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Hydrogels of Poly(hydroxyethyl Methacrylate) and Hydroxyethyl Methacrylate–Glycerol Monomethacrylate Copolymers

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Synopsis

Hydrophilic three-dimensional polymer networks (hydrogels) were prepared from hydroxyethyl methacrylate (HEMA) and the copolymer of HEMA and glycerol monomethacrylate (GMMA). The equilibrium water content of the hydrogels in water was investigated as a function of the initial dilution of the polymerization mixture, the type of solvent, and the hydrophilicity of the polymer. The initial dilution was found to have a decisive effect on the swelling or deswelling of hydrogels after the completion of the gel formation. With relatively less hydrophilic hydrogels, there is a critical initial dilution to produce the gel which does not swell or deswell in water after the gel formation. This "isovolumic" initial dilution shifts toward a higher dilution as the hydrophilicity of the hydrogels increases; however, when hydrophilicity of the polymer rises above a certain point, gels always swell in water. Permeability of oxygen through hydrogels was also studied.

INTRODUCTION

In a previous study,[1] swelling properties of hydrophilic gels (hydrogels) prepared by simultaneous crosslinking and polymerization of hydrophilic monomers have been reported. Results of the study indicate that when a three-dimensional network is prepared in a relatively poor solvent, the effect of the thermodynamic interaction of the solvent and the polymer is overwhelmingly greater than the effects due to other factors, such as the number of crosslinks and the relative swelling of the polymer at the time of crosslinking.[2–5]

The crosslinking polymerization, in general, may involve the phase separation of the resulting polymer, depending on the extent of solvent–polymer interaction. The resulting polymer gels may undergo syneresis or further swelling upon the completion of the polymerization.[6] When hydrogels become opaque or translucent, the systems seemingly become heterogeneous. The critical point at which a hydrogel changes its structure from homogeneous to heterogeneous has significance from both an academic and

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an applied point of view, since a transparent and highly permeable hydrophilic membrane has potential applications in medicine, especially in ophthalmology.

In this work an attempt was made to investigate the effect of some important factors in polymerization on the shift of the critical point where gels became heterogeneous, and to study the swelling behavior of homogeneous gels. Permeability of the oxygen molecule through the hydrogel membranes was examined to confirm the heterogeneity of translucent to opaque hydrogels. Oxygen permeability is considered an important factor when polymer membranes are used in biological systems.

To obtain a more complete profile of the swelling of hydrogels, a more detailed study of hydroxyethyl methacrylate (HEMA) hydrogels was repeated in this study and it was extended to copolymers of HEMA and glycerol monomethacrylate (GMMA) as models of progressively more hydrophilic polymer networks.

For the most part, the concentration of initiator and the amount of crosslinking agent were kept at a fixed level. Should these factors be changed, a similar series of experiments could be carried out for each level of those factors for a complete investigation. However, in order to simplify the experimental procedure, only a limited number of experiments were done in special cases where the effects of those factors are manifested with maximum amplitude.

No attempt was made, in this study, to correlate the amount of crosslinking agent to the number of effective crosslinks in the resulting hydrogels which would include the crosslinks due to the chain transfer reaction as well as the topological entanglement of polymer segments.

EXPERIMENTAL

HEMA obtained from the Borden Chemical Company was distilled at 45°C. under vacuum of 25 μ mercury.

Tetraethyleneglycol dimethacrylate (TEGDMA), also from the Borden Chemical Company, was used as the crosslinking agent without further purification.

Glycerol monomethacrylate (GMMA) was obtained through the ring-opening reaction of glycidyl methacrylate (2,3-epoxypropyl methacrylate) by catalysis with aqueous sulfuric acid. The method of preparation of GMMA is similar to the method described by Refojo.[7] Glycidyl methacrylate is available as a commercial product from the Borden Chemical Company.

As the initiator of polymerization, the redox system of ammonium persulfate, $(NH_4)_2S_2O_8$, and sodium metabisulfite, $Na_2S_2O_5$, was used. Aqueous solutions of both were prepared fresh and the required amount of the solutions were added to the polymerization mixtures. The amount of initiator is described in this paper as the amount of the persulfate in the polymerization mixture.

All hydrogels were prepared in the form of thin films to facilitate and expedite equilibration, drying, and measurement of dimensions. The film was cast between two 4 × 4 in. sheets of Pyrex glass by using a silicone rubber gasket (Dow Corning, Medical Silastic) of 20 mil thickness. After transferring the polymerization mixture into the cell, it was polymerized at 55°C. in an oven for 90 min.

When polymerization was completed, the glass plates were separated and the dimensions of the film noted. It was then allowed to equilibrate in distilled water for 1 week with frequent exchange of distilled water. On completion of equilibration in water, the size of the film was again noted for the calculation of the volume change. At least two sheets of hydrogels were prepared from each polymerization mixture.

