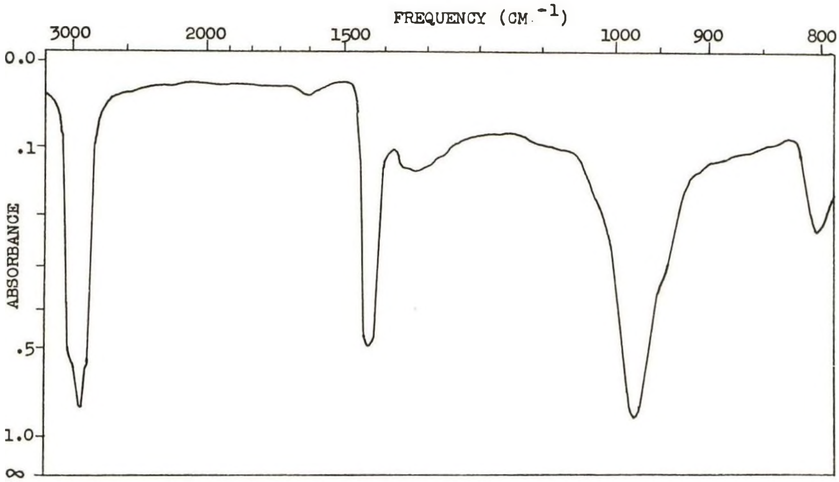


Fig. 2. Infrared spectrum of crystalline 1,6-polyhexatriene.

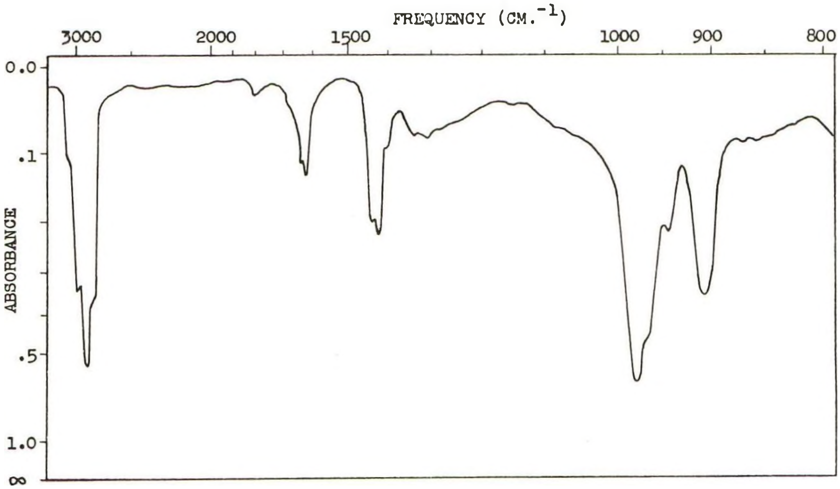


Fig. 3. Infrared spectrum of 1,4-polyhexatriene.

An examination of Fischer-Hirschfelder models disclosed that a 1,2-polytriene structure is significantly hindered, while a polymer structure built up of 1,4-polymer units was quite free of steric limitations. On this basis, it was concluded that steric factors had led to the unexpected 1,4 direction of polymerization, together with an appreciable amount of 1,6-polymer units.

1,6-Polyheptatriene and 2,7-Polyoctatriene. *trans,trans*-Heptatriene and *trans,trans,trans*-octatriene responded well to highly reactive catalyst systems (e.g., $VOCl_3$–i-Bu_3Al) at low temperatures. Soluble, film-forming, amorphous polymers were obtained in good yield, and less insolubilization was encountered than was observed with hexatriene under similar catalyst conditions. This was undoubtedly due to the relatively lower amount, or absence of, vinyl groups in heptatriene and octatriene monomers. The infrared spectra for both polymers were nearly identical to that for amorphous 1,6-polyhexatriene, except for the presence of methyl absorption at 1370 cm.$^{-1}$ and absence of vinylic bands at 915–900 cm.$^{-1}$

Anionic Polyhexatriene. Hexatriene was found to be exceptionally responsive to anionic initiation. *n*-Butyllithium-initiated polymerization in tetrahydrofuran gave high molecular weight polymer which was readily soluble in the polymerization solvent, as well as aromatic hydrocarbons. Since little difficulty was encountered with crosslinking while storing the polymer as a solution, it was well suited for post-reaction studies. However, butyllithium was quite nonselective in the direction of polymerization and a number of modes of enchainment resulted. In addition to the *trans,trans*, the *cis,trans*, the nonconjugated vinyl, and the *trans* groups which were found in 1,4-poly- and 1,6-polyhexatriene, the anionic polymer exhibited an absorption band at 900 cm.$^{-1}$ (Fig. 4) which was attributed to conjugated vinyl groups. The presence of such groups would have resulted

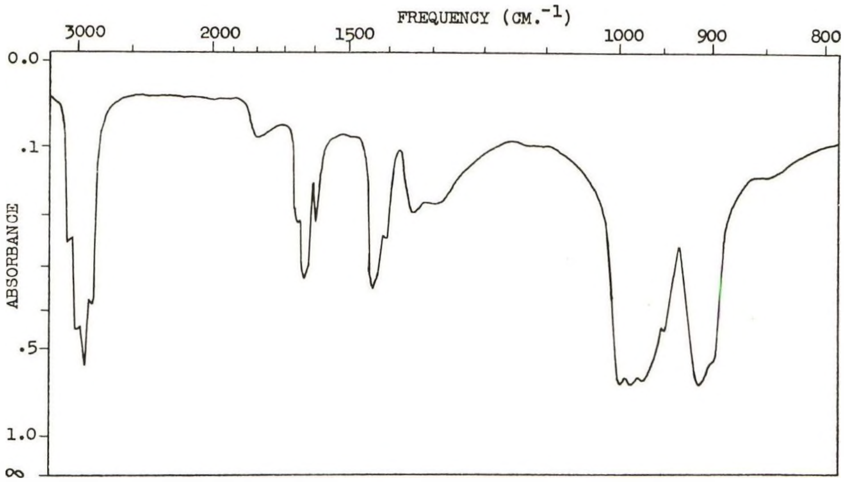


Fig. 4. Infrared spectrum of anionic polyhexatriene.

from a 1,2 mode of enchainment. Although nonconjugated *cis* absorption was not detected, the likelihood of its formation cannot be eliminated.

The elastomeric nature of solvent-cast films from anionic polyhexatriene suggested that the polymer was quite random in structure. Heptatriene and octatriene were also polymerized under anionic conditions, but the molecular weights attained were quite low in comparison to the hexatriene polymers, possibly because of low monomer purity. The infrared spectra were quite similar to that for anionic polyhexatriene; however, vinylic bands (915–900 cm.$^{-1}$) were absent in the polyoctatriene spectrum, as expected.

Cationic and Emulsion Polyhexatriene. Attempts to polymerize hexatriene with cationic initiation were somewhat disappointing. While the more vigorous Lewis acids, such as BF_3 and $AlCl_3$, led to extensively crosslinked polymers, the weaker cationic initiators (BF_3 etherate, $SnCl_4$) were feeble in their activity and at best resulted only in low molecular weight 1,6-polyhexatriene.

High molecular weight, soluble polyhexatriene was prepared by emulsion polymerization. The polymer was melt-pressed at 110°C. to a smooth, tough elastomeric film. The infrared spectrum indicated a unique polymer structure with predominantly *cis,trans* conjugated diene enchainment (970 cm.$^{-1}$) and only a minor amount of *trans,trans* absorption (985 cm.$^{-1}$) which prevailed in most of the coordination polymers.

Conjugative Activation of Internal Olefins

Special mention is warranted for the homopolymers from the internal olefin *trans,trans,trans*-2,4,6-octatriene. Natta[6] found that while internal olefins, such as *trans*- and *cis*-2-butene could be copolymerized (up to 50%) with ethylene by using coordination catalysts, they could not be homopolymerized. Unpublished work in this laboratory has shown that *trans,trans*-2,4-hexadiene, which is a vinylog of *trans*-2-butene, can be homopolymerized in a 1,4-manner to yield a low molecular weight grease. The high molecular weight 1,6-polyoctatriene homopolymer obtained in this work suggests that the conjugative effect on the stability of the triene intermediate is sufficient to overcome any steric factors inhibiting homopolymerization of the lower vinylogs of internal olefins. This "conjugative activation" was manifest in anionic polymerizations; *trans*-2-butene and *trans,trans*-2,4-hexadiene failed to homopolymerize with *n*-butyllithium, while *trans,trans,trans*-2,4,6-octatriene did yield a low molecular weight homopolymer.

Infrared Assignments and Correlation with Structure

The infrared spectra of the triene polymers were very distinctive and exhibited intense absorption bands associated with conjugated dienic unsaturation. Infrared spectra were obtained with Perkin-Elmer Model 21 and Infracord spectrophotometers, using thin polymer films or KBr pellets.

Carbon-hydrogen stretching vibrations in the 3100–3000 cm.$^{-1}$ region showed little variation from recorded examples.[7] Vinylic C–H was noted at 3090 cm.$^{-1}$ and *cis* and *trans* C–H stretching at 3010 cm.$^{-1}$ The C=C stretching bands in the 1680–1600 cm.$^{-1}$ region were noted only for 1,4-polyhexatriene and anionic polyhexatriene. Bands at 1643, 1630, and 1597 cm.$^{-1}$ were believed to be associated with conjugated *trans*, nonconconjugated vinyl, and conjugated vinyl, respectively. No absorption in this region was detected for the 1,6-polytrienes.

The 1000–900 cm.$^{-1}$ region, associated with carbon-hydrogen out-of-plane deformations, proved to be the most distinctive region for identification of the polymer structures. Two intense absorption bands were noted for all of the 1,6-polytrienes, at 985 and 970 cm.$^{-1}$ The 985 cm.$^{-1}$ band was identified as the absorption associated with *trans,trans*-diene structures. This was based on the ready disappearance of the band upon Diels-Alder reactions of the polymers with reactive dienophiles.[4] The absorption at 970 cm.$^{-1}$, always present as a shoulder to the 985 cm.$^{-1}$ band, was considered indicative of *cis,trans*-diene structure This absorption was usually little affected by dienophilic reactions. These two assignments were reinforced by the *trans,trans* and *cis,trans* bands reported[8] for the corresponding isomers of conjugated linoleates at 988 and 982 cm.$^{-1}$ Although the 970 cm.$^{-1}$ band was close to the normal location for isolated *trans* absorption, it was ruled out as such by the absence of a corresponding amount of vinylic absorption (see structure V). Then, too, under certain circumstances (in α-olefin–triene copolymers), the 970 cm.$^{-1}$ was partially removed by Diels-Alder reactions.

A strong band at 910 cm.$^{-1}$ was assigned to nonconjugated vinyl, since it was not affected by dienophiles, while conjugated vinyl absorption, which was easily removed by Diels-Alder reactions, was assigned to the absorption at 900 cm.$^{-1}$. The customary vinyl band at 990–1000 cm.$^{-1}$ was obscured by the intense *trans,trans* absorption.

EXPERIMENTAL

trans-1,3,5-Hexatriene (I)

A procedure similar to that reported by Woods and Schwartzman[9] was used to prepare hexatriene. A 350-g. portion of 2,4-hexadiene-1-ol (sorbyl alcohol) was dropped into a 2.5 × 50 cm. Pyrex column packed with 8–14 mesh Alcoa alumina at such a rate as to maintain the temperature at 260–280°C. The crude products were swept with nitrogen at a pressure of 5–10 mm. into two traps cooled with Dry Ice. The crude product was separated from water and the hexatriene was separated from the major impurity (cyclohexadiene) by crystallization and filtration at −50°C. The hexatriene thus obtained was refined by two recrystallizations from methanol, at −50 and −25°C. The product was extracted thoroughly with water, dried with calcium sulfate, and distilled at 130 mm. (b.p. 33–34°C.) from calcium hydride. A yield of 149 g. (52%) of *trans*-1,3,5-hexatriene was obtained; b.p. 80°C., m.p. −11.5°C. (lit.:[10] b.p. 80°C., m.p. −11.7°C.). The product was 99.8% pure, determined by chromatographing over a β,β-oxydipropionitrile column at 30°C. Hexatriene was stored at −15°C. over calcium hydride.

3,5-Heptadien-2-ol

This intermediate for heptatriene preparation was synthesized by the dropwise addition of a solution of 134 g. (1.40 moles) of 2,4-hexadien-1-al in 200 ml. of tetrahydrofuran to 1.50 moles of methylmagnesium bromide in 500 ml. of tetrahydrofuran in a 2-liter flask cooled to 15°C. After addition was complete, the mixture was stirred for 2 hr. at room temperature and hydrolyzed with 500 ml. of saturated ammonium chloride solution. The tetrahydrofuran was distilled off under vacuum and the product was fractionated to give 139.5 g. (89%) of 3,5-heptadien-2-ol, b.p. 49–50°C./2.3 mm., $n_D^{25} = 1.4860$.

trans,trans-1,3,5-Heptatriene (II)

The dehydration of 3,5-heptadiene-2-ol to 1,3,5-heptatriene was performed by use of the same alumina column employed for preparing hexatriene. A column temperature of 250–275°C. and a pressure of 3 mm. afforded the best yield of product. The crude product was purified in the same manner as hexatriene, except that the final recrystallization from methanol was carried out at 0°C. A 42% yield of pure *trans,trans*-1,3,5-heptatriene was obtained, m.p. 27°C., b.p. 101–102°C. (lit.:[11] b.p. 100–102°C.). In contrast to hexatriene, heptatriene was found to polymerize as a solid at −15°C.; therefore, it was stored in Dry Ice and used within a short time after preparation.

trans,trans,trans-2,4,6-Octatriene (III)

The starting material for octatriene was 2,4-octadien-6-ol, prepared in 82% yield by the addition of ethylmagnesium bromide to 2,4-hexadien-1-al.[12] The conditions for dehydration were identical to those for heptatriene. A 34% yield of all-*trans*-2,4,6-octatriene was realized; m.p. 52°C., b.p. 42°C./8 mm. (lit.:[12] m.p. 52°C., b.p. 44–45°C./11 mm.). This triene was also stored in Dry Ice to prevent polymerization.

1,6-Polyhexatriene (Amorphous)

All coordination polymerizations were carried out under anhydrous conditions with the use of flame-dried glassware and solvents stored over calcium hydride. All catalyst and monomer transfers were performed with syringes. A solution of 0.17 g. (0.4 mmole) of tetraphenyl titanate and 0.02 ml. (0.2 mmole) of vanadyl trichloride in 55 ml. of chlorobenzene was cooled to −25°C. in a 100-ml. flask equipped with stirrer and blanketed with nitrogen. A 3-ml. portion (3.0 mmoles) of a 1*M* solution of diethylaluminum chloride in heptane, to which a molar equivalent of anisole had been added, was injected into the flask. Hexatriene (5 ml., 0.045 mole) was added, and the solution was stirred at −25°C. for 24 hr. This viscous solution was carefully poured into cold, acidified ethanol (3% HCl) to precipitate a white polymer and inactivate the catalyst. The polymer was washed well with cold acidified ethanol and absolute ethanol and dissolved in benzene. Small amounts of residual alcohol could be removed by partial evaporation of benzene or with calcium hydride. Removal of small amounts of insoluble material was accomplished by centrifugation. (In order to preserve the soluble nature of the triene polymers, it was necessary to purify them in this manner, since solid, dry polymer almost always became crosslinked.) The polymer could be stored for considerable periods of time as a benzene solution. The yield of polymer (determined by evaporating the benzene from an aliquot of the polymer solution and weighing the residue) was 2.75 g.; 78%; η_{inh} (0.5% in benzene at 30°C.) = 0.61. Clear, flexible films were cast from benzene solution. The infrared spectrum was indicative of 1,6-enchainment, along with a minor amount of 1,2-polymer. Strong absorption bands were noted at 3010, 2925, 2852, 985, and 970 cm.$^{-1}$, moderate bands at 1445 and 1425 cm.$^{-1}$, and weak bands at 947 and 910 cm.$^{-1}$

1,6-Polyhexatriene (Crystalline)

A solution of 0.05 ml. (0.5 mmole) of vanadyl trichloride in 60 ml. of chlorobenzene in a 100-ml. flask was stirred at −30°C. under a slight flow of nitrogen. A 2 ml. portion (2.0 mmoles) of a 1*M* solution of triisobutylaluminum in cyclohexane was added, followed by 5 ml. (0.045 mole) of hexatriene (it was essential that the monomer be at least 98% pure). The solution was stirred for 2.5 hr. at −30°C., after which time the flask was choked with a slurry of swollen polymer. The catalyst was inactivated and the polymer was precipitated by the addition of cold acidified (3% HCl) ethanol. The polymer was collected by filtration and washed well in a Waring Blendor, first with cold acidified ethanol and then with cold ethanol.

The polymer was dried superficially by pressing between filter paper. It was immediately melt-pressed in a Carver press at 110°C. for 30 sec., followed by water quenching. Very thin films (less than 1 mil) were smooth, flexible, and tough, and slightly hazy, while thicker films were opaque. The infrared spectrum displayed strong absorption bands at 3010, 2925, 2852, 1445, and 985 cm.$^{-1}$, indicating nearly exclusive *trans*,-*trans*-conjugated diene structure resulting from a 1,6-mode of polymerization. The x-ray goniometer trace disclosed two sharp peaks at $2\theta = 21.6°$ and 23.3°, which completely disappeared upon melting at 250°C. and did not reappear upon cooling.

1,4-Polyhexatriene

A solution of 4.8 mmoles of triethylaluminum in 10 ml. of *n*-heptane was placed in a 50-ml. flask, equipped with stirrer and blanketed with nitrogen, and cooled with ice. A 5-ml. portion (3.5 g., 0.045 mole) of hexatriene was added, followed by 0.50 ml. (1.6 mmoles) of titanium tetraisopropoxide. The deep red solution was stirred at 0°C. for 48 hr., after which time a viscous solution had formed. The catalyst was inactivated with acidified ethanol and additional dilution with cold ethanol precipitated a quantity of gummy polymer. This polymer was washed well with alcohol and dissolved in benzene.

Clear, tough, elastomeric films were cast from benzene solution, η_{inh} (0.5% in benzene) = 0.51. As was the case for most of the solvent-cast films, this film became insoluble after drying. The films were oxidized extensively after 24 hr. in air. The structure of 1,4-polyhexatriene was deduced from the infrared spectrum, which showed a strong vinylic band at 910 cm.$^{-1}$ in addition to the 985 and 970 cm.$^{-1}$ bands noted for 1,6-polyhexatriene.

1,6-Polyheptatriene

This polymer was prepared by the same procedure described for crystalline 1,6-polyhexatriene. Insoluble polymer did not appear during the polymerization and the polymerization was continued for an additional 24 hr. The viscous solution was treated with cold acidified ethanol and ethanol to yield a colorless, fluffy polymer. This was purified as the benzene solution. The yield was 84%, η_{inh} (0.5% in benzene at 30°C.) = 0.73. Clear, flexible films which were obtained by solvent casting showed infrared spectra nearly identical to that of amorphous 1,6-polyhexatriene. A slight trace of vinyl absorption at 900–910 cm.$^{-1}$ was observed, as well as a weak band due to methyl absorption at 1370 cm.$^{-1}$ (not present in polyhexatriene).

2,7-Polyoctatriene

A solution of 1.5 ml. (1.5 mmoles) of a 1*M* 1:1 complex of diethylaluminum chloride and anisole in cyclohexane was added to a solution of 0.25 mmole of vanadyl trichloride in 20 ml. of chlorobenzene in a 50-ml. flask equipped with stirrer and blanketed with nitrogen. The purple, heterogeneous mixture was cooled to −35°C., and 4 ml. of a *n*-heptane solution containing 2.0 ml. (1.56 g.) of *trans,trans,trans*-2,4,6-octatriene was added. After 1 hr. at −35°C. the thick mixture was inactivated with cold, acidified ethanol and purified in the same fashion as polyheptatriene. A benzene solution containing 1.2 g. (77%) of polymer was obtained, η_{inh} (0.5% in benzene at 30°C.) = 0.99. The infrared spectrum was similar to that for amorphous 1,6-polyhexatriene and polyheptatriene, except for complete absence of vinyl absorption (910–900 cm.$^{-1}$) and the presence of a sharp methyl absorption band at 1370 cm.$^{-1}$.

Anionic Polyhexatriene

A 30-ml. volume of tetrahydrofuran, which had been distilled from *n*-butyllithium, was added by syringe to a flask equipped with a stirrer and protected with an atmosphere of dry nitrogen. The solvent was cooled with ice, and 0.24 mmole of *n*-butyllithium in hexane was added. To this was added dropwise 10 ml. (0.09 mole) of hexatriene, resulting in a red-orange solution. The solution thickened rapidly over 30 min. A trace of ethanol was added to inactivate the catalyst resulting in a clear, viscous solution. The yield of polymer (by aliquot) was 5.7 g. (80%), η_{inh} (0.5% in tetrahydrofuran at 30°C.) = 1.15.

Clear, elastomeric films were cast from tetrahydrofuran solution. The infrared spectrum of the film showed absorption bands of nearly equal intensities at 995 (vinyl), 985 (*trans,trans*-diene), 970 (*cis,trans*-diene), 910 (nonconjugated vinyl), and 900 cm.$^{-1}$ (conjugated vinyl).

Anionic Polyheptatriene and Polyoctatriene

The procedure for polymerizing *trans,trans*-1,3,5-heptatriene and *trans,-trans,trans*-2,4,6-octatriene with butyllithium was essentially the same as for hexatriene. However, neither heptatriene nor octatriene reached the degree of polymerization attained by hexatriene. The gummy polymers obtained from both trienes were washed well with alcohol during isolation. The inherent viscosity found for polyheptatriene was 0.13 (0.5% in THF at 30°C.); for polyoctatriene, η_{inh} = 0.09. It was not ascertained whether the low molecular weight was due to monomer impurities or to some other cause. The infrared spectra for both anionic polymers were quite similar to anionic polyhexatriene, with the exception of the absence of vinylic bands (910–900 cm.$^{-1}$) for polyoctatriene.

Emulsion Polyhexatriene

Oxygen-free water (20 ml.), 0.4 g. of Ivory soap, 0.02 g. of dodecyl mercaptan, 0.2 g. of potassium persulfate, and 6.0 ml. (4.3 g., 0.054 mole) of *trans*-1,3,5-hexatriene were combined in a 100-ml. bottle. The contents were agitated for 48 hr. at room temperature and then poured into 50 ml. of methanol. White, rubbery polymer which precipitated was washed well with methanol and dried by pressing between filter paper. The polymer was melt-pressed at 100°C. to a clear, slightly elastomeric film. The infrared spectrum showed a strong absorption at 970 cm.$^{-1}$, a weak shoulder at 985 cm.$^{-1}$, and only a trace of vinyl absorption at 910 cm.$^{-1}$.

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Résumé

La polymérisation du 1,3,5-hexatriène, du 1,3,5-heptatriène et du 2,4,6-octatriène, initiée par des catalyseurs différents, montre que les triènes forment une classe distincte de monomères conduisant à des polyoléfines insaturées. Avec un système catalytique de coordination soluble, on obtient des polymères solubles de poids moléculaires élevés possédant un enchaînement 1,6 prédominant; ce mode de polymérisation fournit des groupes 1,3-diényles dans la chaîne principale du polymère. On a préparé un 1,6-polyhexatriène stéréospécifique, possédant une cristallinité d'un type nouveau, basé sur une repétition d'unités *trans*, *trans*-1,3-diène par une polymérisation à basse température au moyen d'un catalyseur trichlorure de vanadyle-triisobutyl-aluminium.

Zusammenfassung

Die Polymerisation von 1,3,5-Hexatrien, 1,3,5-Heptatrien und 2,4,6-Octatrien mit verschiedenen Katalysatoren liess die Triene als eine besondere Klasse von Monomeren erscheinen, die zu ungewöhnlichen ungesättigten Polyolefinen führen. Lösliche hochmolekulare Polymere mit vorwiegender 1,6-Verkettung wurden mit einem löslichen Koordinationskatalysatorsystem dargestellt; diese Polymerisation lieferte 1,3-Dienylgruppen in der Polymerhauptkette. Ein stereospezifisches 1,6-Polyhexatrien von einem neuartigen Kristallinitätstyp mit *trans*-, *trans*-1,3-Dienbausteinen wurde durch Tieftemperaturpolymerisation mit einem Vanadyltrichlorid–Triisobutylaluminiumkatalysator dargestellt.

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Post-Modification of Conjugated Triene Polymers Via the Diels-Alder Reaction*

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Synopsis

Polymers from 1,3,5-hexatriene, 1,3,5-heptatriene, and 2,4,6-octatriene were modified by means of the Diels-Alder reaction. Several dienophilic agents were reacted with the polytrienes containing conjugated diene groups to yield cyclic structures incorporated into, and appended to, the polymer backbone. The mild conditions of the post-reactions proved to be convenient for the conversion of highly unsaturated polyhydrocarbons into unique polymers bearing functional substituents. It was proposed that the incomplete reaction of tetracyanoethylene with the 1,3-dienyl groups of the polymer substrates was a result of steric hindrance of the ring structures of the polymer adducts.

INTRODUCTION

Little use has been made of the Diels-Alder reaction in the modification of preformed polymers. A recent paper[1] has described the modification of unsaturated polyesters by utilizing the olefinic site in the polymer as the dienophile in reactions with monomeric dienes. The synthesis of polyhydrocarbons containing a considerable amount of conjugated diene structure[2] suggested that the reaction of these polymers with dienophiles might be a convenient synthetic route to polymers modified with unusual cyclic structures. Some highly reactive dienophiles, containing strong electronegative substituents, have been described[3,4] in recent years and were considered ideal for their reaction with polytrienes under the mild conditions necessary to minimize attendant crosslinking of the polymer substrates.

DISCUSSION

Several polymers which had been synthesized earlier[2] were utilized as the diene substrates for Diels-Alder post-reactions. The polymers studied most were those from 1,3,5-hexatriene, 1,3,5-heptatriene, and 2,4,6-octatriene, which were polymerized in a 1,6 fashion through the conjugated

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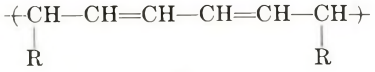
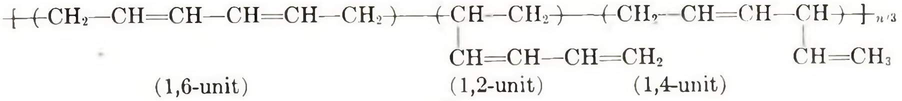
triene system. The resulting structures (Ia) contained a preponderance of *trans,trans*-diene units with a lesser amount of *cis,trans*-diene groups.



$$-\!(\underset{\displaystyle R}{\underset{|}{CH}}-CH{=}CH-CH{=}CH-\underset{\displaystyle R}{\underset{|}{CH}})\!-$$

Ia

Anionic polyhexatriene (Ib), which contained a mixture of conjugated in-chain diene groups from 1,6 enchainment, conjugated vinyl, *trans*-dienes from 1,2 polymerization, and nonconjugated vinyl and *trans*-unsaturation from a 1,4 mode of polymerization was also studied.

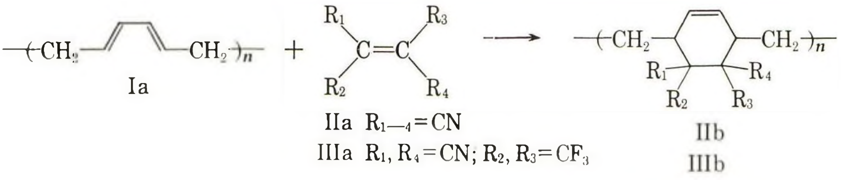


$$\left[(CH_2-CH{=}CH-CH{=}CH-CH_2)-(\underset{CH=CH-CH=CH_2}{\underset{|}{CH}}-CH_2)-(CH_2-CH{=}CH-\underset{CH=CH_3}{\underset{|}{CH}})\right]_{n/3}$$

(1,6-unit) (1,2-unit) (1,4-unit)

Ib

Several types of reagents, ranging from maleic anhydride to the more potent dienophiles of the tetracyanoethylene variety, were used. The net effect of the reaction was to transform polyhydrocarbons into polymers containing cyclohexene rings (II–V), with various polar groups substituted on the cyclohexene moiety. In addition, the reaction of the polytrienes with sulfur dioxide was shown to yield cyclic sulfone structures (VI).



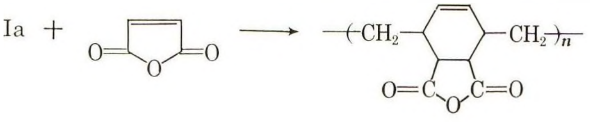
Ia

IIa R_{1-4}=CN

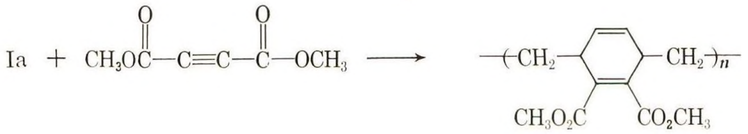
IIIa R_1, R_4=CN; R_2, R_3=CF_3

IIb

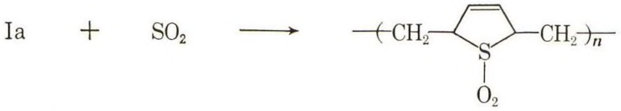
IIIb



IV

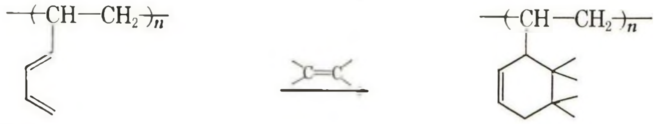


V



VI

When 1,6-polytrienes (Ia) were used as the polymeric diene substrates, the cyclic units were incorporated into the polymer backbone, whereas the conjugated vinyl,*trans*-diene units of anionic polyhexatriene (Ib) gave cyclic structures appended to the polymer chain (VII).



1, 2—polymer VII

Typical Diels-Alder reactions which were carried out with the polytrienes have been summarized in Table I. Tetracyanoethylene (TCNE), due to its strong dienophilic activity,[3] was the reagent most frequently reacted with the polymers. The reactions were carried out in tetrahydrofuran or benzene solution. When benzene was employed as the solvent, the change in the polar nature of the polymer resulting from the incorporation of cyano or trifluoromethyl groups was demonstrated by precipitation of the modified polymer from the nonpolar solvent. Polymers which were prepared from 1,6-polytrienes and the cyano- and cyanotrifluoromethyl-substituted ethylenes (IIa and IIIa) could not be melt-pressed into clear films because of decomposition above 200°C. (this is similar to the behavior of polyacrylonitrile). Films were obtained by casting from polymer solutions. The films obtained from the polymeric adducts of the dienophiles IIa and IIIa and 1,6-polytrienes were stiffer (higher modulus of elasticity) and less flexible than the unmodified polyhydrocarbon substrates.

The reaction of tetracyanoethylene with anionic polyhexatriene, an elastomer containing an assortment of olefinic structures resulting from 1,2-, 1,4-, and 1,6-polymerization (Ib), gave polymers which were solvent-cast to tough, flexible, and somewhat elastomeric films. This was undoubtedly due to the amorphous, copolymeric nature of the original unmodified polymers. Dielectric measurements of these modified films, which probably had a high degree of chain mobility as well as a substantial concentration of polar cyano groups, disclosed a significant increase from the dielectric values of the unsubstituted polytriene films.

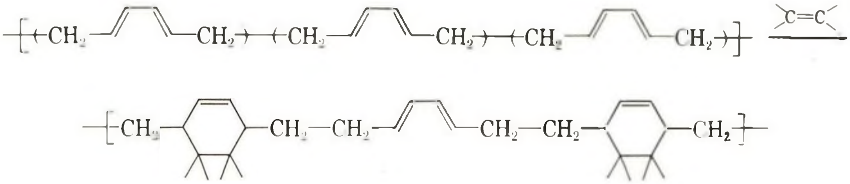
The 1,3-diene groups in the polymers reacted in a typical Diels-Alder fashion. The reaction of *trans,trans*-diene groups with dienophiles occurred more rapidly than the *cis,trans* type and was conveniently followed by observing the diminution of the 985 cm.$^{-1}$ infrared absorption band. The infrared band at 970 cm.$^{-1}$, attributed to *cis,trans* absorption, rarely showed any significant decrease in intensity. This was not unexpected, since it has been reported that *trans,trans*-dienes undergo the Diels-Alder reaction at a rate five times that of *cis,trans*-dienes.[5] It was also found that the reaction of the *trans,trans*-dienyl groups of homopolytrienes never reached completion, even when using tetracyanoethylene at elevated temperature for prolonged periods. The reason for this incomplete reaction became apparent when Fischer-Hirschfelder molecular models of the post-reacted polymers were studied. The steric restrictions which would be imposed by converting every successive diene group into a cyclohexene

TABLE I
Typical Post-Reactions of Polytrienes

Base polymer	Polymer η_{inh}[a]	Solvent	Dienophile	Time, hr.	Temp., °C.	Adduct η_{inh}[b]	Remarks
1,6-Polyhexatriene	0.61	Benzene THF	TCNE	4	25	0.52	45% reaction of *trans,trans*-diene units
1,6-Polyheptatriene	0.88	Benzene	TCNE	24	25	0.62	50% reaction of *trans,trans*-units
2,7-Polyoctatriene	0.99	THF	TCNE	24	25	0.64	43% reaction of *trans,trans*-dienes
Anionic polyhexatriene	1.15[b]	THF	TCNE	4	25	0.98	38% reaction of *trans,trans*- and *trans*,vinyl dienes
1,6-Polyhexatriene	0.61	THF	$CN(CF_3)C{=}C{-}CN(CF_3)$	5	65	0.63	45% reaction of *trans,trans*-units; C-F bands in infrared
1,6-Polyhexatriene	0.61	Toluene	Maleic anhydride	72	25	—	55–60% reaction of *trans,-trans*-units; infrared bands at 1820, 1765, and 1240 cm.$^{-1}$
1,6-Polyhexatriene	0.61	Toluene	Sulfur dioxide	5	65	—	<10% reaction of *trans,-trans*-units; sulfone bands at 1300 and 1125 cm.$^{-1}$
1,6-Polyhexatriene	0.61	Benzene	Dimethyl acetylenedicarboxylate	5.5	80	—	>75% reaction of *trans,-trans*-dienes; infrared bands at 1750–1700 and 1250 cm.$^{-1}$

[a] 0.5% in benzene at 30°C.
[b] 0.5% in tetrahydrofuran at 30°C.

unit in the polymer chain are so great that it is probable that the reaction of no more than every other diene unit would be possible:



EXPERIMENTAL

A general procedure which was employed for reacting polytrienes with tetracyanoethylene can be illustrated by the reaction with 1,6-polyhexatriene.

1,6-Polyhexatriene–Tetracyanoethylene Adduct

A solution of 2.0 g. (0.025 equiv.) of 1,6-polyhexatriene,[2] η_{inh} (0.5%, benzene, 30°C.) = 0.61, in 25 ml. of benzene was treated with a solution of 3.2 g. (0.02 mole) of tetracyanoethylene[3] in 15 ml. of tetrahydrofuran. After 4 hr., the original red color of the solution had changed to a pale yellow-green. Methanol was added to precipitate a quantity of white polymer, which was washed well with methanol and dried at room temperature under vacuum. A 3-g. yield of colorless polymer was obtained which was insoluble in benzene, but completely soluble in tetrahydrofuran. The polymer had an η_{inh} (0.5% in THF at 30°C.) of 0.52. Clear films were cast from tetrahydrofuran solution. The infrared spectrum (Fig. 1) disclosed that much of the *trans,trans*-diene absorption band at 985 cm.$^{-1}$ had

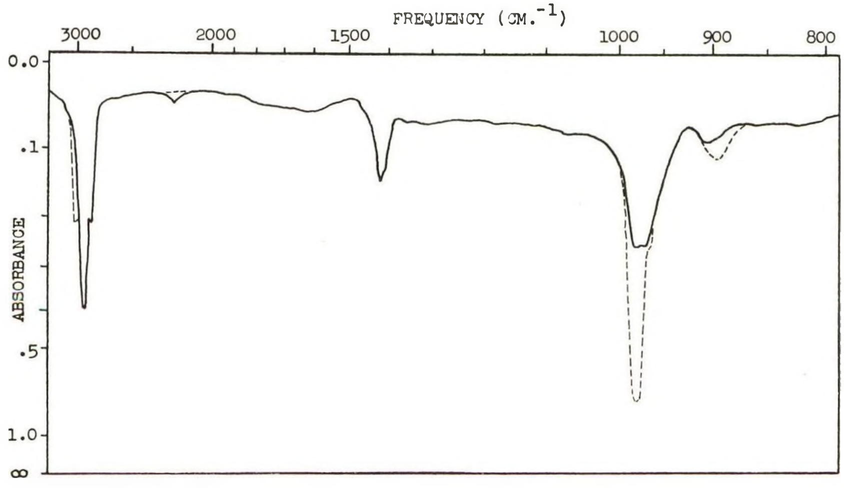


Fig. 1. Infrared spectrum of amorphous 1,6-polyhexatriene. (- - -) Unreacted polymer; (——) Polymer adduct with tetracyanoethylene.

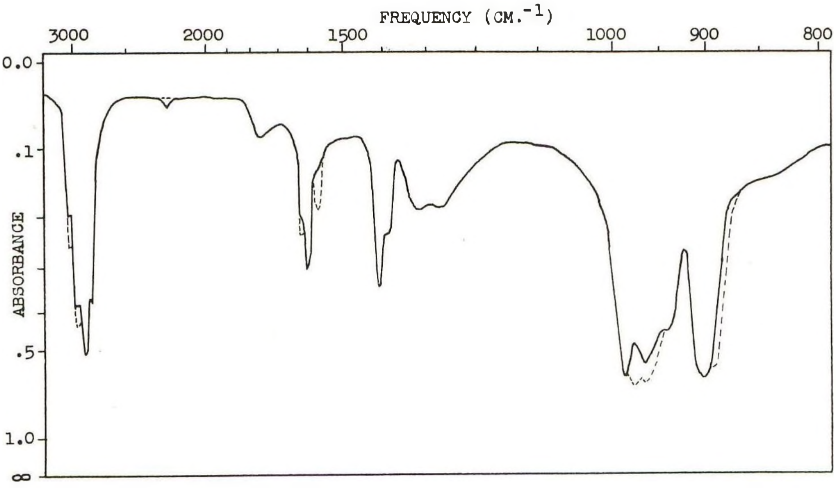


Fig. 2. Infrared spectrum of anionic polyhexatriene. (- - -) Unreacted polymer; (——) Polymer adduct with tetracyanoethylene.

been removed, while the *cis,trans*-diene shoulder at 970 cm.$^{-1}$ was virtually unchanged. A relatively weak cyano absorption band had appeared at 2220 cm.$^{-1}$. The nitrogen analysis of 18.20% indicated approximately 45% of the theoretical diene content had been reacted with TCNE.