One film was cut into four squares, each 3 × 3 cm. The surfaces were dried with bibulous paper, weighed, and then dried in aluminum dishes at 105°C. until they reached constant weights. From these readings the water content of each piece was determined and the mean of the four values (which agreed within 0.5%) was used to describe the water content of each film.

RESULTS AND DISCUSSION

HEMA Hydrogels

Effect of Solvent and Initial Dilution

Poly(HEMA) is not soluble in water and, accordingly, when more than about 40% water is used in the polymerization mixture, hydrogels become translucent to opaque, indicating that precipitation of the polymer occurs at higher concentrations of water. The addition of ethylene glycol—a better solvent for the polymer than water—into the monomer solution makes it possible to obtain transparent gels with higher amounts of solvent in the polymerization mixture.

Once the transparent hydrogels are obtained, they can be equilibrated in water and the solvent can be eventually changed to water. In this exchange process of the solvent, transparent gels become turbid, but regain transparency when the original solvent has been completely replaced by water.

Thus, with the use of ethylene glycol the amount of solvent in the polymerization mixture can be extended beyond the upper limit where hydrogels become heterogeneous with water, and the effect of initial dilution on the swelling of the hydrogels can be examined in a wider range of dilution. However, the tripartite system of monomer–water–ethylene glycol necessitates the study of a phase diagram for a three-components system.

In this series of experiments, 1.5% of monomer was replaced by TEGDMA, crosslinking agent, and the initiator concentration was kept constant at 0.012% of ammonium persulfate and 0.024% of sodium metabisulfite in the polymerization mixture. Concentrations of solvent in the poly-

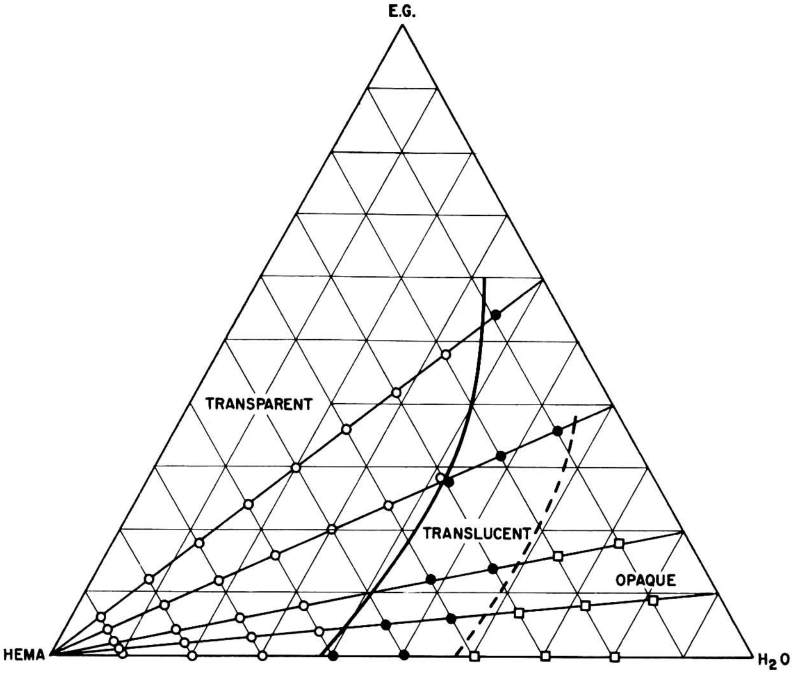

Fig. 1. Transparency of HEMA hydrogels in HEMA–H_2O–ethylene glycol system: (○) transparent gels; (●) translucent gels; (☐) opaque gels.

merization mixture were changed from 10% to 90% in 10% increments and the following water/ethylene glycol ratios were used: 100/0, 90/10, 80/20, 60/40, and 40/60. The transparency of hydrogels is summarized in a phase diagram shown in Figure 1.

The water contents of gels after they are equilibrated in water are shown in Figure 2. The results indicate that the equilibrium water content of homogeneous hydrogel in pure water does not depend on the composition of the solvent in which polymerization took place; but the critical initial dilution, at which precipitation of the polymer occurs, increases with the increasing amount of ethylene glycol in the solvent. Thus, the addition of ethylene glycol in monomer solutions does not increase the equilibrium water content of the homogeneous gels, but it prevents the precipitation of the polymer or the formation of heterogeneous gels.

Although the dependence of the water content on the initial dilution is more evident than it was found in the previous study,[1] it is relatively small and does not depend on the composition of the solvent.

When a gel becomes translucent or opaque, the water content in the gel increases sharply and deviates from its linear dependence on the initial dilution, indicating water is held in a heterogeneous fashion in translucent or opaque gels. Results with heterogeneous hydrogels are less reproducible.

There is an indication that HEMA gels may be transparent with equilibrium water content less than about 41% and opaque when the

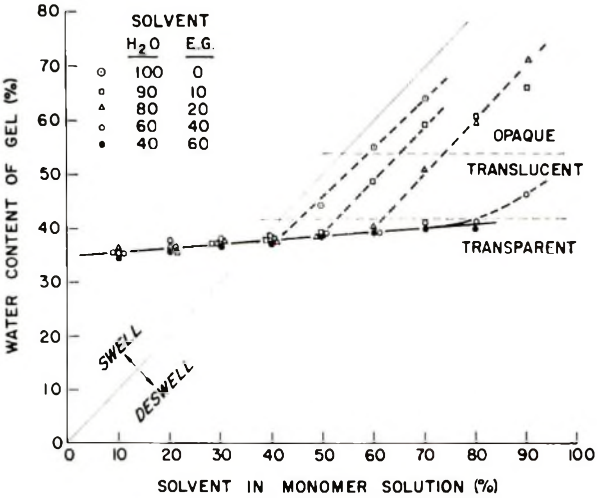

Fig. 2. Effect of the initial dilution of monomer solution and the composition of the solvent on the water content of HEMA hydrogels.

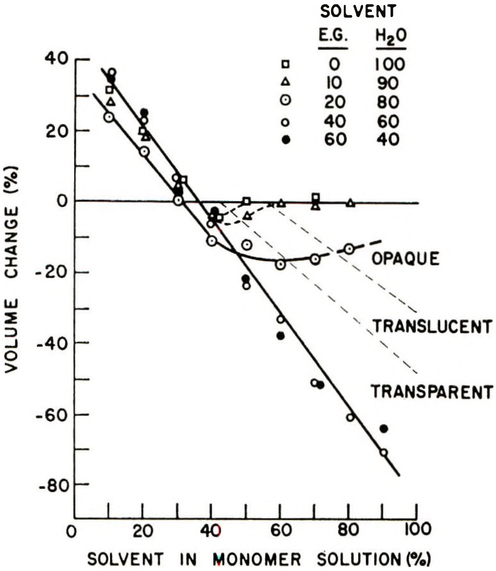

Fig. 3. Effect of the initial dilution of monomer solution on the volume change of HEMA hydrogels in water.

equilibrium water content is higher than 54%. Gels that have an equilibrium water content between 41% and 54% are translucent and their turbidity increases with the water content.

Gels which remain above the diagonal line in Figure 2 should swell when they are equilibrated in water after the completion of the polymerization, and gels which are plotted below the line should deswell upon equilibration in water. This relationship is clearly demonstrated by the volume change of the gel upon equilibration in water, in Figure 3. The volume changes were calculated from the ratio of linear deformation, assuming isotropic swelling or deswelling of the gels.

It is interesting to note that the volume change is almost linearly dependent on the initial dilution as long as the gels stay clear (homogeneous gels) and does not depend on the composition of the solvent. In other words, after a gel is formed, swelling or deswelling upon equilibration in water is not due to the exchange of solvent but is mainly due to the structural factor of gels.

The results also indicate that "isovolumic" gels, which do not change volume (in water) after the completion of gel formation, can be obtained with HEMA, with the use of approximately 35% solvent in the polymerization mixture, regardless of the composition of the solvent. The term "isovolumic" gels, of course, refers to the swelling of the gels in water only. They may swell or deswell when they are immersed in drastically different solvents.

Effect of Initiator Concentration

Varying the concentration of initiator—and consequently changing the kinetic chain length or the concentration of the growing free radicals—was expected to alter the water content of a given hydrogel. For example, sponges of hydrogels can be obtained by polymerization with an extremely high concentration of initiators.[8] For this experiment, a hydrogel close to the border line of transparent (homogeneous) gels (found on the phase diagram with the initiator concentration of the previous experiments) was chosen. A solvent of 80% water and 20% ethylene glycol, and solvent

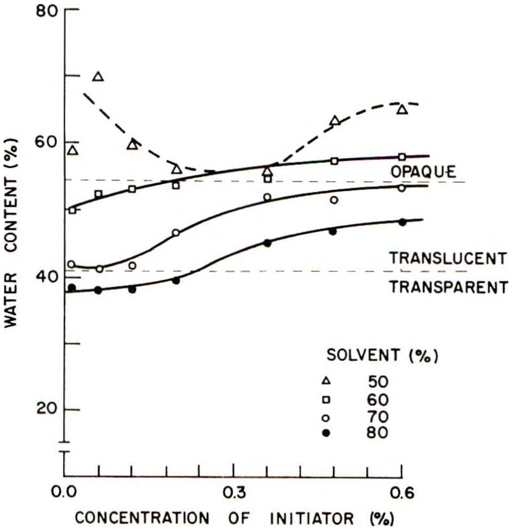

Fig. 4. Effect of the concentration of initiators on the water content of HEMA hydrogels (solvent: 80 H_2O/20 ethylene glycol).