The same general technique was also used to prepare adducts of tetracyanoethylene with 1,6-polyoctatriene and 1,6-polyheptatriene.

Anionic Polyhexatriene–TCNE Adduct

This reaction was carried out in tetrahydrofuran, the polymerization solvent. The reaction product was solvent-cast to clear films which were less elastomeric than films from the unmodified polyhexatriene. The infrared spectrum of the polymeric adduct (Fig. 2) showed complete removal of the shoulder at 900 cm.$^{-1}$, which had been attributed to the conjugated vinyl group resulting from a 1,2 mode of polymerization. Some of the *trans,trans*-diene absorption band (985 cm.$^{-1}$) had also been removed. Nitrogen analysis indicated 38% of the theoretical amount of TCNE had reacted.

1,6-Polyhexatriene–1,2-Dicyano-1,2-di(trifluoromethyl)ethylene Adduct

1,6-Polyhexatriene was reacted in refluxing tetrahydrofuran with 1,2-dicyano-1,2-di(trifluoromethyl)ethylene.[4] Although the adduct remained reasonably high in molecular weight (η_{inh} in THF = 0.63), the films from the polymer tended to be brittle, perhaps as a result of extreme steric hindrance in the polymer chain. The infrared spectrum was somewhat similar to those for polyhexatriene–TCNE adducts. In addition to partial removal of the 985 cm.$^{-1}$ band and appearance of a weak cyano band (2220 cm.$^{-1}$), carbon–fluorine absorption bands were noted in the

1250–1150 cm.$^{-1}$ region. Nitrogen analysis indicated that approximately 45% reaction had occurred.

1,6-Polyhexatriene–Maleic Anhydride Adduct

A solution of 1.6 g. (0.02 equiv.) of 1,6-polyhexatriene and 2.0 g. (0.02 mole) of maleic anhydride in 10 ml. of toluene was stirred at room temperature for three days. The addition of diethyl ether precipitated a white polymer which was washed well with ether and redissolved in tetrahydrofuran. Clear films were cast from the solution. The infrared spectrum showed that 55–60% of the *trans,trans*-absorption band at 985 cm.$^{-1}$ had been removed. The appearance of strong absorption bands at 1820, 1765, and 1240 cm.$^{-1}$ was also indicative of the addition of maleic anhydride.[6]

1,6-Polyhexatriene–Sulfur Dioxide Adduct

A solution of 1.6 g. (0.02 equiv.) of 1,6-polyhexatriene in 10 ml. of toluene in a pressure bottle was cooled to −15°C. and 5 ml. of liquified sulfur dioxide was added. The bottle was sealed, placed in a wire cage, and agitated for 5 hr. at 65°C. After the bottle was chilled and opened, the excess sulfur dioxide was allowed to evaporate. The solution was poured into methanol to precipitate a white polymer, which was dried under reduced pressure and dissolved in tetrahydrofuran. A clear, stiff film was cast from this solution. The infrared spectrum of the film indicated that only about 10% of the *trans,trans*-diene band at 985 cm.$^{-1}$ had been removed. However, the presence of strong absorption bands at 1300 and 1125 cm.$^{-1}$ demonstrated that cyclic sulfone structures had been incorporated into the polymer.[6] An attempt to carry this reaction to a higher degree of completion at 100°C. for 64 hr. resulted in the formation of black polymer which was soluble in tetrahydrofuran but formed only very brittle films.

1,6-Polyhexatriene–Dimethyl Acetylenedicarboxylate Adduct

A solution of 2.0 g. (0.025 equiv.) of 1,6-polyhexatriene, 4.6 g. (0.030 mole) of dimethyl acetylenedicarboxylate and 0.1 g. of hydroquinone in 15 ml. of benzene was refluxed for $5^1/_2$ hr. The solution was then poured into methanol to precipitate light yellow polymer. The polymer was washed well with methanol and dried under reduced pressure. The polymer was dissolved in tetrahydrofuran, and clear films were obtained from the solution. The infrared spectrum indicated that nearly all of the *trans,trans*-diene absorption band at 985 cm.$^{-1}$ had disappeared. The appearance of strong carbonyl absorption bands in the 1750–1700 cm.$^{-1}$ region and a 1250 cm.$^{-1}$ band were additional evidence of the incorporation of dimethyl acetylenedicarboxylate.

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Résumé

Des polymères du 1,3,5-hexatriène, 1,3,5-heptatriène et 2,4,6-octatriène ont été modifiés au moyen de la réaction de Diels-Alder. On a fait réagir plusieurs agents diénophiles avec les polytriènes contenant des groupes diènes conjugués pour produire des structures cycliques incorporées et attachées à la chaîne principale du polymère. Des conditions douces de post-réaction sont indispensables pour transformer les hydrocarbures polymériques fortement insaturés en un polymère unique portant des substituants fonctionnels. On a proposé que la réaction incomplète du tétracyanoéthylène avec les groupes 1,3-diényle des substrats polymériques résultait de l'encombrement stérique des structures cycliques du polymère produit.

Zusammenfassung

Polymere aus 1,3,5-Hexatrien, 1,3,5-Heptatrien und 2,4,6-Octatrien wurden mit Hilfe der Diels-Alder-Reaktion modifiziert. Einige Dienophile wurden mit den konjugierte Diengruppen enthaltenden Polytrienen unter Bildung zyklischer, in die Polymerkette eingebauter und an diese angehängter Strukturen zur Reaktion gebracht. Die milden Bedingungen der Nachreaktion erwiesen sich für die Umwandlung von hochgradig ungesättigten Polykohlenwasserstoffen in ungewöhnliche, Funktionalsubstituenten tragende Polymere als brauchbar. Es wird angenommen, dass die unvollständige Reaktion von Tetracyanäthylen mit der 1,3-Dienylgruppe der Polymersubstrate ein Ergebnis der sterischen Hinderung der Ringstrukturen der Polymeraddukte ist.

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α,ω-Glycols from Isobutylene and Some Derived Block Copolymers

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Synopsis

Butyl rubber containing 2 mole-% of isoprene was ozonized and reduced producing polyisobutylene glycol. Hydroxyl equivalent determinations on the glycol and elemental analyses of the chain extended polymers indicate the glycol to be difunctional. Possible structures of the glycol and extended polymer are suggested.

INTRODUCTION

In a recent publication, Hayashi and Marvel[1] described the preparation of α,ω-glycols of polybutadiene, polyisoprene, and their hydrogenated derivatives using a lithium naphthalene catalyst. This particular study is an extension of that work and involves α,ω-glycols of polyisobutylene.

The polyisobutylene glycols were prepared by the ozonization of a butyl rubber, followed by reduction in a manner similar to that described by Greenwood[2,3] with the use of dry methylcyclohexane as solvent and lithium aluminum hydride in tetrahydrofuran as the reducing agent. The resulting solutions were decomposed with dilute sulfuric acid and the organic layers washed, dried, and, finally, evaporated to dryness leaving highly viscous liquids.

Infrared analysis of the resulting polymers indicated the presence of OH groups (bands at 3400 cm.$^{-1}$) and also the complete absence of carbonyl groups. The results are given in Table I.

The sample of butyl rubber (M.D. 503) was described as a fast curing high Mooney butyl of 800,000 molecular weight containing 2 mole-% of isoprene almost exclusively of the 1,4-configuration.[4] Ozonolysis of this rubber should, theoretically, give a polyisobutylene unit with a number-average molecular weight of 2848.

It can be seen from Table I that the number-average molecular weights approximate quite closely to the theoretical values except in early experiments. In these early experiments, the ozonolysis was discontinued as soon as ozone was observed in the waste gas. In the later experiments, the solutions were thoroughly saturated with ozone. It seems probable that the

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* Postdoctoral Research Associate supported by Textile Fibers Department, E. I. du Pont de Nemours and Company, Inc., 1962–63.

TABLE I

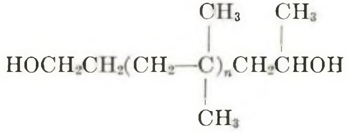
	Yield, %	Viscosity at 30.0°C.[a]		Hydroxy equivalents[b]	Molecular weight[c]	n	CH analysis			
							Found		Calcd.[d]	
		In benzene	In THF				C, %	H, %	C, %	H, %
PIBG 6	71.2	—	0.099	2568, 2562	5110	90				
PIBG 8	85.2	—	0.100	2390, 2397	4787	84				
PIBG 9	95.6	0.070	0.087	1375, 1375	2750	47	84.69	14.41	85.65	14.18
PIBG 11	90.1	0.077	0.094	1531, 1508	3038	52	83.88	14.09	84.72	14.19
PIBG 12	98.4	—	0.089	1584, 1545	3129	54	84.48	14.15	84.76	14.20
PIBG 16	99.5	0.073	0.090	1333, 1313	2646	46	84.23	14.39	84.63	14.15
PIBG 17	90.3	0.075	0.092	1310, 1273	2583	45	84.14	14.19	84.63	14.15
PIBG 18	96.0	0.082	0.093	1329, 1352	2681	46	84.90	14.39	84.63	14.15

[a] Inherent viscosity in the concentration range of 0.5–1.0%.

[b] Hydroxy equivalents determined by the acetic acid/pyridine method.[5]

[c] Number-average molecular weight calculated from the hydroxy equivalents.

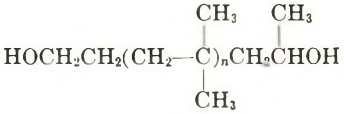
[d] Calculated from the model:



$$HOCH_2CH_2(CH_2{-}\overset{CH_3}{\underset{CH_3}{C}})_nCH_2\overset{CH_3}{C}HOH$$

glycols PIBG 6 and PIBG 8 were not completely degraded and still contain some unsaturation, although this was not apparent from the infrared spectra.

The glycols prepared in later experiments all had hydroxy equivalents of approximately half that of the theoretical number-average molecular weight, a good indication that the polymer was difunctional. The polymer should then have the structure I:

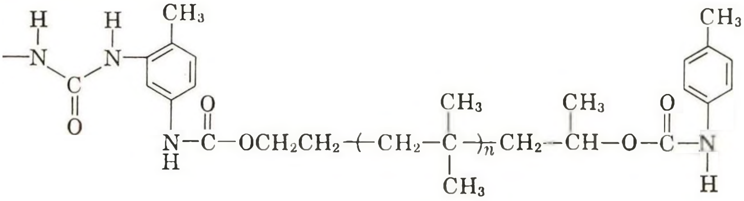


$$HOCH_2CH_2(CH_2-\overset{CH_3}{\underset{CH_3}{C}})_nCH_2\overset{CH_3}{C}HOH$$

I

The theoretical C and H analyses of such glycols agree quite closely with the experimental values which were obtained.

The glycols were then treated with 2 moles of 2,4-toluenediisocyanate to form the urethane and then with water to join the urethane units with urea linkages (II)



II

Another possible scheme involves urethane linkages at the 2 position of the diisocyanate, but this is unlikely as the isocyanate group *ortho* to the methyl group of the 2,4-toluenediisocyanate is much less reactive than the *p*-isocyanate group.[6]

Two experimental methods were used to extend the glycols, and only the experiments carried out in the absence of solvent and catalyst led to completely soluble products. The method utilizing a catalyst gave higher viscosities but a considerable amount of insoluble product was obtained. This is possibly due to trace amounts of 1,2 structure in the original butyl rubber leading to a trifunctional polyol which could crosslink on chain extension with 2,4-toluenediisocyanate.

The overall molecular weights of the chain extended polymers were not as high as obtained in previous work with butadiene glycols and this is due, possibly, to the fact that the secondary alcohol of the polyisobutylene glycol is less reactive than the primary alcohol.

EXPERIMENTAL

Materials

Tetrahydrofuran was supplied by Matheson, Coleman and Bell and dried over calcium hydride.

Methylcyclohexane was pure grade supplied by the Phillips Petroleum Company, dried over calcium hydride.

Butyl Rubber, M.D. 503 from Enjay Chemical Company, Division of Humble Oil and Refining Company, was made available through Dr. A. J. Ultee of Orlon-Lycra Division of E. I. du Pont de Nemours and Company.

Lithium aluminum hydride was as supplied by Metal Hydrides, Inc., 95 + % pure.

2,4-Toluenediisocyanate was supplied by du Pont, Elastomer Chemicals Department as Hylene T and purified by distilling under reduced pressure of nitrogen.

Polyisobutylene Glycol

Butyl rubber (49.06 g.) was dissolved in one liter of dry methyl cyclohexane in a 2-liter, three-necked flask containing a mechanical stirrer, sintered glass gas inlet, and a thermometer and the whole chilled to −10°C. When the required temperature was reached, the thermometer was replaced by a gas outlet consisting of a water condenser leading to a drying tube and, finally, to a gas bubbler which contained a solution of sodium iodide.

Ozone was then passed through the solution until it was thoroughly saturated. This was done by allowing the gas to pass through the solution for 2 hr. after iodine had been observed in the sodium iodide solution. In initial experiments, the flow of ozone was stopped soon after ozone was noted in the waste gas. This resulted in a less highly degraded polymer. Dry nitrogen was then passed through the solution to remove dissolved oxygen.

The outlet condenser and the sintered glass inlet were then removed and replaced by a thermometer and a dropping funnel containing a filtered solution of lithium aluminum hydride (3.35 g.) in tetrahydrofuran (440 ml.). The reducing agent was then added at such a rate as to keep the temperature below −5°C. Upon addition of the lithium aluminum hydride, the solution became highly viscous but reverted to a more mobile state on addition of excess reducing agent.

The whole was allowed to warm to room temperature, the dropping funnel replaced by a condenser, and the mixture refluxed for 30 min. The solution was again chilled to −10°C. and the excess hydride decomposed with dilute sulfuric acid. The organic layer was then separated, washed with dilute acid and water, and dried over sodium sulfate.

The product (PIBG 9, Table I) was a highly viscous liquid and was obtained in 95% yield.

Chain Extension of the Polyisobutylene Glycols

1. Polyisobutylene glycol PIBG 9 (2.778 g.) and 2,4-toluenediisocyanate (0.371 g.) were heated at 80–85°C. under dry nitrogen for 16 hr., the mixture being stirred continuously. The mixture was then dissolved in dry tetrahydrofuran, and wet tetrahydrofuran (5% solution of water in tetrahydrofuran) was added in 2-ml. portions until the infrared spectrum of extracted samples showed the absence of isocyanate groups.

The polymer was precipitated, washed, and dried.

The yield was 2.951 g. of soluble product (94.2%) and there was no insoluble product. The inherent viscosity of this product was 0.26 (0.8% polymer in tetrahydrofuran at 30°C.).

ANAL. Calcd. for urethane–urea polymer: C, 82.41%; H, 13.15%; N, 1.83%. Found: C, 82.10%; H, 13.10%; N, 1.95%.

2. Polyisobutylene glycol PIBG 12 (Table I) (4.869 g.) was heated with 2,4-toluenediisocyanate (0.565 g.) and dibutyl tin dilaurate (0.041 g.) under dry nitrogen for 3 days at 78°C. The resulting mixture was dissolved in tetrahydrofuran and portions of wet tetrahydrofuran added as in previous experiments until all the isocyanate groups were used up.

The solution contained some insoluble material, and this was filtered off. The polymer was then precipitated as before.

The yield was 3.480 g. of soluble product (64.0%) and 1.539 g. of insoluble product (28.3%).

The inherent viscosity of the soluble polymer was 0.33 (0.9% polymer in tetrahydrofuran at 30°C.).

ANAL. Calcd. for urethane–urea polymer: C, 82.77%; H, 13.27%; N, 1.64%. Found: C, 83.5%; H, 13.31%; N, 1.71%.

We wish to thank Dr. A. J. Ultee of the Textile Fibers Department of E. I. du Pont de Nemours and Company, Inc., arranging for the gift of the butyl rubber. The financial support of the Textile Fibers Department is gratefully acknowledged. We should also like to thank Micro-Tech Laboratories, Inc., for elemental analyses of our samples.

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Résumé

Un caoutchouc butylique contenant deux pourcent molaire d'isoprène a été ozonisé et réduit en formant un polyisobutylène glycol. Les déterminations de l'équivalent hydroxyle sur le glycol et les analyses élémentaires des chaînes de polymère indiquent que le glycol est bifonctionnel. Des structures possibles du glycol et du polymère sont proposées.

Zusammenfassung

Butylkautschuk mit zwei Molprozent Isopren wurde ozonisiert und unter Bildung von Polyisobutylenglycol reduziert. Bestimmung des Hydroxyläquivalents des Glycols und Elementaranalyse der kettenverlängerten Polymeren zeigen, dass das Glycol difunktionell ist. Mögliche Strukturen für das Glycol und das verlängerte Polymere werden vorgeschlagen.

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Cohesive Energy Density and Internal Pressure of High Polymers

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Synopsis

A method for estimating the intermolecular pair potential in high polymers from density data alone is illustrated. The cohesive energy density and internal pressure of several polymers are calculated in this way. The results agree satisfactorily with various other estimates.

Several years ago Gibbs and DiMarzio began a series of papers[1–5] concerned with applications of the lattice theory to polymers and in particular to discussion of the glass transition. The use of a lattice as a basis for describing liquids may be objected to on theoretical grounds, but the fact remains that useful results are obtained from such a description and in the absence of anything better pragmatism wins the day. One result of the papers of Gibbs and DiMarzio is that the pair interaction potential can be estimated from specific volume data alone. From this may be calculated the cohesive energy density (ced), and the internal pressure, p_i. It is a trivial step from the work of Gibbs and DiMarzio[2,3] to these equations, but because the results agree with other estimates and hence give support to the theory it is good to take that step. In addition a basis is provided for interpreting the observation of Allen et al.[6] that for many polymers the ratio of internal pressure to cohesive energy density is about 1.3. Allen et al.[6] also report that for many polymers

$$d \ln p_i/dT = -2\alpha_L$$

as was first noted for liquids of small molecules.[7,8] Here α_L is the thermal coefficient of expansion of the liquid. The following development permits some comments on this relation also.

Derivation of the Equations

The papers of Gibbs and DiMarzio[2,3] provide the foundation for what follows, and where convenient their notation is adherred to. The internal energy is assumed divisible into three parts. The first is the cohesive energy term arising from intermolecular interactions. Gibbs and DiMarzio called this the "hole" energy and took the system with no holes as a reference of zero energy. For the present purpose the system of completely isolated chains provides a more logical zero point and is used. This change is of no real significance, but changes the form of the equation slightly.

The second term is the contribution made by interaction of adjacent bonded groups. This energy, denoted U_{Intra}, is assumed to be independent of the chain environment. The third term, denoted U_v, includes everything else: i.e., vibrational energy, electronic energy, etc. Like the second, it is assumed to be independent of chain environment. In these terms the internal energy is written:[2,3]

$$U = -(z\alpha S_x q n_x/2) + U_{\text{Intra}} + U_v \tag{1}$$

In this, z is the lattice coordination number, α is the pair interaction potential on a per mole basis, and n_x is the moles of x-mer chains. For long chains q is closely approximated by $x(z - 2)/z$. The factor S_x is defined by

$$S_x = qn_x/(qn_x + n_0) \tag{2}$$

where n_0 is the moles of "holes" or unoccupied sites in the system. The volume, V, of the system is given by[2,3]

$$V = C(xn_x + n_0) \tag{3}$$

where C, the volume per mole of sites, will be discussed later. Division of the cohesive energy by the volume gives the cohesive energy density (ced):

$$\text{ced} = (z - 2)\alpha S_x V_x/2C \tag{4}$$

where $V_x = xn_x/(xn_x + n_0)$ is the volume fraction of x-mers.