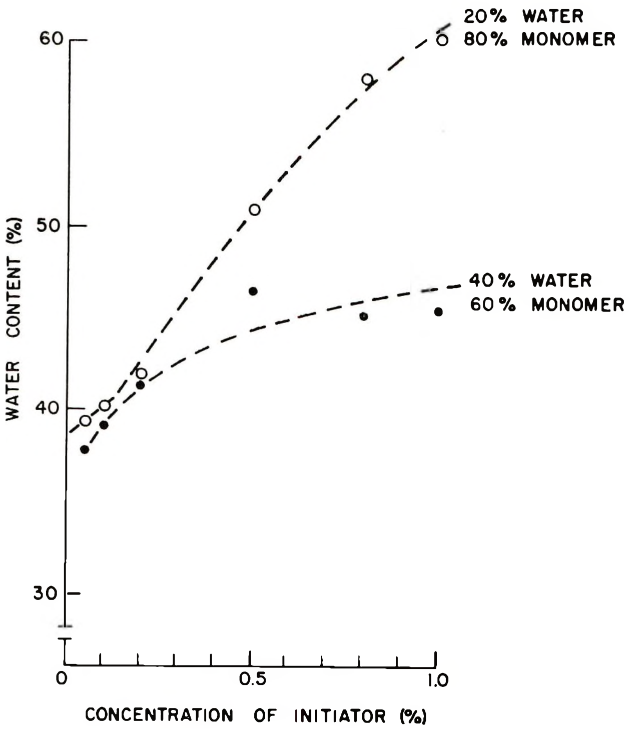

Fig. 5. Effect of the concentration of initiators on the water content of HEMA hydrogel (solvent: 100% H_2O).

concentrations of 50, 60, 70, and 80% were used for polymerization mixtures with different initiator concentrations. The films were prepared as before. The amounts of ammonium persulfate used were 0.012, 0.06, 0.2, 0.4, 0.5, and 0.6%; double the amount of sodium metabisulfite was paired with each concentration of ammonium persulfate in the polymerization mixture.

The equilibrium water content of the hydrogels was plotted against the concentration of initiator (percentage of ammonium persulfate) in Figure 4. Similar experiments with 100% water as solvent were done, and the results are shown in Figure 5. The results indicate that both the transparency and the equilibrium water content depend not only on the initial dilution and type of solvent, but also on the concentration of initiator (i.e., the number of the growing radicals). This effect is most evident in Figure 5. With formulae which yield completely opaque gels, the initiator concentration seems to lose its significance.

Swelling of Hema Hydrogels in Aqueous Solutions

Effect of Solvent Composition on the Swelling of Isovolumic Gels in Saline Solution. When a hydrogel equilibrated in water only is placed in a different type of aqueous solution, the gel will swell or deswell, depending

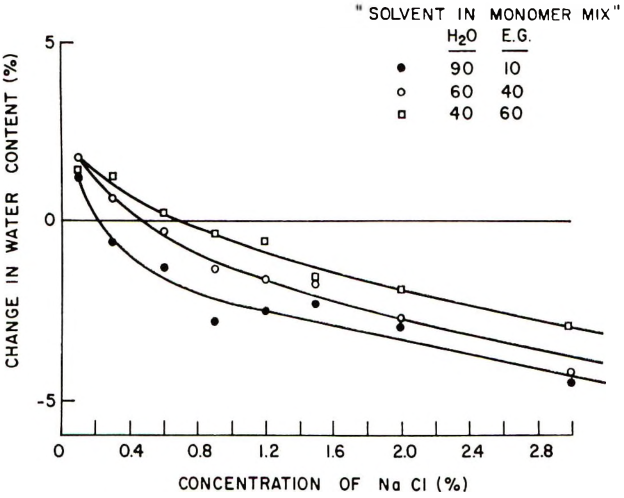

Fig. 6. Changes in water content of HEMA hydrogels in saline solutions.

on the chemical potential of water in the solution and on the specific interaction of solute with the polymer of the hydrogel.

The effect of the NaCl concentration in saline solution on the swelling of isovolumic hydrogels was investigated with gels prepared in three different solvent compositions. The result, as shown in Figure 6, was a change from the equilibrium water content in pure water.

The results indicate that the change of water content in an isovolumic gel in saline solution depends on the solvent composition in which the gel is formed. These changes seem to be less in gels which were formed in the presence of an increased amount of ethylene glycol, a better solvent than water.

Effect of Crosslinks on the Swelling of Isovolumic Gels in Saline and Artificial Tear Solutions. Although the effect of crosslinks on the swelling of HEMA gels in pure water was previously found to be negligible,[1] the increase of crosslinks was expected to reduce changes in the hydration of gels placed in different aqueous solutions.

In this experiment an isovolumic hydrogel is prepared by a solvent of 90% water and 10% ethylene glycol (the solvent which showed the most shrinking in saline solution of the three gels mentioned in the preceding section). The amounts of crosslinking agent used were: 1.5, 2.0, 3.0, 4.0, and 5.0% in total monomer.

After small pieces of film, 3 × 3 cm. square, were immersed in 3% saline solution and in an artificial tear solution for 10 days, the water contents were measured and changes from the equilibrium water content in pure water were calculated.

The artificial tears used in this experiment were prepared by the following formula:[9] gelatin, 0.3 parts; chlorobutanol, 0.3 parts; Locke's solution 30.0 parts. Locke's solution was made up as follows: NaCl, 0.9 parts;

KCl, 0.024 parts; $CaCl_2$, 0.042 parts; dextrose, 0.1 parts; sodium bicarbonate, 0.02 parts; distilled water, 100.0 parts.

The results are summarized in Table I. Table I indicates that crosslinks reduce the swelling and deswelling of HEMA gels in aqueous solutions. This reduction, however, is not great, and the effect seems to level off rapidly with the increasing amount of crosslinking agent.

TABLE I

Effect of Crosslinks on the Swelling of Hydrogels in Aqueous Solutions

Amount of crosslinking agent, %	Change in water content, %	
	3% Saline	Artificial tears
1.5	−4.53	8.00
2.0	−6.07	7.05
3.0	−5.57	6.40
4.0	−5.58	6.35
5.0	−5.58	5.65

HEMA–GMMA Copolymer Hydrogels

Since poly(GMMA) is a water-soluble polymer, the copolymers of GMMA and HEMA may be considered as models of hydrophilic polymers which increase their hydrophilicity with an increasing amount of GMMA. Therefore, the effect of hydrophilicity of a polymer on the swelling of hydrogels can be examined with these copolymers by methods similar to those applied to HEMA gels in the previous sections.

In this series, the solvent was fixed at 90% water and 10% ethylene glycol. TEGDMA, 2% in the total monomers, was used as the crosslinking agent. The initiator concentration was fixed at 0.012% ammonium persulfate and 0.024% sodium metabisulfite in the polymerization mixture. The amount of GMMA in copolymers was changed from 10% to 90% in 10% increments.

Effect of Monomer Ratio and Initial Dilution

Although 10% ethylene glycol was added as a solvent in order to increase both the solubility of TEGDMA in monomer solutions in low monomer concentration ranges and the solubility of HEMA-rich copolymers, it was expected that, in these experiments, the effect of ethylene glycol is much less and that all series could be prepared with 100% water. Therefore, a solvent which consists of 90% water and 10% ethylene glycol was treated as one phase of solvent, and the phase diagram of two monomers and one solvent was constructed in order to find the range wherein the homogeneous hydrogels can be formed. The phase diagram is shown in Figure 7.

The phase diagram suggests that these two monomers may not copolymerize in all ratios and that, at higher solvent concentrations, two homopolymers and a copolymer may be crosslinked together, yielding apparently

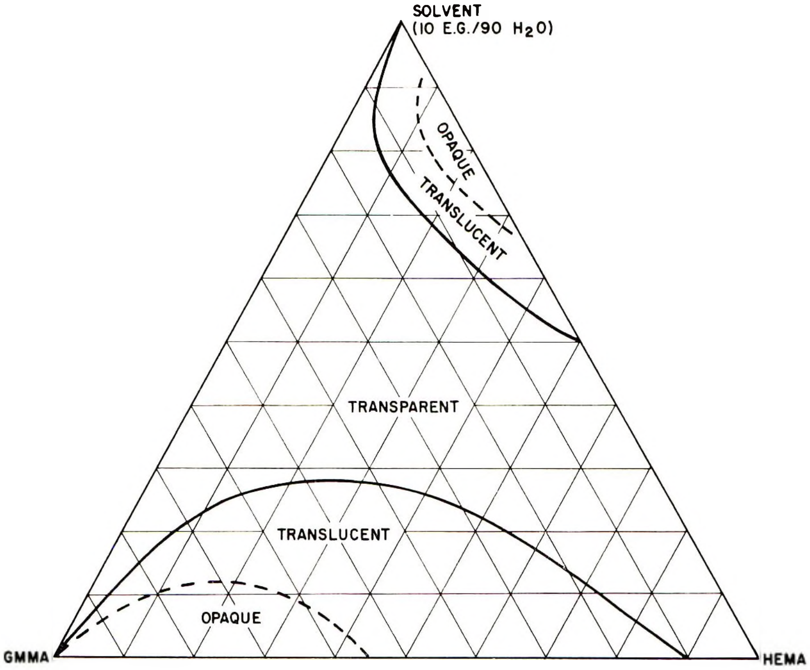

Fig. 7. Transparency of GMMA–HEMA hydrogels in HEMA–GMMA–solvent (10 ethylene glycol/90 H_2O) system.