The internal pressure is defined to be

$$p_i = (\partial U/\partial V)_T \tag{5}$$

Reference to eq. (1) and the assumptions on which it is based shows that only the cohesive energy is volume-dependent. Therefore

$$p_i = -(zqn_x/2)[\alpha(\partial S_x/\partial V)_T + S_x(\partial\alpha/\partial V)_T] \tag{6}$$

At this point the pair interaction potential, α, must be examined. For the present purpose it is convenient to approximate it by an inverse cube proportionality to C. This corresponds approximately to an inverse sixth power of the pair separation. C is assumed independent of pressure; i.e., all of the compressibility is ascribed to changes in n_0. This assumption is undoubtedly false, but at low pressures it is believed to be a good approximation. From these considerations it follows that $(\partial\alpha/\partial V)_T = 0$. From the definitions of S_x and V $(\partial S_x/\partial V)_T$ is readily obtained. Substitution gives

$$p_i = zS_x^2\alpha/2C \tag{7}$$

From eqs. (4) and (7) is found

$$p_i/\text{ced} = z/(z - 2)(S_x/V_x) \tag{8}$$

in general S_x/V_x will be slightly less than unity, and, if $z = 8$, p_i/ced will be slightly less than $^4/_3$ as found by Allen et al.[6]

One may attempt to rationalize the choice of $z = 8$ by noting that the body-centered cubic lattice to which this corresponds is compatible with the tetrahedral lattice that would be appropriate if only bonded carbon atoms were considered.[2] The large difference between the bonded and nonbonded carbon–carbon distance severely weakens this argument, however, and it appears that at this time the choice of coordination number must be considered as arbitrary.

Allen et al.[6] also report that

$$d \ln p_i/dT \approx -2\alpha_L \tag{9}$$

In the present notation this corresponds to

$$d \ln p_i/dT = -2(d \ln C/dT) - [2/(xn_x + n_0)](dn_0/dT) \tag{10}$$

From eq. (7) is obtained

$$d \ln p_i/dT = -(d \ln C/dT) + (2d \ln S_x/dT) + (d \ln \alpha/dT) \tag{11}$$

The required derivatives are readily obtained from the above discussion. Substitution gives

$$d \ln p_i/dT = -4(d \ln C/dT) - (S_0/V_0)[2/(xn_x + n_0)](dn_0/dT) \tag{12}$$

Equation (12) does not agree with eq. (10). In the following section experimental results will be compared with these two equations and we shall find that they favor eq. (12).

In order to use the equations obtained above an expression for C is needed in terms of experimentally accessible quantities. For polyethylene this is easy. In terms of the model every CH_2 group occupies one lattice site. Working from here and using the appropriate bonded and nonbonded dimensions of atoms given by Pauling[9] one can readily estimate the volume required for various substituents. From this the number of cell sites per monomer unit can be determined. The factor x in the equations now refers not to the number of carbon atoms in the backbone but to the number of sites occupied per chain. Insofar as the substituents can be treated as branches this change in significance will have no effect on the form of the equations.[10] The equation for C is then

$$C = V_x M_x/\rho \tag{13}$$

in which M_x is the mean molecular weight of a site-filling unit and ρ is the density.

It is not necessary to go into detail here regarding the equations by which α is obtained from specific volume data. Gibbs and DiMarzio[2,3] have derived these, and their results are

$$\ln (V_0^{(z/2)-1}/S_0^{z/2}) = z\alpha S_x^2/2RT \tag{14}$$

TABLE I
Comparison of Estimates of the Solubility Parameter and of Internal Pressure

1	2	3	4	5	6	7	8	9	10	11	12	13
						δ, (cal./cc.)$^{1/2}$		p_i, cal./cc.		$-10^4\ d \ln p_i/dT$		
Polymer	$10^4\alpha_L$, deg.$^{-1}$	$10^4\alpha_g$, deg.$^{-1}$	T, °K.	ρ, g./cc.	M_x	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	$2\times10^4\alpha_L$
Polyethylene	6.36[a]	2.1[b]	293	0.855[a]	14	7.8[c]	8.0	78 ± 2[e]	84			
						7.9[d]						
						8.35[e]						
Polypropylene	4.8[f]	1.9[f]	330	0.886[f]	14	9.2[c]	9.4		118			
Polyisobutylene	5.67[g]	1.48[h]	293	0.935[g]	14	8.0[c]						
						8.05[i]	8.3	80[e]	91	13.9[e]	12.2	8.4
						8.1[j]						
						7.8[k]						
Natural Rubber	6.63[m]	2.0[m]	298	0.908[m,n]	68/5	7.9[l]						
						8.1[o]	8.3	88.5[m]	90	21.1[m]	20.2	13.3
						8.15[p]		88.0[e]		17[e]		
						8.35[i]						
Polyvinylchloride	5.2[q]	2.1[q]	355	1.406[n,r]	97/4	9.4[k]						
						9.7[j]	9.8					
						10.8[c]						
Polystyrene	5.33[t]	2.30[u,v]	373	1.05[w]	104/7	8.5[s]						
						8.6[k]	10.3					
						9.0[c]						
						9.1[x]						

[a] Data of Doolittle.[11]
[b] Data of Dannis.[12]
[c] Data of Hayes.[13]
[d] Data of Richards.[14]
[e] Data of Allen et al.[6]
[f] Data of Beck et al.[15]
[g] Data of Bekkadahl.[16]
[h] Data of Simha and Boyer.[17]
[i] Data of Scott and Magat.[18]
[j] Data of Burrell.[19]
[k] Data of Bristow and Watson.[20]
[l] Data of Gee.[22]
[m] Data of Scott.[21]
[n] Density at 298°K. All others are at 293°K.
[o] Data of Bristow and Watson.[23]
[p] Data of Small.[24]
[q] Data of Wood.[25]
[r] Data of Schildknecht.[26]
[s] Data of Boyer and Spencer.[30]
[t] Data of Fox and Flory.[27]
[u] Data of Fox and Flory.[28]
[v] Data of Gordon and Macnab.[29]
[w] Extrapolated value.
[x] Data of Staverman.[31]

and

$$\frac{1}{xn_x + n_0}\,\frac{dn_0}{dt} = \frac{(z\alpha/2RT^2)V_0S_x^2}{(z/2)S_x - (z\alpha S_0S_x^2/RT) - [(z/2) - 1]V_x} \qquad (15)$$

In deriving eq. 15 they neglected the dependence of α on T. To include it does not seriously complicate things; thus, using the relation between α and C given earlier we write in place of eq. (15):

$$\frac{1}{xn_x + n_0}\,\frac{dn_0}{dT} = \frac{(z\alpha S_x^2V_0/2RT)[(1/T) + (3d\ln C/dT)]}{(z/2)S_x - (z\alpha S_0S_x^2/RT) - [(z/2) - 1]V_x} \qquad (16)$$

The pair potential, α, can be eliminated between eqs. (14) and (16) and a value for xn_x/n_0 obtained. From this and eq. (14) the pair potential may be calculated. This is a tedious process, but a table has been computed relating the experimentally accessible quantity $T(\alpha_L - \alpha_g)/(1 + 3T\alpha_g)$ to the terms $z\alpha S_x/2RT$ and $z\alpha S_x^2/2RTV_x$ which are required for estimation of the (ced) and p_i. Here $\alpha_L = -d\ln\rho/dT$ above the glass transition at the temperature T and $\alpha_g = d\ln C/dT = -d\ln\rho/dT$ below the glass transition.

Discussion of Results

With the aid of the table discussed above, the results in columns 8, 10, and 12 of Table I were obtained from the data in columns 2–6. These may be compared with other experimental estimates tabulated in columns 7, 9, 11, and 13. Because cohesive energy density is most often reported in terms of the solubility parameter δ [equal to the square root of (ced)] this is the form adopted here. This also makes the agreement look better, but the reader will doubtless not be misled by this. With two exceptions the results were either calculated directly at 293°K. or corrected to this temperature. In these two instances it was more convenient to obtain the results at 298°K. The difference is insignificant.

In comparing the estimates of δ it is clear that only for polystyrene is the agreement bad. This may be explained by failure of the assumption that the pendant group may be treated as a simple branch.[10]

TABLE II
Relation between the Expansion Coefficients and the Terms $z\alpha S_x/2RT$ and $z\alpha S_x^2/2RTV_x$

$\frac{T(\alpha_L - \alpha_g)}{1 + 3T\alpha_g}$	$\frac{z\alpha S_x}{2RT}$	$\frac{z\alpha S_x^2}{2RTV_x}$
0.0680	2.88	2.86
0.0815	2.68	2.66
0.1030	2.43	2.40
0.1196	2.27	2.24
0.1437	2.09	2.05
0.1828	1.86	1.82
0.2585	1.55	1.50

The available comparisons of internal pressure are not so numerous but the agreement is generally good. The agreement between the estimated value for natural rubber (90 cal./cc.) with that from Scott[21] is particularly satisfying in that the data used for the estimate (columns 2, 3, and 5) are from the same source. The agreement shown in columns 11 and 12 for the temperature variation of internal pressure is also satisfactory whereas the agreement with the simple equation reported by Allen et al.[6] (6) is bad. It should be noted, however, that their value of α_L for polyisobutylene is considerably higher than the one used here and that their α_L gives good agreement between their experimental result and the simple equation.

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Résumé

On explique une méthode d'estimation du potentiel entre deux moléculas dans les hauts polymères à partir uniquement de données de densité. La densité de l'énergie de cohésion et la pression interne de plusieurs polymères ont été calculées de cette facon. Les résultats sont en ben accord avec beaucoup d'autres données.

Zusammenfassung

Eine Methode zur Bestimmung des intermolekularen Paarpotentials bei Hochpolymeren lediglich aus Dichtedaten wird angegeben. Dle Kohäsionsenergiedichte und der innere Druck mehrerer Polymerer werden auf diese Weise berechnet. Die Ergebnisse stimmen befriedigend mit verschiedenen anderen Bestimmungen überein.

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Kinetics of Sorption of Water Vapor by Hydrophilic Polymers. Potassium and Lithium Forms of Poly(vinyl Methyl Ether–Maleic Acid)

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Synopsis

The rates of desorption of water vapor from the lithium and potassium forms of poly(vinyl methyl ether-maleic acid) were measured at several initial concentrations and temperatures. A few absorption experiments were performed, and the resulting curves were anomalous. The sorption rates were slower for the lithium form than for the potassium form and the rates for both forms were dependent upon the penetrant concentration. Sorption coefficients, defined by analogy with diffusion coefficients, were determined from the initial rates of desorption and were used to characterize the desorption rates. Limiting-sorption coefficients were determined and found to be much smaller than the diffusion coefficients for water vapor in polymers which are more hydrophobic.

Introduction

The sorption of water vapor by hydrophobic polymers is characterized by Fickian sorption curves and diffusion coefficients which are independent of or only slightly dependent on the penetrant concentration.[1] These properties are observed even at temperatures below the glass transition of the penetrant–polymer systems. In contrast, the sorption of water vapor by very hydrophilic polymers, e.g., poly(vinyl alcohol) and sodium poly(acrylate), is characterized by anomalous sorption curves and rates which depend on the penetrant concentration.[2–4] This different sorption behavior in the hydrophilic polymers appears to be the result of greater polymer–polymer interaction which restricts the segment mobility and polymer–penetrant interaction which may increase the segment mobility as the concentration of penetrant increases, but which may also contribute to the activation energy.

In this study the sorption properties of the potassium and lithium forms of a polycarboxylic acid were investigated and compared. These two metal ions were chosen because they differ appreciably in the degree of their interaction with the carboxylic acid groups and with water.

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Experimental Procedures

The poly(vinyl methyl ether–maleic acid) was provided as the anhydride by the General Aniline and Film Corporation. An aqueous solution of the polymer was filtered and dialyzed first against $1M$ HCl and then against deionized water until the chloride ions were undetectable in either the water or the polymer solution. The casting solutions were prepared by titrating solutions of the polymer with KOH or LiOH to 0.1 of a pH unit below the pH corresponding to the respective second stoichiometric points of the polydicarboxylic acid. Between the first and second stoichiometric points the pH of the solution was significantly lower in the LiOH titration than in the KOH titration. The solutions were cast on mercury and dried at 50°C. to form the membranes. The resulting membranes were clear, brittle when dry, and tacky at moderate humidities. Cloudy, structurally weak membranes resulted if excess base was used in the titration. The thickness of the dry membranes was determined with a micrometer caliper with a precision of $\pm 2\mu$.

The temperatures of the glass transition, T_g, of the various forms of the polymer were determined with a dilatometer similar to the one described by Russell and Van Kerpel.[5] The volume of a 1-g. sample of the polymer membrane was determined as the temperature was raised at a constant rate of 1.0°C./min. Typical curves of specific volume versus temperature are shown in Figure 1. The coefficient for the thermal expansion under these

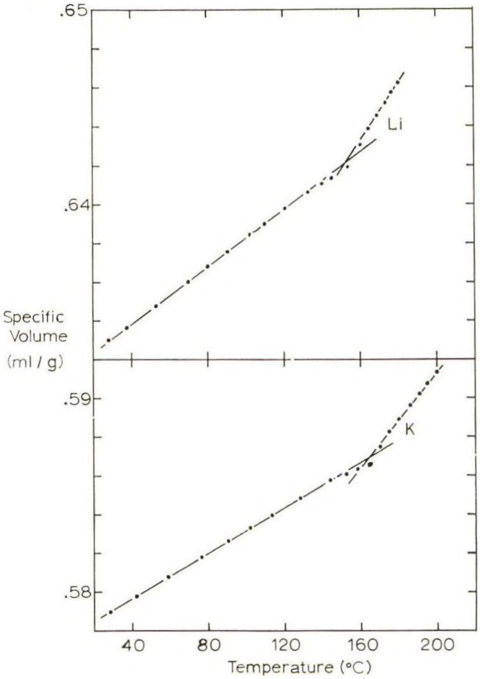

Fig. 1. Specific volume versus temperature for the lithium and potassium forms.

conditions was calculated for temperatures below T_g. The values of T_g were reproducible within ±2°C. The density of a polymer form was calculated from the difference in the mass of mercury required to fill the dilatometer to a prescribed height at a constant temperature with and without a weighed sample of the polymer. The precision of the method was ±0.01 g./cm.^{3}

The sorption apparatus and its operation were described previously.[4] The temperature was controlled within ±0.2°C. and the quartz-spiral balance was accurate to ±0.02 mg., with a maximum load of 50 mg. The water vapor pressure was controlled during the sorption experiments by maintaining a constant temperature at the vapor source. Integral sorption and desorption experiments were performed. Desorption data are more complete because the time required to completely desorb the membranes was excessively long, while equilibrium could be established with even very low vapor pressures in a much shorter time. The membranes were conditioned at 65°C. for several hours in the sorption apparatus. The desorbed weight was constant over the temperature range used in the experiments, 40–60°C.

Results

The physical properties of the various forms of the dry membranes are listed in Table I.

TABLE I
Properties of the Dry Membranes

Form	T_g, °C.	Density at 25°C., g./cm.^{3}	Thickness, μ	Coefficient of thermal expansion at 25°C., °C.$^{-1}$
Potassium	163	1.73	50	9.6×10^{-5}
Lithium	155	1.58	38	11.4×10^{-5}
Acid	115	1.37	—	—

Reduced absorption and desorption curves were prepared by plotting the fraction of the water gained or lost, $M_1/M_1(e)$, versus $t^{1/2}$. A typical graph is presented in Figure 2. M_1 is the absolute value of the difference between the water concentration in the membrane (grams water/gram of dry polymer) at time t and the initial concentration, and $M_1(e)$ is the water concentration in the membrane in equilibrium with the vapor. The absorption curves were anomalous, i.e., sigmoid in shape, so the average-diffusion coefficients could not be determined. In order to reduce the rates to a manageable form and simplify the consideration of their significance, and average sorption coefficient, $\bar{R}$, was determined. $\bar{R}$ is defined by analogy with the average diffusion coefficient, $\bar{D}$, by either

$$\bar{R} = 0.049(L^2/t_{1/2}) \tag{1}$$

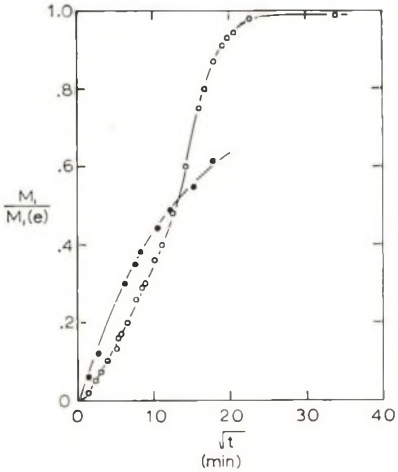

Fig. 2. Reduced sorption and desorption curves for the potassium form at 60°C. and a water vapor activity of 0.025: (○) sorption; (●) desorption.

or

$$\bar{R} = (\pi/16)(KL)^2 \tag{2}$$

where L is the dry thickness, $t_{1/2}$ is the time required for $M_1/M_1(e)$ to reach 1/2, K is the initial slope of the reduced sorption curve, and $\bar{R}$ may be either $\bar{R}_d$ for desorption of $\bar{R}_a$ for absorption. A similar approach has been used to extract diffusion coefficients from swelling rates of polymers in solvents.[6]

TABLE II

Sorption Results and Limiting Sorption Coefficients

Form	T, °C.	a_1	$M_1(e)$, g./g.	$\bar{R}_a \times 10^{12}$, cm.²/sec.	$\bar{R}_d \times 10^{12}$, cm.²/sec.	$R_0 \times 10^{12}$, cm.²/sec.
Potassium	60.0	0.025	0.0638	110	205	7.3
		0.008	0.0458	93.4	115	
		0.004	0.0296	43.6	39.2	
		0.002	0.0200		26.0	
		0.0006	0.0146		15.7	
	50.0	0.0086	0.0545		59.0	2.8
		0.0022	0.0338		19.4	
	40.0	0.058	0.1062		270	1.1
		0.0217	0.0757		81.0	
		0.0018	0.0329		7.4	
Lithium	60.0	0.082	0.055		11.5	0.73
		0.040	0.035	4.1	4.1	
	50.0	0.100	0.067		6.6	0.24[a]
	40.0	0.150	0.101		10.2	0.068
		0.045	0.044		0.63	

[a] Determined by extrapolation of the single value of $\bar{R}_d$ by assuming the same concentration dependence of $\bar{R}_d$ as at 40.0 and 60.0°C.

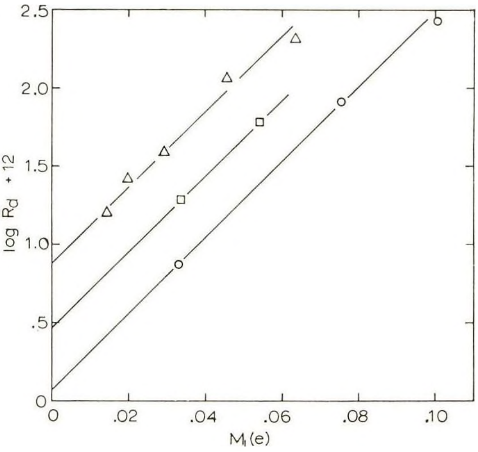

Fig. 3. Average desorption coefficient versus the vapor concentration at equilibrium for the potassium form: (○) 40°C.; (□) 50°C.; (△) 60°C.

If the reduced sorption is linear to $t_{1/2}$, then eq. (1) is equal to eq. (2) and $\bar{R} = \bar{D}$, where $\bar{D}$ is the average diffusion coefficient. The initial slope of desorption, i.e., eq. (2), was used in this work. A limiting sorption coefficient, R_0, is defined by

$$\lim_{a_1, M_1(e) \to 0} \bar{R} = R_0 \tag{3}$$

where a_1 is the activity of the water vapor. The R_0 values were determined by extrapolating a plot of log R_d versus $M_1(e)$ to $M_1(e) = 0$, as shown in Figure 3, for the potassium form. A linear extrapolation was made and the equation

$$\bar{R}_d = R_0 \exp \{ bM_1(e) \} \tag{4}$$

described the data at low concentrations with b independent of the temperature in the range investigated. An exponential dependence of $\bar{R}_d$ on $M_1(e)$ was also found for the hydrophilic membranes previously studied.[4] The values of average and limiting sorption coefficients for the potassium and lithium forms are listed in Table II. No kinetic data are reported for the acid form because a constant desorbed weight could not be obtained.

The average activation energies, $\bar{E}$, were determined from graphs of $\ln(R_0)$ versus $1/T$ (Fig. 4). The value of the preexponential term, A_0, in the Arrhenius-type equation,

$$R_0 = A_0 \exp \{ -\bar{E}/RT \} \tag{5}$$

was also, calculated. The transition-state theory for diffusion in a system of negligible change in volume gives,[7]

$$A_0 = \lambda^2(ekt/h) \exp \{ \Delta S^{\ddagger}/R \} \tag{6}$$

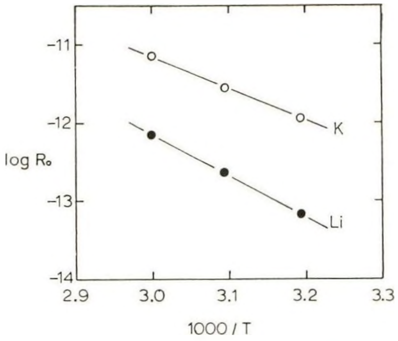

Fig. 4. Plot of log R_0 vs. $1000/T$ for the lithium and potassium forms.

where $\Delta S^\ddagger$ is the molar entropy of activation for the process and λ is the distance between equilibrium sites. Table III summarizes the results obtained by treating R_0 as described.

TABLE III
Sorption-Kinetics Parameters

Form	b	$\bar{E}$, kcal./mole	A_0, cm.²/sec.	$\lambda(e^{-\Delta S^\ddagger/R})^{1/2}$, A.
Potassium	57	19.6	54	1.7×10^2
Lithium	50	25.1	2.4×10^3	3.8×10^3

The method of Zimm and Lundberg[6] was used to calculate values of the clustering factor, G_{11}/v_1, for the membranes. Although the points were not numerous, several reliable values all in the range of -14 to -3 were obtained. This result indicates that in the range of concentrations used the water is not clustered, but is on preferred sites so that each penetrant molecule excludes more than its own volume. In an ideal solution, $G_{11}/v_1 = -1$, which indicates that the addition of a penetrant molecule excludes only its own volume in the system.

The volumes of the ionic polymers per metal ion were calculated from the equivalent weight and the density. The volumes of the metal ions, calculated from the crystal radii, were then subtracted from the total volume per metal ion to give the volume of the polymer plus the free volume per metal ion. The results were 110 A.³ per potassium ion and 97 A.³ per lithium ion. These values indicate that the free volume per metal ion is greater in the potassium form than in the lithium form.

Comparison of Lithium and Potassium Forms

The values of R_0 are an order of magnitude smaller for the lithium form than for the potassium form of the polymer. This result is reflected in the larger activation energy for the lithium form, although the preexponential factor is also larger and compensates in part for the increased activation energy. The smaller R_0 for the lithium form is expected simply on the basis that its free volume is less than that of the potassium form.[1] The carboxylic acid groups of the polymer apparently interact more strongly with the lithium ions, as shown by the titration results which indicate stronger complexing by the lithium ions than the potassium ions. The more restricted structure of the lithium form accounts for the result that at a given water concentration in the polymer a higher vapor activity is required for the lithium form than for the potassium form, despite the greater free energy of hydration for lithium ions in water solutions.

The interaction between the penetrant and the metal ions may influence the sorption rate, especially at low concentrations, if the ions are the preferred sites. The greater energy required to detach a water molecule from a lithium ion than a potassium ion may be significant; however, no assignment of this influence on the sorption rate is readily evident because the simple free-volume consideration is consistent with the results.

Comparison with Hydrophobic Polymers

The values of R_0 for both forms are 10^{-4} to 10^{-5} times the values of D_0 for the more hydrophobic membranes. A method of comparing sorption properties is shown in Figure 5, where $\bar{E}/T$ is plotted versus log A_0 for fourteen water vapor–hydrophobic polymer systems and for the hydrophilic polymer systems. The systems represented in Figure 5 are described in Table IV. The points for the hydrophobic polymers at temperatures above and below T_g lie close to the empirical line obtained by the method of least squares, while the points of the hydrophilic polymers are significantly displaced from the line. The empirical line nas the same slope as that expected from the Arrhenius equation:

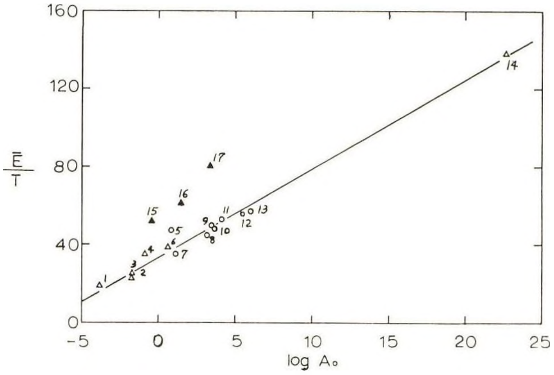

Fig. 5. Plot of $\bar{E}/T$ vs. log A_0 for diffusion of water vapor in various polymers: (○) T above T_g; (△,▲) T below T_g. Description of each system is given in Table IV.

$$\bar{E}/T = -2.30\,R \log D_0 + 2.30\,R \log A_0 \tag{7}$$

with D_0 constant. The correlation emphasizes that D_0 differs little in the hydrophobic polymers. The line may be interpreted as an indication that the sorption mechanism remains unchanged for the series of polymers.[9] Thus it may be argued that the sorption mechanism in the hydrophilic polymers differs from that in the hydrophobic polymers.

TABLE IV
Table of Systems Plotted in Figure 5

Point number	Polymer	T, °C.	T_g, °C.	Reference
1	Cellulose acetate	30	69	12
2	Ethyl cellulose	25	43	13
3	Poly(vinyl chloride–acetate)	37	30, 60–70	14
4	Poly(ethylene terephthalate)	25	69	13
5	Rubber hydrochloride	25	25	13
6	Poly(methyl methacrylate)	30	105	12
7	Poly(methyl acrylate)	40	9	15
8	Poly(vinyl acetate)	40	30	15
9	Poly(vinyl acetate)	30	30	2
10	Poly(ethylene)	25	−30	13
11	Baked linseed oil	30	—	12
12	Poly(propylene)	25	−18	13
13	Poly(vinyl chloride–acetate)	70	30, 60–70	14
14	Poly(vinyl chloride)	30	82	12
15	PVM/MA–poly(vinyl alcohol)	50	85, 115	16
16	Potassium form, PVM/MA	50	163	This paper
17	Lithium form, PVM/MA	50	155	This paper

Barrer[10,11] interprets such a linear relationship between $\bar{E}/T$ and log A_0 in terms of the extent of participation of the polymer in the diffusion step. Specifically, A_0 is related to the number of degrees of freedom, or size of the zone, in which the activation energy is distributed. In a given medium for a series of penetrants a linear relationship is predicted if it is assumed that the size of the zone of disturbance is proportional to $\bar{E}/T$. The displacement of the points of the hydrophilic polymers from the empirical line is to a smaller A_0 than predicted at a given $\bar{E}/T$ or to a larger $\bar{E}/T$ at a given A_0. This displacement is interpreted by Barrer's theory to mean that the activation energy for diffusion is more localized in the hydrophilic than in the hydrophobic polymers, which would indicate that the polymer–penetrant interaction is significant in the diffusion step of the water vapor–hydrophilic polymer systems.

The possibility exists that the identification of R_0 as D_0 is incorrect, and until a method of determining D_0 in an unequivocal manner is used for the systems of this investigation, the above arguments must be considered as tentative. However, the method used here should give limiting values of whatever process is occurring, which apparently differs from the diffusion in hydrophobic polymers. A comparison of $\bar{E}/T$ and A_0 seems justified, since the Arrhenius-type plots are linear.

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Résumé

On a mesuré les vitesses de désorption des vapeurs d'eau des dérivés lithiées et potassés du copolymère (éther vinyl-méthylique–acide maléique) à différentes concentrations initiales et températures. Un certain nombre d'expériences d'absorption ont été effectuées et les courbes obtenues sont anormales. Les vitesses de sorption sont plus lentes dans le cas du lithium que dans le cas du potassium et les vitesses dans les deux cas dépendent de la concentration de l'agent diffusant. Les coefficients de sorption, définis par analogie avec les coefficients de diffusion, sont déterminés à partir des vitesses initiales de désorption et sont utilisés pour caractériser les vitesses de désorption. Des coefficients de désorption limites ont été déterminés et sont plus petits que les coefficients de diffusion de la vapeur d'eau dans des polymères plus hydrophobes.

Zusammenfassung

Die Geschwindigkeit der Desorption von Wasserdampf von der Lithium- und Kaliumform der Poly(vinylmethyläthermaleinsäure) wurde bei mehreren Ausgangskonzentrationen und Temperaturen gemessen. Einige Absorptionsversuche wurden durchgeführt und dabei anomale Kurven erhalten. Die Sorptionsgeschwindigkeit war für die Lithiumform niedriger als für die Kaliumform, und für beide Formen hingen die Geschwindigkeiten von der Konzentration des penetrierenden Stoffes ab. In Analogie zum Diffusionskoeffizienten definierte Sorptionskoeffizienten wurden aus der Anfangsdesorptionsgeschwindigkeit bestimmt und zur Charakterisierung der Desorptionsgeschwindigkeit verwendet. Grenzsorptionskoeffizienten wurden bestimmt und erwiesen sich in stärker hydrophoben Polymeren als kleiner als die Diffusionskoeffizienten für Wasserdampf.

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Polymerization of Higher Aldehydes. VII. Tacticity of Elastomeric Polyacetaldehyde*,†

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Synopsis

High resolution NMR spectroscopy was used to determine the tacticity of elastomeric polyacetaldehyde. Spectra obtained at elevated temperatures and in solutions of carbon tetrachloride and tetrachloroethylene showed a weak line on the high field side of a strong line in both the methyl group and the CH group regions. Comparison of these results with those obtained on related model compounds indicated that the weak lines can be attributed to the isotactic structure and that the strong lines can be assigned to the heterotactic structure. After the lines were narrowed by spin-decoupling procedures, the area measurement results suggested that polyacetaldehyde is a highly random polymer.

INTRODUCTION

Elastomeric polyacetaldehyde has been investigated extensively in recent years.[3] Its physical structure has been determined to be amorphous,[4] and its stereochemical structure has been considered to be atactic.[5] In a recent study, however, Letort and Richard[6] suggested that the chemical structure might be ordered in a syndiotactic configuration because of the type of polymerization (crystallization polymerization) employed, although no confirming evidence was given.

High resolution nuclear magnetic resonance spectroscopy (NMR) has been used successfully in the determination of tacticity of polymers. The first study reporting its use was done on the amorphous polymer, poly(methyl methacrylate).[7] A number of other studies followed, including the determination of tacticity of polytrifluorochloroethylene[8] and poly(vinyl chloride).[9] In the latter case, the spectral lines were narrow enough to show multiplet splittings due to spin-spin interactions. Since those splittings interfered with the measurement, a new experimental technique called

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* After the submission of our paper a communication appeared by J. Brandrup and M. Goodman,[2] who had worked independently from us on the determination of the tacticity of elastomeric polyacetaldehyde. We have been in communication with J. Bandrup and M. Goodman and are in full agreement with their results. A further paper by Goodman and Brandrup, "The Investigation of Polyacetaldehyde Structure by High Resolution Nuclear Magnetic Resonance," will appear in the January 1965 issue of this Journal.

† Presented before the Division of Analytical Chemistry at the 147th Meeting of the American Chemical Society, Philadelphia, Pennsylvania, April 9, 1964.

spin decoupling was used to collapse the multiplet splittings into single chemically shifted lines so that the determination could be made. With this technique the scope of NMR in making tacticity determinations has been increased greatly.

Polymers with heteroatoms in the polymer chain have not been investigated by high resolution NMR. Such polymers offer an advantage in the NMR determination because there is no interference from $—CH_2—$ groups in the backbone chain. In the case of polypropylene, the protons of the $—CH_2—$ group had to be replaced with deuterium before the determination could be made.[10] Oxygen in the backbone chain of polyacetaldehyde facilitates the NMR examination in two ways: (*a*) there is no interference from a CH_2 group and (*b*) the oxygen atom in the chain has a rather large inductive effect on the tertiary proton by shifting its resonance line to very low fields with a resulting large separation of its line from that of the methyl protons.

EXPERIMENTAL

Materials

Acetaldehyde was polymerized, freshly distilled acetaldehyde in ether-pentane (1:2) at −78°C. being used, with BF_3 etherate as the initiator. The polymer was endcapped with acetic anhydride/pyridine at room temperature. It was dissolved in ether, washed with sodium carbonate solution and several times with distilled water. After drying, 0.1% of Age-Rite (β,β'-dinaphthyl-*p*-phenylenediamine) was added to the ether solution and the ether was evaporated under reduced pressure (0.1 mm.). After this treatment, the polyacetaldehyde was free of paraldehyde which is present in small amounts in some cationic acetaldehyde polymerizations.

Polyacetaldehyde samples of both very high molecular weight and moderate molecular weight were prepared for examination. The inherent viscosity of a 0.1% butanone solution of the high molecular weight polyacetaldehyde was 2.73 before and 2.58 after capping. Since the NMR studies reported here involved the use of elevated temperature, it was necessary that the polyacetaldehyde be endcapped in order to give it the stability required.[3,11] A polyacetaldehyde of moderate molecular weight had the following inherent viscosities: the uncapped polymer gave 0.42 in 0.5% butanone solution at 20°C., and the acetate-capped polymer gave 0.36 in butanone and 0.33 in tetrachlorethylene.

In order to determine the extent of degradation during the NMR measurements, a polymer sample was treated under exactly the same conditions as were required for the NMR measurement. After 25 min. at 93°C., the inherent viscosity was 0.27 in tetrachloroethylene at 20°C. The solvent was evaporated at 0.1 mm. at room temperature and finally at 70°C. for 1 hr. The volatiles were collected in a trap cooled in liquid nitrogen. Infrared examination did not show any paraldehyde in the tetrachloroethylene. Test experiments showed that as little as 1% of paraldehyde could be detected. The weight loss of polyacetaldehyde during this operation was about 5%; the final measurement of the inherent viscosity in butanone at 20°C. was 0.27.

Paraldehyde was obtained from a freshly opened bottle of Merck U.S.P. material. It was purified by removing acidic impurities with sodium carbonate and by distilling it from fresh potassium carbonate. Paraldehyde was analyzed by gas chromatography to determine whether it was a single compound, a mixture of the two possible steroisomeric forms, or a mixture containing some of the less volatile tetramers. Samples of paraldehyde were analyzed on nine different columns at temperatures varying from 70 to 100°C. Only one peak was found in each case. At a column temperature of 140°C., the compound decomposed on most columns, giving additional peaks characteristic of decomposition patterns. Another sample of paraldehyde was analyzed on a chromatographic column of aluminum oxide. A 20-g. portion of the sample dissolved in 100 ml. of pentane was analyzed on a chromatographic column of aluminum oxide. A 20-g. portion of the sample dissolved in 100 ml. of pentane was placed on 600 g. of aluminum oxide. Within the first 400 ml. of pentane eluate, more than 80% of the paraldehyde was removed. No appreciable minor impurities were detected. This main fraction showed only a single peak in the chromatographic analysis. Samples of the technical grade paraldehyde also showed essentially the same results from the chromatographic and the gas chromatographic analyses. The results tend to confirm that paraldehyde is a single compound.

Metaldehyde was obtained commercially and was recrystallized from methylene chloride following a Soxhlet extraction. Since metaldehyde can actually exist in four different stereoisomers, care was taken to be sure that only the all-*cis* cyclic isomer was used in the examination. Two of the four isomers have been fairly well characterized. The "normal" metaldehyde (m.p. 246°C.) was studied by Pauling and Carpenter,[12] and the Fourier analysis indicated it to be the all-*cis* isomer. The other metaldehyde (m.p. 46°C. and called metaldehyde II) was first isolated and identified by Craven.[13] We have found it in small amounts (less than 0.5%) in one sample of commercial metaldehyde. It is probably the *cis,trans,cis, trans* isomer.

Both possible isomers of parachloral were obtained from Dr. B. C. Anderson of the Central Research Department of E. I. du Pont de Nemours & Co., Inc.

Equipment

The Varian Associates A-60 NMR spectrometer was used for obtaining the chemical shift data on each sample. Tetramethylsilane (TMS) was used as the internal reference for these data.

The Varian Associates DP-60 NMR spectrometer equipped with a temperature controller of our own design for cooling the magnet, Varian Associates magnet flux stabilizing devices, V-4340 variable temperature NMR probe assembly, and the V-4331-THR Dewar probe insert was used to per-form the spin-decoupling experiments at elevated temperatures in conjunction with the Nuclear Resonance Specialities PD-60 homonuclear spin decoupler.

Sample Preparation

Polyacetaldehyde was dissolved in both reagent grade carbon tetrachloride and tetrachlorethylene at a concentration of about 10% for the examination by NMR. Chemical shift measurements were made at ambient temperature and 93°C., and the spin-decoupling experiments were performed at 90°C.

Paraldehyde was examined as a neat liquid at 0° – 134°C. The spin decoupling experiments were performed at a temperature of 105°C.

Metaldehyde was examined in tetrachlorethylene at a concentration of about 10%. The temperature used for the examination was 100°C.