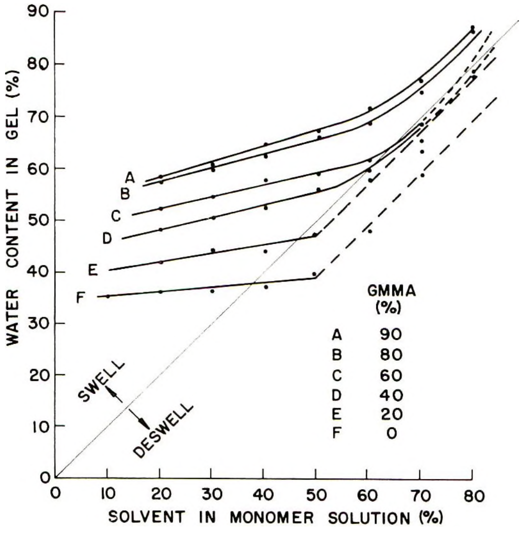

Fig. 8. Effect of the composition of copolymers and the initial dilution on the water content of HEMA–GMMA hydrogels.

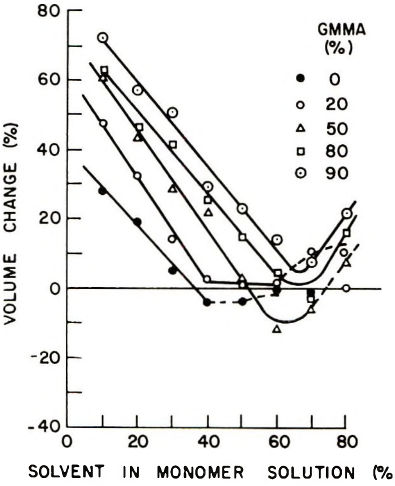

Fig. 9. Effect of the initial dilution of monomer solution on the volume change of HEMA–GMMA hydrogels in water.

homogeneous, transparent hydrogels. Even if they are not real copolymers in the strictest sense, transparent and apparently homogeneous crosslinked three-dimensional networks furnish interesting models of hydrogels with different degrees of hydrophilicity.

Some of the equilibrium water contents in pure water are shown in Figure 8. The results show that the water content increases with the amount of GMMA in hydrogels, indicating that the water content depends on the hydrophilicity of the polymer segment which forms hydrogels. The dependence of the swelling of gels on the initial dilution is more evident with the increasing amount of GMMA in hydrogels and, consequently, with the increasing hydrophilicity of the gels.

A trend similar to that found with HEMA gels was found here; that is, as soon as the gel becomes heterogeneous, the dependency of the water content on the initial dilution deviates from a linear relationship and increases sharply. The slope of copolymer gels with a higher GMMA content shows a tendency to curve up at higher initial dilutions. This tendency may be due to less effective crosslinking at lower polymer concentration.

Both the equilibrium water content and the dependency on the initial dilution (slope of line in Fig. 8) seemed to increase with increasing hydrophilicity. This suggested that (*1*) the swelling of a hydrogel which takes place after the gel formation would increase with the more hydrophilic gels, and (*2*) the isovolumic initial dilution would not be observed when the hydrophilicity of gels reaches a certain degree. These phenomena were indeed found in measurements of volume changes, some of which are shown in Figure 9.

Isovolumic initial dilutions, in which gels are so formed that no further swelling nor deswelling will occur in water, can be estimated from a graph similar to Figure 8 and also from a graph similar to Figure 9. The esti-

TABLE II
Effect of GMMA Content on the Isovolumic Initial Dilution

GMMA in copolymer, %	Isovolumic initial dilution, solvent in monomer solution, %
0	37
10	42
20	46
30	53
40	60
50	61
60	62
70	70[a]
80	70[a]
90	70[a]

[a] Initial dilution with the least volume change.

mated isovolumic initial dilutions obtained by averaging values from the two methods are listed in Table II.

When the amount of GMMA in copolymers reaches about 70%, the isovolumic initial dilution no longer exists and, consequently, the hydrogels always swell after the gel formation is completed. However, even in this range, there seems to be a minimum in volume change dependent upon the initial dilution. Roughly estimated values are also included in Table II.

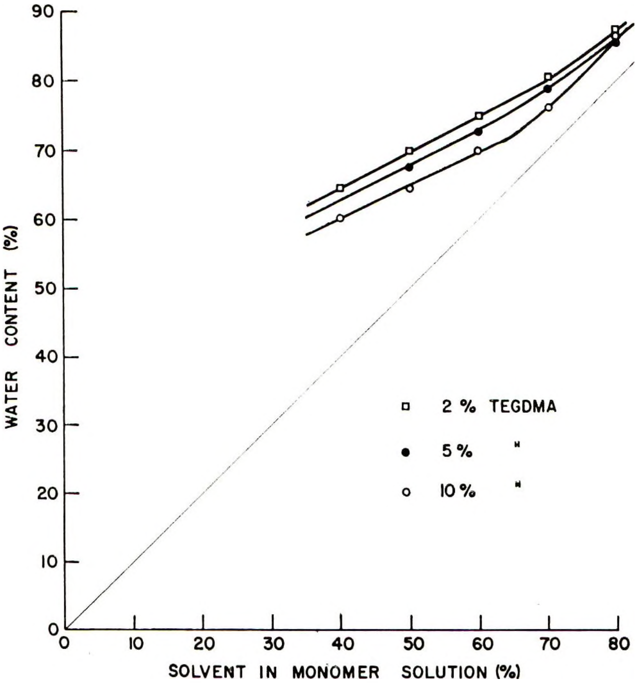

Fig. 10. Effect of crosslinks on the water content of GMMA hydrogels.