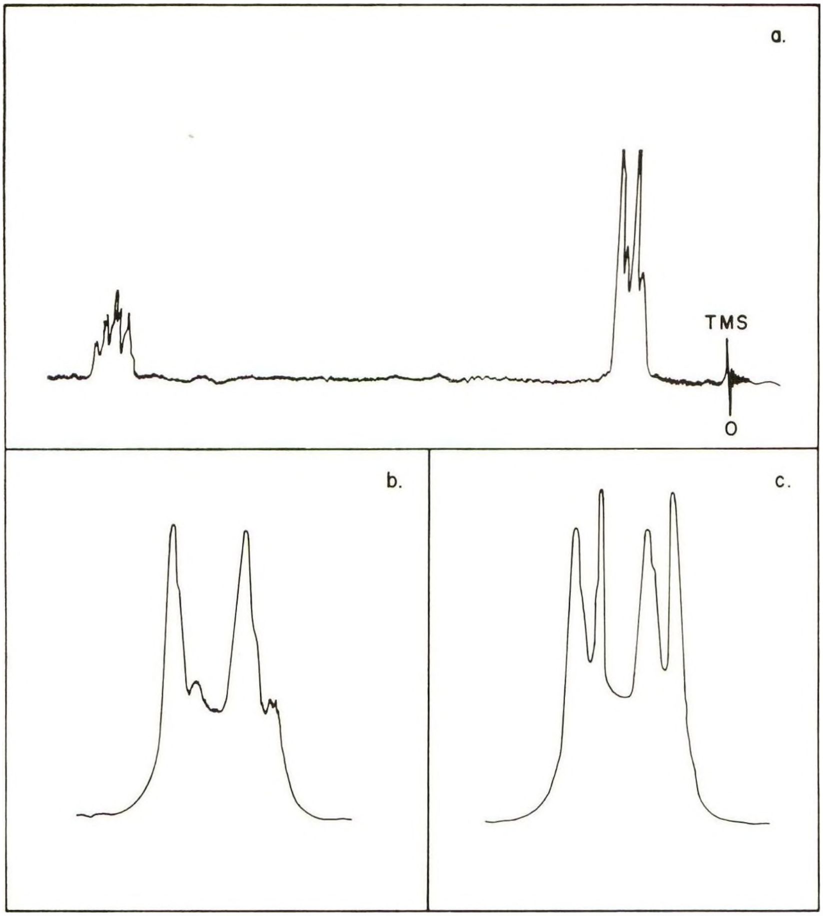

Fig. 1. NMR spectra of a 10% solution of polyacetaldehyde in perchloroethylene at 93°C.: (*a*) undecoupled spectrum; (*b*) undecoupled methyl spectrum; (*c*) undecoupled methyl spectrum plus paraldehyde.

The two isomers of parachloral were examined in reagent grade carbon tetrachloride at a concentration of about 50%. Only room temperature scans were obtained.

RESULTS

The high resolution NMR spectrum of polyacetaldehyde in tetrachloroethylene is shown in Figure 1*a*. The chemical shift values for the lines seen in this figure are given in Table I. They are expressed in parts per million (ppm) relative to the high field reference line of tetramethylsilane (TMS). The spectrum is seen to consist of two sets of lines. The low field lines appearing at −5.10 ppm are attributed to the tertiary proton and the high field lines appearing at about −1.30 ppm are attributed to the methyl protons. The multiplet splitting in both sets of lines is a result of the spin-spin interaction between the two types of protons in polyacetaldehyde. The coupling constant determined for this interaction was 5.1 cycle/sec. Since multiplet splittings have been observed only occasionally in polymer spectra because of line broadening, it was somewhat unexpected to have observed the splitting in this spectrum. Weak shoulders are seen on the high field side of both sets of lines, but they are seen more clearly for the methyl lines. Figure 1*b* shows the methyl lines under higher resolution with the weak lines being readily distinguished from the strong lines. In Table I, it is seen that the chemical shift estimated for the strong methyl lines was −1.32 ppm, and the chemical shift estimated for the weak methyl lines was −1.30 ppm. These weaker lines are attributed to a stereochemical species that is different from the species that gives rise to the stronger lines. By spin decoupling the spin-spin interaction between the tertiary proton and the methyl protons, the line widths of both sets of lines were narrowed to the extent that the weak shoulder lines were separated more completely from the stronger lines. The spin-decoupling experiment consisted of irradiating the methyl protons with 219.5 cycle/sec. frequency at a power level ($\gamma H_2/2\Pi > 5.1$ cycle/sec.) greater than the cou-

TABLE I

			Chemical shifts, ppm relative to TMS	
Sample	Temp., °C.	Solvent	CH group	CH_3 group
Acetaldehyde	32	Deuterated chloroform	−9.80	−2.20
Paraldehyde	105	—	−5.02	−1.28
Metaldehyde	100	Tetrachloroethylene	−4.99	−1.31
Polyacetaldehyde	93	Tetrachloroethylene	−5.10	−1.32, −1.30

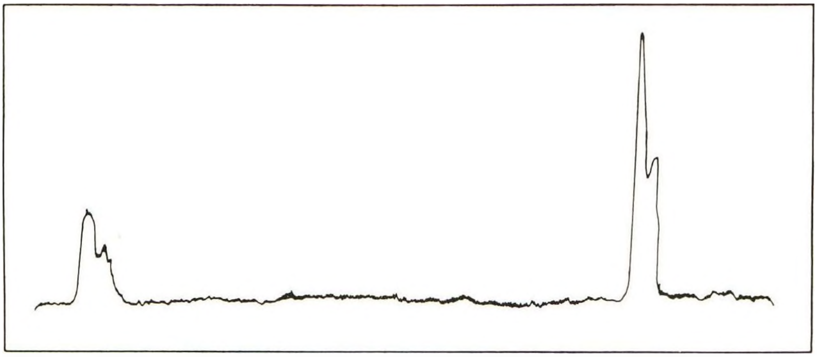

Fig. 2. Decoupled NMR spectrum of a 10% solution of polyacetaldehyde in CCl_4 at 90°C.

pling constant of the interaction in order to observe the collapse of the tertiary proton pattern into the two chemically shifted lines. Then, it consisted of irradiating the teritiary proton with the same frequency at about the same power level in order to observe the collapse of the pattern for the methyl protons into the two chemically shifted lines. Figure 2 shows the decoupled spectrum of polyacetaldehyde. The separation of the weaker line in each pair was large enough to determine its area relative to that of the stronger line; the area of the latter was about two to three times larger than the area of the weaker line.

In order to relate these NMR observations of polyacetaldehyde to its stereoregular conformations, several model compounds were examined under conditions similar to those used for polyacetaldehyde. One of these was paraldehyde, the cyclic trimer of acetaldehyde. Table I lists the chemical shifts of the two lines seen for paraldehyde. The line due to the tertiary proton appears at −5.02 ppm and the line due to the methyl proton appears at −1.28 ppm. These shifts were relatively constant over the temperature range studied. The spin-spin coupling interaction between the two proton groups showed a coupling constant of 5.2 cycle/sec. The irradiating frequency of 223.6 cycle/sec. at a power level ($\gamma H_2/2\Pi$) greater than 5.2 cycle/sec. was used to decouple this interaction. The decoupling experiment was performed to compare the results with those obtained from polyacetaldehyde.

Another model compound examined was one of the steroisomers of metaldehyde. It is the all-*cis* cyclic tetramer of acetaldehyde. In this form the metaldehyde is a rigid flat molecule extending the methyl groups from the four corners of the square. From Table I it is seen that the lines due to the tertiary proton and methyl protons appear at about the same position as those for paraldehyde. Because of the low solubility of the solution even at 100°C., very little multiplet splitting was observed.

Two other model compounds examined were the isomers of parachloral. Their NMR spectra are shown in Figure 3. As expected, the *cis* isomer

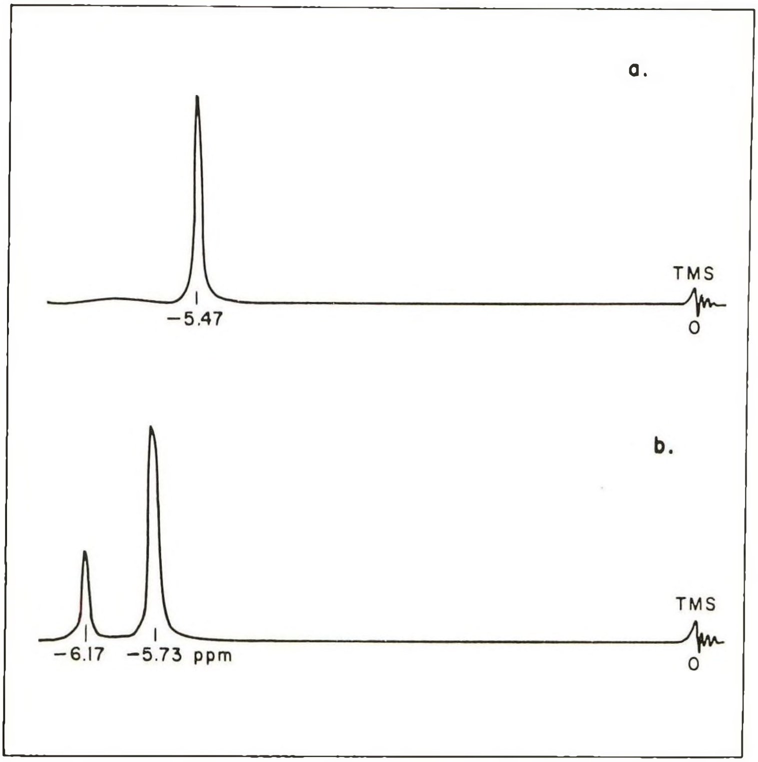

Fig. 3. NMR spectra of 50% solutions of parachloral: (*a*) *cis* isomer; (*b*) *trans,cis,trans* isomer.

shows only one line, appearing at −5.47 ppm. The other isomer (*trans, cis,trans*) shows two lines with a 2:1 ratio in its intensities. The more intense line appears at the higher field position of −5.73 ppm, while the less intense line appears at the lower field position of −6.17 ppm. The more intense line appearing at nearly the same position as the line for the all-*cis* isomer can be assigned, therefore, to the protons *cis* to each other.

DISCUSSION

Table I, which summarizes the chemical shift results of the compounds studied, except for the parachlorals, shows a similarity in position of the methyl lines for paraldehyde and metaldehyde with the weak methyl lines for polyacetaldehyde. However, because of the small difference in chemical shift between the strong and weak methyl lines for polyacetaldehyde, and because of the difference in value for the chemical shift of the methyl protons of paraldehyde and the weak lines for polyacetaldehyde, a small amount of paraldehyde was added to the NMR tube containing the solution of polyacetaldehyde in order to obtain a direct comparison of the methyl lines. Figure 1*c* shows the methyl spectrum of polyacetaldehyde and paraldehyde. This spectrum was obtained in a manner which was identical to that shown in Figure 1*b*. The only difference is the paraldehyde. From Figure 1 it becomes immediately apparent that the weak lines in the methyl spectrum of polyacetaldehyde are coincident with the methyl lines for paraldehyde. The coincidence in line position for the methyl protons of paraldehyde and the weak lines for polyacetaldehyde indicates that there is a similarity in structure between these two species. Paraldehyde, showing only one set of lines for the tertiary proton and the methyl protons even on decoupling must, therefore, be an all-*cis* isomer. If it were the *trans,cis,trans* isomer, two sets of lines would be observed in both regions, The metaldehyde isomer examined during this study was known to be the all-*cis* one as stated earlier in the Experimental section. The similarity in line position for its methyl protons with the weak methyl lines for polyacetaldehyde indicates that there is a structure similarity between these two species also. Thus, since both paraldehyde and metaldehyde are indicated to be the all-*cis* isomers, it follows then that the weaker lines in the spectrum of polyacetaldehyde can be attributed to the isotactic type of stereochemical structure assuming that both proton groups are shielded nearly identically in the rings and in the isotactic structure of the polymer. This assumption is reasonably sound since it is known that only small structural differences frequently cause significant and sometimes large differences in shielding, as in the case of the *cis* lines for the two different parachloral isomers. With the assignment of the weaker lines in the spectrum of polyacetaldehyde to isotactic structure, the stronger lines can be assigned either to syndiotactic or heterotactic structure. If they were assigned to syndiotactic structure, polyacetaldehyde would be a block copolymer of isotactic and syndiotactic sequences. Since this would result in different polymer properties, these lines must be assigned to heterotactic structure. Some syndiotactic structure could be present in polyacetaldehyde but because of the low amount of it, lines attributable to it could be masked by the large heterotactic lines.

Table II summarizes the results obtained by previous investigators who have employed successfully the use of high resolution NMR in the determination of tacticity of stereoregular polymers. Chemical shift results of the CH group region show the syndiotactic CH line to be at lower fields than the isotactic CH line for two of the three polymers listed. The shift difference between the syndiotactic CH lines and the isotactic CH lines, is, however, the same for all three polymers. In the case of the CH_2 group, there appears to be little difference in the chemical shift values between the isotactic lines and the syndiotactic lines. For deuterated polypropylene there seems to be essentially no difference at all. Chemical shift results of the methyl region show the largest difference in value between the isotactic and the syndiotactic lines. For the two examples shown in the table, the isotactic methyl line appears at lower fields than the syndiotactic methyl line. This relationship in the methyl region is just the opposite to that seen for the CH group region.

The data in Table II were compiled to show the results of work done pre-

TABLE II
Chemical Shifts of Proton Groups in Stereoregular Polymers

Polymer	Chemical shifts, ppm relative to TMS							
	CH group			CH_2 group		CH_3 group		
	Iso-tactic	Hetero-tactic	Syndio-tactic	Iso-tactic	Syndio-tactic	Iso-tactic	Hetero-tactic	Syndio-tactic
Polystyrene[a]	−2.50	−2.39	−2.18	—	—	—	—	—
Poly(vinyl alcohol)[b]	−3.32	−3.65	−3.97	—	—	—	—	—
Poly(vinyl chloride)[c]	−4.19	−4.41	−4.52	−2.22	−2.04	—	—	—
Poly(vinyl methyl ether)[c]	—	—	—	−1.85	−1.77	—	—	—
Polypropylene (deuterated)[d]	—	—	—	−0.95	−0.95	—	—	—
Poly-α-methylstyrene[e]	—	—	—	—	—	−0.82	−0.35	−0.14
Poly(methyl methacrylate)[f]	—	—	—	—	—	−1.22	−1.05	−0.91

[a] Data of Brownstein et al.[14]
[b] Results obtained in authors' laboratories.
[c] Data of Bovey et al.[9]
[d] Data of Stehling.[10]
[e] Data of Brownstein et al.[15]
[f] Data of Bovey and Tiers.[7]

viously on stereoregular polymers and to relate these results, if possible, with those obtained from this study. Unfortunately, because none of the examples shown is exactly analogous in structure to polyacetaldehyde, i.e., they do not include both CH and methyl groups in one determination, the results in Table II cannot be compared directly with those obtained from polyacetaldehyde. Only those results obtained from the model compounds described earlier can be used to determine the stereochemical structure of polyacetaldehyde.

A report by previous investigators on probability studies and polymer formation indicates that completely random polymers show heterotactic lines to be about twice as intense as syndiotactic lines and isotactic lines.[4] By assigning the weaker lines in the spectrum of polyacetaldehyde to isotactic structure and the stronger lines to heterotactic structure, it is seen that polyacetaldehyde nearly approaches the completely random situation.

We wish to thank Dr. B. C. Anderson for supplying us with highly purified samples of α- and β-parachloral and for his advice concerning these samples.

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Résumé

On a utilisé la spectroscopie RMN à haute résolution en vue de déterminer la tacticité du polyacétaldéhyde. Les spectres obtenus à haute température et en solution dans le tétrachlorure de carbone et de tétrachloréthylène ont révélé une raie faible du côté des champs plus élevés, tant à côté de la raie intense du groupe méthyle que de celle du groupe CH. La comparaison de ces résultats avec ceux obtenus aud épart des composés-modèles s'y rapportant a montré que les raies faibles peuvent être attribuées à la structure isotactique et que les raies intenses correspondent à la structure hétérotactique. La mesure de la surface des raies, amincies par le processus de découplage des spins, suggère que le polyacétaldéhyde est un polymère hautement statistique.

Zusammenfassung

Hochauflösungs-NMR-Spektroskopie wurde zur Bestimmung der Taktizität von Polyacetaldehyd benützt. Die bei höheren Temperaturen und in Tetrachlorkohlenstoff- und Tetrachloräthylenlösung erhaltenen Spektren zeigten eine schwache Linie auf der Seite hoher Feldstärke einer starken Linie sowohl im Methylgruppen- als auch im CH-Gruppenbereich. Ein Vergleich dieser Ergebnisse mit solchen an verwandten Modellverbindungen zeigt, dass die schwachen Linien der isotaktischen Struktur und die starken Linien der heterotaktischen Struktur zugeordnet werden können. Nach Verengung dieser Linien durch Spinentkopplungsverfahren liess die Flächenmessung erkennen, dass Polyacetaldehyd ein hochgradig ungeordnetes Polymeres ist.

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Kinetics of the Polymerization of Divinylbenzene Isomers

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Synopsis

The overall rates of polymerization of *m*- and *p*-divinylbenzene, a 2:1 mixture of the *meta* and *para* isomers, and commercial divinylbenzene have been followed viscometrically. Data at 60 and 80°C. show that the *meta* isomer polymerizes most rapidly. Ratios of rates show differences in activation energies. An effect on the overall rates is tentatively attributed to the increased resonance stabilization of the *p*-vinylphenyl-derived radical which further decreases the already low reactivity of the styrene-derived radical. The possibility that steric factors contribute significantly to the rate difference is considered to be unlikely.

In previous studies,[1] it was noted that pure *m*-divinylbenzene copolymerizes differently from the pure *para* isomer and mixtures of the two isomers. Specifically, under conditions which gave satisfactory bead copolymers with 8–16% of the pure *para* isomer, the *meta* isomer invariably gave conglomerated aggregates of ill-formed beads. Since this difference may result from differences in rates of polymerization and copolymerization, studies of the relative rates of polymerization of pure *meta*, pure *para*, a 2:1 mixture of pure *meta* and *para*, and the commercial mixture of divinylbenzenes were undertaken and will be described herein. Studies of copolymerization rates will be presented later.

EXPERIMENTAL

Materials

Styrene (Distillation Products Co.) was purified by distillation, n_D^{20} 1.5469 (reported,[2] n_D^{20} 1.5468), single peak in vapor-phase chromatography. Commercial divinylbenzene (Koppers Co.) was distilled before use, n_D^{25} 1.5623. The vapor-phase chromatographic characterization of this material has been described previously.[3] The *m*-divinylbenzene was separated by preparative V.P.C. from the commercial mixture of divinylbenzenes by the procedure described previously,[3] n_D^{25} 1.5755 (reported,[4] n_D^{25} 1.5748) and, as determined by vapor-phase chromatography, consists of 99% *meta* and

1% *para* isomers. The *p*-divinylbenzene was synthesized from phenylenediacrylic acid as described previously[4] and purified by vapor-phase chromatography, m.p. 30.2–30.8°C., n_D^{35} 1.5857 (reported,[4] m.p. 29.5–30°C.). The 2:1 *m*:*p*-divinylbenzene was separated from commercial material by the process described previously,[3] n_D^{25} 1.5790. Toluene was purified by distillation and the benzoyl peroxide was precipitated from chloroform solution with methanol.

Procedure

Polymerizations were run with freshly distilled, polymer-free monomer. Erratic results were obtained with monomer stored under nitrogen at −20°C. for any length of time. For the rate measurements, the viscometer (the same one for all experiments) was placed in a constant temperature bath and flushed with nitrogen prior to introduction of the sample. The initiator was weighed and dissolved in purified toluene to give the concentration specified on the figures. To 5 ml. of this solution, 0.5047 g. of monomer was added to give an 11.64% solution. The solution was mixed well and 4.6 ml. of it was injected into the large arm of the viscometer at time zero. A blanket of nitrogen was maintained in the large arm. Efflux times were recorded at intervals and are plotted in Figures 1–4. In standardizing experiments (Figs. 1 and 2) with commercial divinylbenzene the concentration of initiator was varied to give a range of rates at 60 and 80°C. The efflux times in duplicate runs checked within less than ±1.0%. Under these conditions, rates at 60 and 80°C. with equal initiator concentrations cover too wide a range of efflux times to permit reasonably accurate measurement of rates of all isomers under one set of conditions.

RESULTS AND DISCUSSION

The preliminary rate measurements with commercial divinylbenzenes are shown in Figures 1 and 2. This monomer was selected to define conditions under which measurable rates would be observed. At 80°C. (Fig. 1),

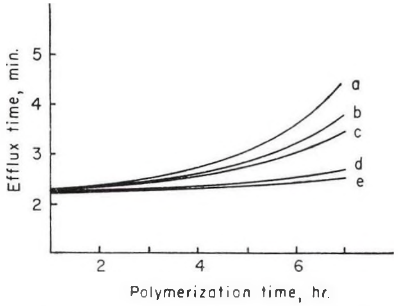

Fig. 1. Rate of polymerization of commercial divinylbenzene in toluene (11.64%) at 60°C. with varying concentrations of benzoyl peroxide initiator: (*a*) 2.81%; (*b*) 1.55%; (*c*) 1.00%; (*d*) 0.31%; (*e*) 0.155%.

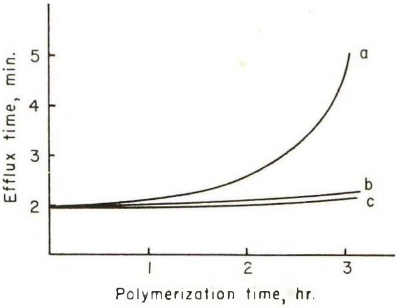

Fig. 2. Rate of polymerization of commercial divinylbenzene in toluene (11.64%) at 80°C. with varying concentrations of benzoyl peroxide initiator: (*a*) 0.155%; (*b*) 0.052%; (*c*) 0.029%.

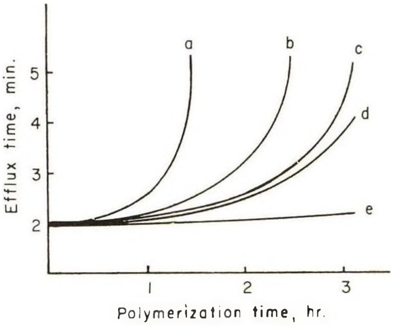

Fig. 3. Rate of polymerization of various divinylbenzenes in toluene (11.64%) at 80°C. with 0.155% benzoyl peroxide initiator: (*a*) pure *m*-divinylbenzene; (*b*) 2:1/*m*:*p*-; (*c*) commercial divinylbenzene; (*d*) pure *p*-divinylbenzene; (*e*) styrene.

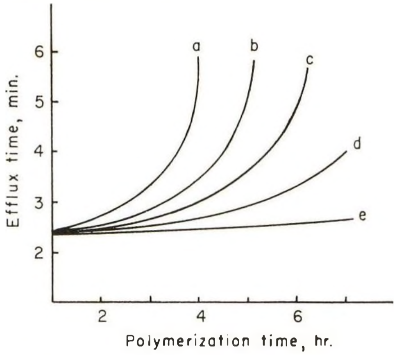

Fig. 4. Rate of polymerization of various divinylbenzenes in toluene (11.64%) at 60°C. with 1.55% initiator: (*a*) pure *m*-divinylbenzene; (*b*) 2:1/*m*:*p*-; (*c*) pure *p*-divinylbenzene; (*d*) commercial divinylbenzene; (*e*) styrene.

there is a range of workable initiator concentrations between 0.029 and 0.155%. The range at 60°C. (Fig. 2) is covered by concentrations of 0.155–2.81%. These data establish that the method, at least under these conditions, is not well suited to the determination of activation energies. Precisely measured rates under comparable conditions are not available.

Under other conditions, such as a narrower temperature range, a different solvent, or careful selection of intermediate initiator concentrations, the data needed for activation energy calculations may be obtainable. Such studies are in process and will be reported later.

The rate conditions defined as described in the preceding paragraph can be used for comparisons of rates based on ratios. For these comparisons the data of Figures 3 and 4 were obtained. The 60°C. data were obtained at 1.55% initiator and the 80°C. data at 0.155% initiator. It is significant that under these conditions there is a differentiation of the rates of reaction of the four materials. It is of interest to note that the rate of polymerization of each of the divinylbenzenes appears to exceed that of styrene considerably. This may be an artifact of the viscosity-measured rates in which small amounts of crosslinking create viscosity changes not involved in the styrene polymerizations.

TABLE I

Ratios of Rate Constants for Polymerization of Divinylbenzene Isomers at 60 and 80°C.[a]

Efflux time, min.	60°C.			80°C.		
	K_m/K_p	$K_m/K_{2:1}$	$K_{2:1}/K_p$	K_m/K_p	$K_m/K_{2:1}$	$K_{2:1}/K_p$
3	1.50	1.26	1.19	2.16	1.56	1.38
4	1.54	1.28	1.21	2.18	1.59	1.37
5	1.56	1.29	1.21	2.23	1.61	1.38
6	1.58	1.29	1.22	2.26	1.62	1.39

[a] Inverse ratio of polymerization times at stated efflux time as given in Figures 1 and 2; thus, $K_m/K_p = t_p/t_m$.

TABLE II

Differences in Activation Energies for Polymerization of Divinylbenzene Isomers at 60 and 80°C.[a]

	60°C.			80°C.		
Efflux time, min.	$E_m - E_p$, kcal.	$E_m - E_{2:1}$, kcal.	$E_{2:1} - E_p$, kcal.	$E_m - E_p$, kcal.	$E_m - E_{2:1}$, kcal.	$E_{2:1} - E_p$, kcal.
3	−0.27	−0.16	−0.12	−0.55	−0.32	−0.23
4	−0.29	−0.16	−0.13	−0.56	−0.33	−0.22
5	−0.30	−0.17	−0.13	−0.57	−0.34	−0.23
6	−0.31	−0.17	−0.14	−0.58	−0.35	−0.23

[a] The values are determined from the expression:

$$E_m - E_p = -RT \ln (K_m/K_p) = RT \ln (t_m/t_p)$$

Comparisons of the ratios of rate constants at 60 and at 80°C. are given in Table I, and differences in activation energies at 60 and 80°C. are given in Table II. The former are equivalent to, and are calculated as, inverse ratios of polymerization time at the same values of efflux time. The ratios are given at the 3, 4, 5, and 6 min. efflux times. At 60°C. the *meta* is 1.54

times as rapid as the *para* and 1.27 times as rapid as the 2:1 *meta–para* mixture. The 2:1 *meta–para* mixture is 1.21 times as rapid as the *para*. At 80°C. these ratios are 2.2; 1.6; and 1.38.

Differences in the activation energies (Table II) are determined by the relation (for *meta* and *para* isomers):

$$E_m - E_p = -RT \ln (K_m/K_p) = RT \ln (t_m/t_p)$$

in which t_m and t_p are polymerization times for the *meta* and *para* isomers and are given in Table II in kilocalories. The differences vary from −0.58 ($E_m - E_p$ at 80°C.) to −0.12 ($E_{2:1} - E_p$ at 60°C.). The *meta* isomer reacts most rapidly. It shows the greatest difference in activation energies at both 60 and 80°C., and the difference is greater at 80°C. than it is at 60°C. This establishes that the activation energy is less for the *meta* isomer than for 2:1 *meta–para* mixture and for *p*-divinylbenzene. The range of differences in E_A covered is probably a few kilocalories in an estimated 6–10 kcal.

Activation energies, such as these we are discussing herein, are recognized as including contributions from four reactions: (*1*) initiation, (*2*) propagation, (*3*) termination, and (*4*) chain transfer to solvent. The first of these is approximately constant (different concentrations of initiator are involved) in our observations, and structural factors in the monomer (*meta* or *para*) probably modify the rates of the other three reactions. A further complication is introduced in that both linear polymerization and cross-linking reactions are involved. The reactions are probably also subject to steric, as well as electronic, factors which result from a variation in the relative accessibility of the *meta* and *para* vinyl groups. These would be expected to appear as differences in frequency factors.

In view of this array of possible contributing factors, it is perhaps premature, on the basis of the data available from these studies, to try to correlate the observed increase in overall rate of polymerization of the *meta* isomer with some specific structural effect on these reactions. It may, however, be reasonable to assume that, in the linear polymerization reactions, the *p*-vinyl group provides additional resonance stabilization in the radical. The *meta* isomer should behave as if it consisted of two separate styrene vinyl groups with no alteration in reactivity from their resonance interaction. This is consistent with results from prior studies[5] of the copolymerization kinetics of the *meta* and *para* isomers. A decrease in rate can thus be ascribed to enhanced resonance stabilization in the *para*-derived radical.

Steric effects may also be involved significantly in the rate differences. It is thought that steric effects are involved in the low propagation constant for styrene ($K_p = 176$) as compared to vinyl acetate ($K_p = 3{,}700$) and are reflected in large differences in frequency factors. Steric factors would presumably be operative in both the linear polymerization and in the cross-linking reactions of the divinyls, and the data indicate that the *meta* groups are less sterically hindered. This is not consistent with the apparent accessibility of the *p*-vinyl groups as shown in three-dimensional models of the 120° polystyrene spiral.

The enhanced rate also seems not likely to be related to differences in the kinetics of the crosslinking reaction. In the crosslinking reaction the second vinyl group can be considered as an alkyl-substituted (*meta* or *para*) styrene. Copolymerization kinetics studies of styrene with both *m*- and *p*-methylstyrene, for example, which would clarify the extent of such differences, are apparently unavailable.[5] It may be unwise to assume this difference to be small but if it is small, one would hypothesize little difference in activation energies of the *m*- and *p*-divinylbenzenes in crosslinking reactions.

There are apparently no data available which will permit comparisons of chain transfer kinetics of *m*- and *p*-substituted vinyl or alkyl styrenes.

Without data on the rate of copolymerization of styrene with *m*- and with *p*-divinylbenzene, it is also premature to state that the difficulties encountered in bead copolymerization with the *meta* isomer are due to the enhanced rate of polymerization of the *meta* isomer. It does appear reasonable, however, to attribute this to a difference or differences in kinetics of polymerization.

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Résumé

Les vitesses globales de polymérisation de mélanges de *meta-*, *para-*, 2:1/*m*:*p*, et de divinylbenzène commercial, ont été suivies par viscosimétrie. Les résultats à 60° et 80° montrent que l'isomère méta polymérise le plus rapidement. Les rapports des vitesses montrent des différences d'énergies d'activation. On a tenté d'attribuer une influence sur les vitesses globales à l'augmentation de la stabilisation par résonance du radical dérivé du para-vinylphényle, qui diminue encore la réactivité déjà faible du radical dérivé du styrène. On considère comme peu probable la possibilité qu'ont les facteurs stériques de jouer un rôle important dans la différence de vitesses.

Zusammenfassung

Die Bruttopolymerisationsgeschwindigkeit von *meta-*, *para-*, 2:1/*m*:*p*-Mischungen und handelsübliches Divinylbenzol wurden viskosimetrisch bestimmt. Die Ergebnisse bei 60° und 80° zeigen, dass das *meta*-Isomere am raschesten polymerisiert. Die Ver-

hältnisse der Geschwindigkeiten lassen Unterschiede in den Aktivierungsenergien erkennen. Ein Einfluss auf die Bruttogeschwindigkeit wird versuchsweise der erhöhten Resonanzstabilisierung des von *p*-Vinylphenyl abgeleiteten Radikals zugeschrieben, welche die schon niedrige Reaktivität des von Styrol abgeleiteten Radikals noch weiter herabsetzt. Es scheint unwahrscheinlich, dass sterische Faktoren merklich zu den Geschwindigkeitsunterschieden beitragen.

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NOTES

Infrared Studies of Chain Conformations in Polyvinyl Chloride

I. INTRODUCTION

The infrared spectrum of PVC has been studied by many investigators using ordinary PVC which is polymerized at high temperatures.[1-7] Some interesting behaviors of the C—Cl stretching modes have been observed using PVC polymerized at low temperatures.[8-12] These studies and x-ray work[13] have shown that the syndiotactic part or the crystalline part is increased by lowering the polymerization temperature. Krimm and co-workers have recently studied the assignment of infrared spectrum of PVC with the help of $(CH_2—CDCl)_n$, $(CHD—CHCl)_n$, $(CHD—CDCl)_n$, and $(CD_2—CDCl)_n$ polymerized at various temperatures.[14]

Another attempt has been made to assign the C—Cl stretching modes by using the concept of internal rotational isomerism. Shimanouchi and Tasumi discussed the C—Cl stretching modes of PVC from the observed frequencies of the C—Cl stretching modes of *d,l*- and *d,d*-2,4-dichloropentane.[15] Shipman, Folt, and Krimm also have observed the C—Cl stretching modes of many primary, secondary, and tertiary organochlorine compounds and have revealed the relation between their frequencies and conformations.[16]

Only two C—Cl stretching modes are expected to appear in the infrared spectrum of syndiotactic PVC from the normal mode treatment[17] and this fact is supported in highly crystalline PVC;[10,14] however, more than two bands are observed in the region of the C—Cl stretching modes of ordinary PVC, and their frequencies and intensities are quite sensitive to the physical state of PVC.[18] A more careful measurement in the region of the C—Cl stretching modes with various kinds of PVC and a model compound, say 2,4,6-trichloroheptane, will aid in understanding the C—Cl stretching modes of PVC which are assigned to the isotactic part and to the boundary between the isotactic part and the syndiotactic part. Complete information of the behavior of the C—Cl stretching modes of PVC can be applied to studying the chain conformation in various states (solution, powder, and film).

II. EXPERIMENTAL AND RESULTS

1. Infrared Spectra of Various PVCs

A. Spectral Changes of PVC Caused by Orientation

Krimm and Enomoto reported that the band at 640 cm.$^{-1}$ was stronger than the band at 615 cm.$^{-1}$ in the infrared spectrum of the unoriented cast film of the ordinary PVC polymerized at 50°C., and their relative intensity ratio was inverted by stretching the case film.[18] It is interesting to examine the same behavior with PVC polymerized at low temperature. The PVCs were prepared at various temperatures by the photosensitized method by the use of uranyl nitrate catalyst[19] and by suspension polymerization with organic peroxide. The cast films were prepared with 50°C. PVC and −30°C. PVC from tetrahydrofurane. The solvent was extracted completely with carbon disulfide. The infrared spectra of their unoriented and oriented specimens were obtained with a grating spectrometer from 550 to 800 cm.$^{-1}$ and are shown in Figure 1.

B. Infrared Spectra of Powder PVC

The infrared spectra of oriented PVC film has been well studied, but only a few studies have been done systematically on the spectrum of powder PVC.[11,18] Figure 2 shows the infrared spectra of powder PVCs polymerized at various temperatures.

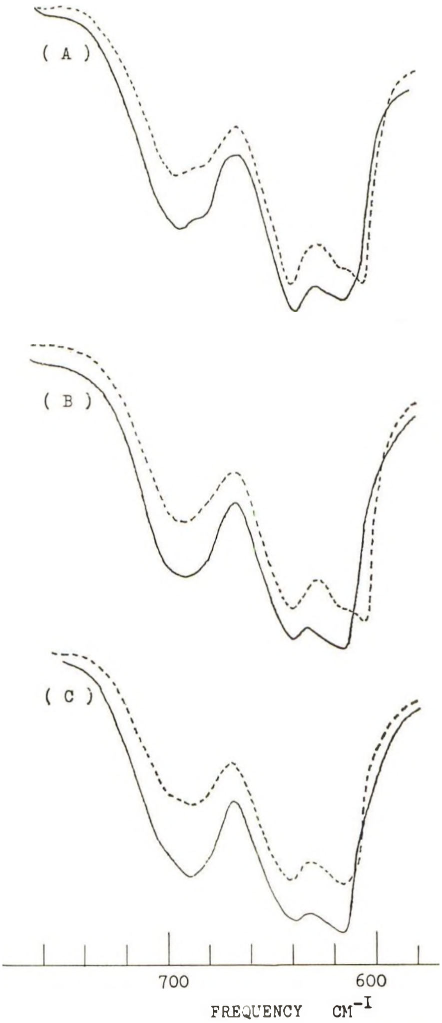

Fig. 1. Spectral changes of cast films by orientation (——) 50°C. PVC; (- -) −30°C. PVC. (*A*) Unoriented film; (*B*) 200% elongated film; (*C*) 600% elongated film.

C. Infrared of PVC at Solutional State

The cyclohexanon gel of PVC,[10,11] the acetone–carbon disulfide gel,[18] and molten PVC were used to observe the amorphous C—Cl stretching modes. The band at 640 cm.$^{-1}$, which was assigned to the crystalline band, overlapped with an amorphous band, because a weak band was still observed at around 640 cm.$^{-1}$ in the spectrum of the amorphous state[14] while the band at 640 cm.$^{-1}$ was reduced by orientation.[18] A dilute solution of PVC is desirable for observing the amorphous C—Cl stretching modes of PVC. An acetone–carbon disulfide mixture is a good solvent for PVC because acetone has no band in the region of the C—Cl stretching modes except for a band near 750 cm.$^{-1}$. This mixture (acetone:carbon disulfide = 1:5) does not have any band from 700 to 550 cm.$^{-1}$ and completely dissolves 120°C. PVC which was expected to have a lower degree of polymer-

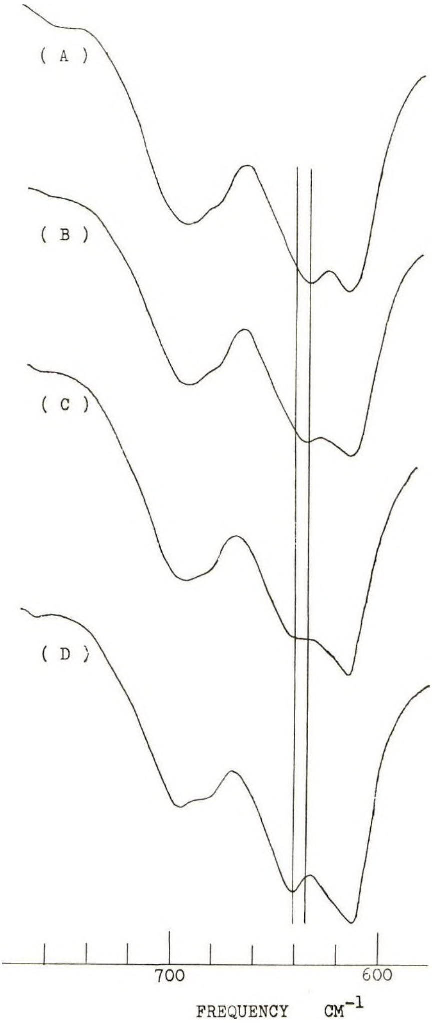

Fig. 2. Infrared spectra of powder PVCs: (*A*) 120°C. PVC; (*B*) 50°C. PVC; (*C*) −30°C. PVC; (*D*) −78°C. PVC.

ization and crystallinity than ordinary PVC. A good infrared spectrum of the 120°C. PVC in solution was obtained and is shown in Figure 3.

D. Infrared Spectrum of Plasticized PVC

A film of plasticized PVC is more easily stretched and has better recovery than a film of rigid PVC. Most PVC plasticizers have some absorption bands in the region of the C—Cl stretching modes of PVC,[20] and it is not easy to remove the bands of the plasticizers completely from the spectra by the compensating method. We examined many plasticizers and discovered that diisobutyl adipate was a good plasticizer for the spectroscopic study of the effect of plasticizer on the chain conformation of PVC because it does not have any interfering bands.