Effect of the Amount of Crosslinking Agent

The effect of the number of crosslinks was investigated by using poly(GMMA) hydrogels with 2%, 5%, and 10% TEGDMA as the crosslinking agent in the total monomer. Both the solvent and the concentration of initiators are the same as mentioned in the preceding section. The results are shown in Figure 10.

The crosslinks seem to reduce the swelling of hydrogels without changing the dependency of the water content on the initial dilution (without changing the slopes on Figure 10); however, the overall effect on the equilibrium water content is rather small compared to that of the initial dilution. In this series, there is also a tendency of the slope to go upward at higher dilutions, thus producing no isovolumic initial dilution with these hydrogels.

Permeability of Oxygen through Hydrogels

Since the diffusion constants of oxygen in some polymers are somewhat similar to those of water in polymers,[10] the permeability of oxygen through hydrogels may give us an interesting means of evaluating differences in the structure of various hydrogels. Oxygen permeability can be easily measured without changing hydration of the hydrogels, whereas the direct measurement of water movement in highly hydrated systems such as hydrogels involves many points of argument in the interpretation of the data. Furthermore, oxygen permeability is an important factor when a polymer membrane is used in contact with biological systems.

Oxygen permeability was measured by using a polarographic oxygen sensor, Beckman oxygen analyzer Model 777, and by creating oxygen flow across the hydrogel membrane between air-saturated water and deoxygenated water (purging oxygen by nitrogen gas). Details of this method will be presented in a separate note.

Results with HEMA gels and HEMA–GMMA gels are listed in Tables III and IV, respectively. These permeability values are plotted against the water contents of hydrogels in Figure 11.

TABLE III
Oxygen Permeability of HEMA Hydrogels

Gel[a]	Water content, %	Permeability $P \times 10^{10}$, cc. STP-cm./cm.^{2}-sec.-cm. Hg
A	35.5	160
B	36.7	170
C	38.2	190
D (translucent)	49.9	760
E (opaque)	58.7	2700

[a] Gels: A: 10% solvent (60 water/40 ethylene glycol); B: 30% solvent (40 water/60 ethylene glycol); C: 40% solvent (60 water/40 ethylene glycol); D: 70% solvent (80 water/20 ethylene glycol); E: 80% solvent (80 water/20 ethylene glycol).

Results indicate that the permeation of oxygen molecules through transparent hydrogel membranes is roughly proportional to the water content of the membrane; however, the permeation is much greater in translucent and opaque gels than in transparent gels of similar hydration. This abrupt increase in permeability when a gel becomes translucent or opaque suggests that these gels are not only optically heterogeneous but also that they are macroscopic aggregates of microgels, although within the range of this work, no visible spongy structures were observed.

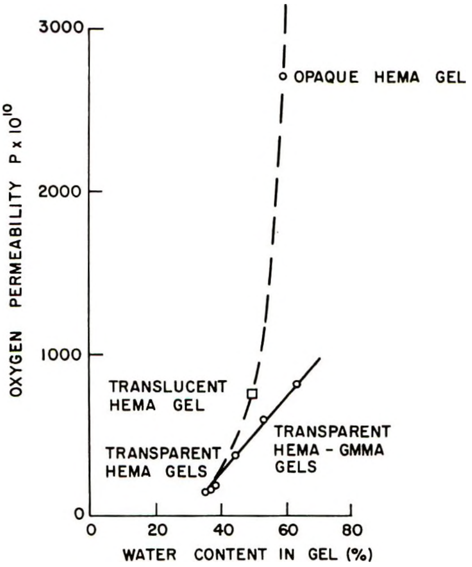

Fig. 11. Effect of water content of hydrogels on the permeability of oxygen.

TABLE IV
Oxygen Permeability of GMMA–HEMA Hydrogels[a]

GMMA in copolymer, %	Water content, %	Permeability $P \times 10^{10}$, cc. STP-cm./cm.^{2}-sec.-cm. Hg
0	39.0	170
20	43.8	380
33	53.0	600
50	63.4	830

[a] All hydrogels were prepared with 50% solvent (90 water/10 ethylene glycol).