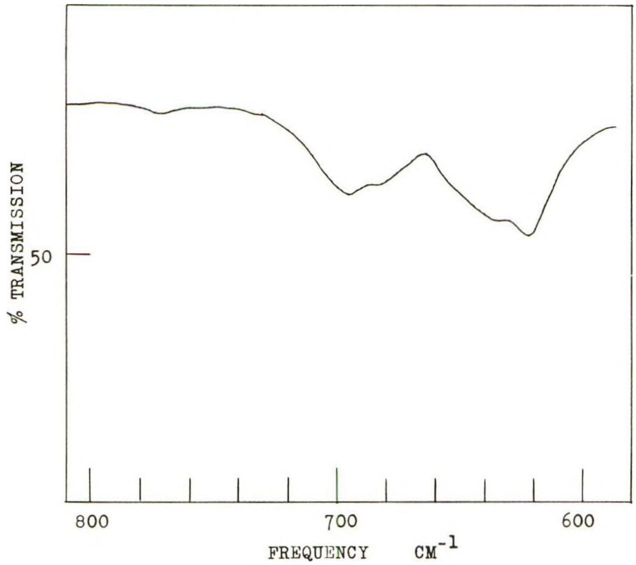

Fig. 3. Infrared spectrum of 120°C. PVC in acetone–carbon disulfide solution.

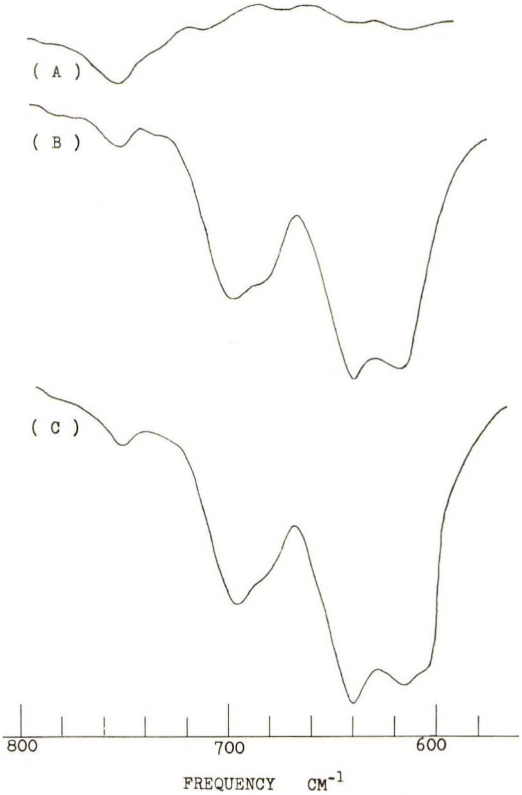

Fig. 4. Infrared spectra of plasticized PVCs: (*A*) diisobutyl adipate; (*B*) plasticized 50°C. PVC with 60 phr diisobutyl adipate; (*C*) plasticized −30°C. PVC with 60 phr diisobutyl adipate.

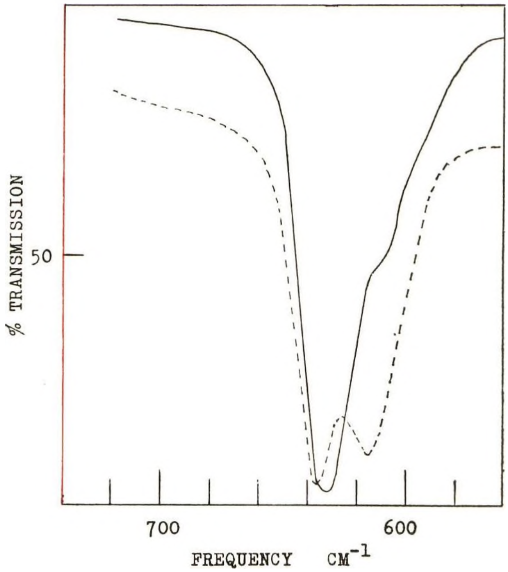

Fig. 5*a*. Raman effect and infrared spectrum of *d,l*-2,4-dichloropentane.

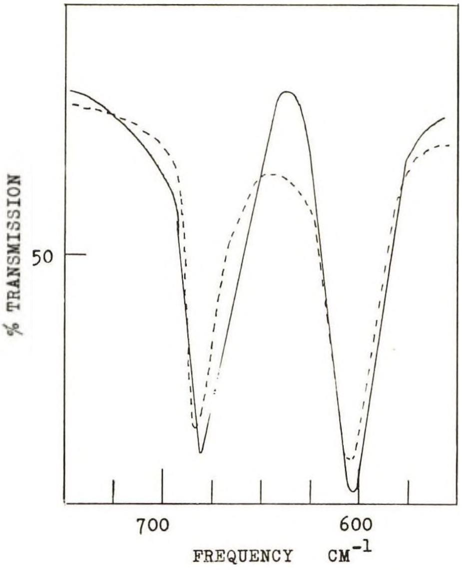

Fig. 5*b*. Raman effect and infrared spectrum of *meso*-2,4-dichloropentane: (——) Raman effect; (- -) infrared spectrum.

2. Infrared Spectra of PVC's Model Compounds

Two optical isomers were separated by gas chromatography in the case of 2,4-dichloropentane, and the infrared spectra of the isomers were quite useful for understanding the chain conformation and the C—Cl stretching modes of PVC. 2,4,6-Trichloroheptane is a better model compound of PVC because it is expected to have three optical isomers (*dld, dll,* and *ddd*). A large amount of 2,4-dichloropentane was prepared to observe the

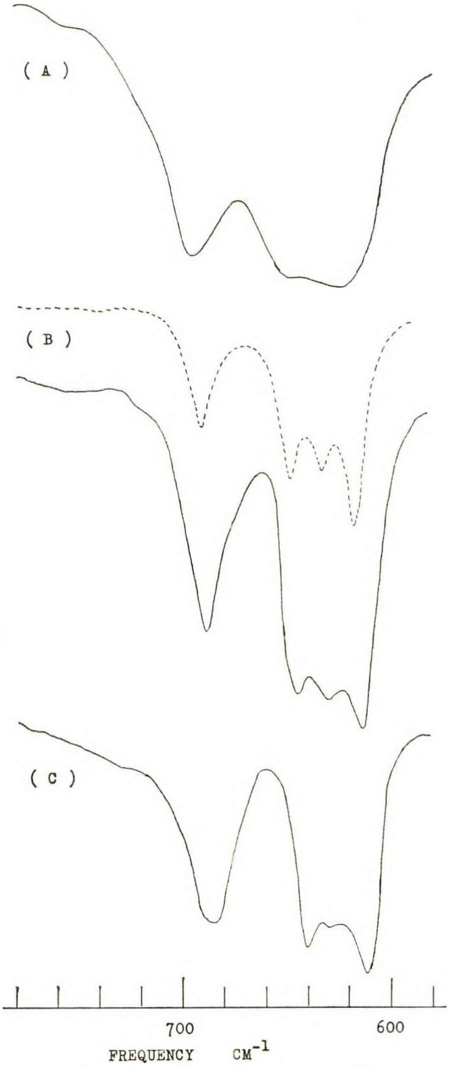

Fig. 6*a*. Infrared spectrum of TCH-I.

Raman effect by a previously developed method.[15] The spectra of both isomers are shown in Figure 5.

2,4,6-Trichloroheptane was prepared by the chlorination of 2,4,6-trioxyheptane with thionyl chloride and pyridine, and it was expected to have three optical isomers (*dld*, *ddl*, and *ddd*). We failed to separate the optical isomers by gas chromatography, but we could obtain the different infrared spectra of the compounds by adjusting the preparative condition which gave the same chemical composition as shown in Table I and Figure 6.

III. DISCUSSION

The effect of orientation on the chain conformation in the cast film of 50°C. PVC was also observed with the −30°C. PVC as shown in Figure 1. The overlapping of a band with the crystalline band near 640 cm.$^{-1}$ is supported by Figures 2 and 3. The frequency

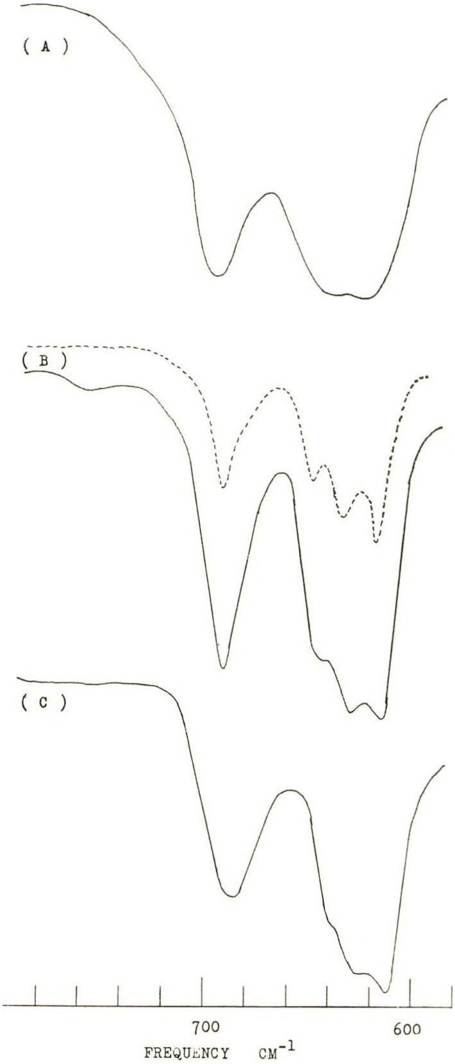

Fig. 6*b*. Infrared spectrum of TCH-II: (*A*) gaseous phase 199 ~ 200°C.; (*B*) room temperature, (——) liquid phase, (- -) 20% CS_2 solution; (*C*) solid phase (cooled by liquid nitrogen).

of the band near 640 cm.$^{-1}$ in the infrared spectra of the powder PVCs varies with the polymerization temperature. The 120°C. and 50°C. PVCs have a peak at 635 cm.$^{-1}$ and the −78°C. PVC has one at 640 cm.$^{-1}$. The −30°C. PVC has a broad band between these values. This frequency shift is undoubtedly due to the chain conformation variations from highly crystalline PVC.[10,11,14] The band at the lower frequency is mainly assigned to the amorphous part, while the higher one is assigned to the crystalline part. The related band is also observed at 635 cm.$^{-1}$ in the infrared spectrum of the 120°C. PVC in solution. Because the intensity of the band at 640 cm.$^{-1}$ is reduced by orientation in the case of the cast film, this amorphous component is probably due to a less favorable chain conformation.

Another spectral change is observed around 690 cm.$^{-1}$. This band was observed to

TABLE I
Chlorination of Heptanetriol

No.	Heptanetriol, mole	Thionyl chloride, mole	Pyridine, mole	Temp., °C.
TCH-I	1	3	3	110
TCH-II	1	3	Trace	90

No.	C, %	H, %	Cl, %
TCH-1	41.61	6.36	52.07
TCH-II	41.64	6.33	52.05
Theoretical value	41.28	6.39	52.33

shift its peak by orientation[11] and the peak of the parallel band appeared at a higher frequency than the perpendicular one. Two components are observed at 695 cm.$^{-1}$ and near 680 cm.$^{-1}$ in the infrared spectra in the unoriented states and the solution states, and both components are shifted to 690 cm.$^{-1}$ by orientation.

The band at around 690 cm.$^{-1}$ was assigned to the C—Cl stretching modes of the bent carbon skeletal structure. Some less favorable bent skeletal structures exist in PVC, and they are changed to the more stable state by orientation from the above experimental fact. The infrared spectra of the model compounds are interesting for explaining the C—Cl stretching modes of PVC. Detailed studies of a series of secondary alkylchlorides[10,15,16] revealed that the frequency of the C—Cl stretching mode depends in particular on the substituents which are *trans* to the Cl atom across both adjacent C—C bonds. Convenient notations were given to classify the modes.[16] When both substituents *trans* to the Cl atom are H atom, the C—Cl stretching mode appears at around 620 cm.$^{-1}$ and is designated as S_{HH}. The band at near 690 cm.$^{-1}$ is S_{HC}, where one substituent *trans* to the Cl atom is an H atom and the other is a C atom.

Table II shows the possible chain conformations of 2,4-dichloropentane and the C—Cl stretching modes. The *d,l* form and the *d,d* form were concluded not to change the chain conformations, as any significant spectral change was not observed by cooling and heating the samples.[15] The *d,l* compound has only the TT form, and the coupling of the two S_{HH} modes appear at 615 and 635 cm.$^{-1}$ As the *meso* compound has the TG* or the GT form, the S_{CH} appears at 687 cm.$^{-1}$ and the isolated S_{HH} at 623 cm.$^{-1}$ where it is located between the coupled S_{HH}s.

Figure 6 shows the infrared spectra of the two kinds of 2,4,6-trichloroheptane which resemble, more than Figure 5, the infrared spectrum of PVC. The band of TCH-I at 645 cm.$^{-1}$ is stronger than that of TCH-II. This band is weaker than the band at 630

TABLE II
Possible Chain Conformations of 2,4-Dichloropentane and the C—Cl Stretching Modes

Optical isomer	Chain conformations (around C—C bond)	C—Cl stretching modes	
		P.I.R. (cm.$^{-1}$)	Raman (cm.$^{-1}$)
dl	TT	S_{HH} 615 (s)	610 (shoulder)
		S_{HH} 636 (vs)	632 (vs)
	GG	Not observed	
dd	TG* (GT)	S_{HH} 623 (vs)	622 (vs)
		S_{HC} 687 (vs)	684 (vs)

cm.$^{-1}$ in the spectrum of pure TCH-I at room temperature; however, the 645 cm.$^{-1}$ band becomes stronger than the 630 cm.$^{-1}$ band in the case of dilute carbon disulfide solution. This tendency is also observed in case of TCH-II, and it is interesting that the intensity of the band at 645 cm.$^{-1}$ of 2,4,6-trichloroheptane varies with changes in the concentration of carbon disulfide. This change is related to the behavior of the band at 640 cm.$^{-1}$ in the infrared spectrum of PVC. When TCH-I is cooled by liquid nitrogen, the band at 630 cm.$^{-1}$ becomes quite weak; however, the same variation is not clearly observed in the infrared spectrum of TCH-II. This suggests that the ratios of the optical isomers in TCH-I are somewhat different from those in TCH-II. While the bands at 645 and 615 cm.$^{-1}$ become sharp when the sample is cooled by liquid nitrogen, the band at 688 cm.$^{-1}$ becomes broad and this suggests that the bands near 690 cm.$^{-1}$ are composed of some other components. This fact will be used to explain why some components appear near 690 cm.$^{-1}$ in the infrared spectrum of PVC.

Many chain conformations of 2,4,6-trichloroheptane are considered with combinations of the *d,l* form and the *d,d* form in Table II. Several conformations shown in Table III are stereochemically possible, but it is not easy to determine the chain conformations and to assign the C—Cl stretching modes at present. Two types of the isolated S_{HH} are observed at 630 and 640 cm.$^{-1}$ while the coupled S_{HH}s which arise from the TTTT form appear at 640 and 615 cm.$^{-1}$ One of these may be the S_{HH} after S_{CH} and the other after S_{HC}. As the TTTT form and the GTGT (the TG*TG*) form are probably the most stable forms, based on the study of 2,4-dichloropentane,[15] the significant spectral change observed in the infrared spectrum of TCH-I may be due to the *dll* isomer in which TCH-I may be rich.

TABLE III
Possible Chain Conformations of
2,4,6-Trichloroheptane and the C—Cl Stretching Modes

Optical isomer	Chain conformation	C—Cl stretching modes
dld	TTTT	S_{HH} S_{HH} S_{HH}
	TTG*G*	S_{HH} S_{HC} S_{CH}
	(GGTT)	S_{HC} S_{CH} S_{HH}
dll	TTTG	S_{HH} S_{HH} S_{CH}
	TTG*T	S_{HH} S_{HC} S_{HH}
	(GGTG)	S_{HC} S_{CH} S_{CH}
ddd	TG*TG*	S_{HH} S_{CH} S_{CH}
	(GTGT)	S_{HC} S_{HC} S_{HH}

The effect of the plasticizer on the chain conformation of PVC is easily understood from Figure 4. The intensity of the band at 640 cm.$^{-1}$ is the same with that at 615 cm.$^{-1}$ in the spectrum of the unoriented pressed film without plasticizer[18] and the former becomes stronger than the latter when the pressed film is plasticized with more than 20 diisobutyl adipate. The crystalline band at 605 cm.$^{-1}$ becomes quite weak in the infrared spectrum of the plasticized −30°C. PVC. This shows clearly that the plasticizer decreases the crystallinity and changes the chain conformation to a less favorable state.

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*A Convenient Preparation for Ethylenesulfonic Acid**

Frequently free ethylenesulfonic acid is required for copolymerizations or homopolymerization. However, no good laboratory method for the preparation of free ethylenesulfonic acid was reported prior to the publication of Breslow and Hulse.[1] Although these workers reported the preparation of large quantities of this acid, it was necessary for them to isolate it from an aqueous solution containing large amounts of dissolved salts. The starting material which they used, sodium ethylenesulfonate, was synthesized from ethanol by the method of Breslow, Hough, and Fairclough.[2] Sodium ethylenesulfonate, however, can be prepared more readily via other routes.[3,4] Thus, it can be made by dehydrohalogenation of sodium 2-bromoethanesulfonate,[5] which is readily available by the procedure of Marvel and Sparberg.[6,7]

We have observed that an ether solution of ethylenesulfonic acid may be obtained conveniently by suspending dry, finely divided sodium ethylenesulfonate in dry ether and saturating the mixture with dry hydrogen chloride. Pure ethylenesulfonic acid may then be obtained by distillation under greatly reduced pressure after removal of the ether from the filtered solution.

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Experimental

Sodium Ethylenesulfonate. A 12*M* solution of sodium hydroxide was added to 464 g. (2.2 mole) of sodium 2-bromoethanesulfonate[6] in a small amount of water until a slightly basic reaction to litmus was noted. The solution was carefully evaporated to dryness on a steam bath (excessive heat left a hard, glassy residue which was alcohol-insoluble and presumed to be polymeric sodium ethylenesulfonate.) The residue was extracted with 95% ethanol to yield 260 g. (2.0 mole) of sodium ethylenesulfonate.

Ethylenesulfonic Acid. Dry, pulverized sodium ethylenesulfonate 108 g. (0.83 mole) and 300 ml of dry ether were placed in a 1-liter flask fitted with an inlet tube, stirrer, and condenser protected by a drying tube. Dry hydrogen chloride (scrubbed with concentrated sulfuric acid) was bubbled through the rapidly stirred slurry until unabsorbed gas issued freely from the outlet of the drying tube. The mixture was allowed to sit for 15 min. to permit the sodium chloride to settle, and the solid was then filtered off on a fritted glass filter. Most of the ether was removed from the filtrate by distillation through a Vigreux column, and the remainder by application of reduced pressure with a water aspirator. The residue of crude ethylenesulfonic acid was distilled in a Hickman still with the aid of a diffusion pump. Under a pressure of approximately 0.01 mm. it was possible to distill the acid at a pot temperature of 95°C. or less. The yield of water-white acid was 87 g. (96%), n_D^{25} 1.4490.

ANAL. Calc. for $C_2H_4O_3S$: neut. equiv., 108.1. Found: neut. equiv., 110.

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