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Résumé

Des réseaux (hydrogels) polymériques, tridimentionnels, hydrophiles, ont été préparés au départ de méthacrylate hydroxyéthylique (HEMA) et le copolymère de HEMA et le mono-méthacrylate de glycéryle (GMMA). La teneur en eau à l'équilibre d'hydrogels dans l'eau a été étudiée en fonction de la dilution initiale du mélange de polymérisation, du type de solvant et du caractére hydrophile du polymère. La dilution initiale exerce un effet décisif sur le gonflement et le dégonflement des hydrogels après la formation du gel définitif. Avec des hydrogels relativement moins hydrophiles, il y a une dilution plus critique pour former un gel qui ne gonfle ou qui ne dégonfle pas dans l'eau aprés formation du gel. Cette dilution initiale isovolumique glisse aux hautes dilutions à mesure que le caractère hydrophile de l'hydrogel croît; toutefois lorsque le caractère hydrophile du polymère dépasse un certain point, les gels gonflent toujours gonflés dans l'eau. La perméabilité de l'oxygène au travers de ces hydrogels a également été étudièe.

Zusammenfassung

Hydrophile dreidimensionale Polymernetzwerke (Hydrogele) wurden aus Hydroxyäthylethacrylat (HEMA) und Copolymeren von HEMA und Glycerin-monomethacrylat (GMMA) hergestellt. Der Gleichgewichtswassergehalt der Hydrogele in Wasser wurde als Funktion der Ausgangsverdünnung des Polymerisationsgemisches, des Lösungsmitteltyps und der Hydrophilität des Polymeren untersucht. Die Ausgangsverdünnung besass einen entscheidenden Einfluss auf die Quellung oder Entquellung der Hydrogele nach Vollendung der Gelbildung. Bei verhältnismässig schwach hydrophilen Hydrogelen besteht eine kritische Ausgangsverdünnung für die Bildung eines Gels, welches nach der Gelbildung in Wasser weder quillt noch entquillt. Diese "Isovolums"-Anfangsverdünnung verschiebt sich mit steigender Hydrophilität der Hydrogele zu einer höheren Verdünnung; wenn jedoch die Hydrophilität des Polymeren über einen gewissen Wert ansteigt, quellen die Gele immer in Wasser. Schliesslich wurde auch die Permeabilität der Hydrogele für Sauerstoff untersucht.

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Polymerization of Butadiene Sulfone

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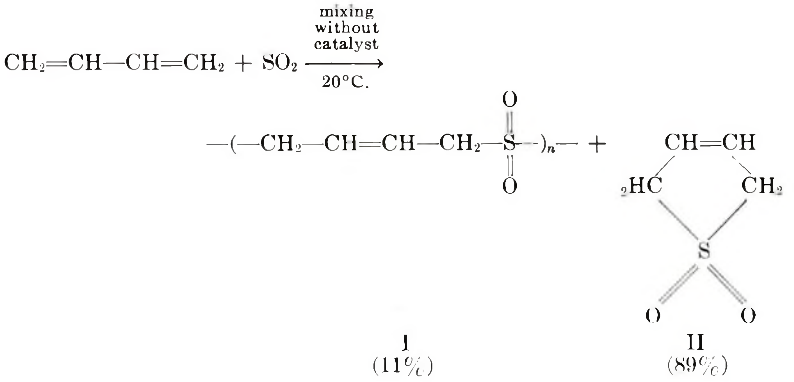
Synopsis

Polymerization of butadiene sulfone ($BdSO_2$) by various catalysts was studied. Azobisisobutyronitrile (AIBN), butyllithium, tri-*n*-butylboron $(n\text{-}Bu)_3B$, boron trifluoride etherate, Ziegler catalyst, and γ-radiation were used as catalysts. Butadiene sulfone did not polymerize with these catalysts at low temperatures (below 60°C.), but polymers were obtained at high temperature with AIBN or $(n\text{-}Bu)_3B$. The polymerization of $BdSO_2$ initiated by AIBN in benzene at 80–140°C. was studied in detail. The obtained polymers were white, rubberlike materials and insoluble in organic solvents. The polymer composition was independent of monomer and initiator concentrations and reaction time. The sulfur content in polymer decreased with increasing polymerization temperature. The polymers prepared at 80 and 140°C. have the compositions $(C_4H_6)_{1.55}$-(SO_2) and $(C_4H_6)_{3.14}(SO_2)$, respectively, and have double bonds. These polymers were not alternating copolymers of butadiene with sulfur dioxide. The polymerization mechanism was discussed from polymerization rate, polymer composition, and decomposition rate of $BdSO_2$. From these results, the polymerization was thought to be "decomposition polymerization," i.e., butadiene and sulfur dioxide, formed by the thermal decomposition of $BdSO_2$, copolymerized.

INTRODUCTION

The preparation of polysulfones by the reaction of sulfur dioxide with olefins has been studied recently.[1–5] Previously, it was reported by Harries,[6] and Ostromuislenskii[7] that the reaction of sulfur dioxide and unsaturated hydrocarbons having conjugated double bonds produced amorphous adducts and crystalline ones. Staudinger described the reaction products from sulfur dioxide and unsaturated hydrocarbons of the butadiene type.[8] He recognized the crystalline product to be a cyclic monosulfone and the amorphous one to be a linear polysulfone, and proposed the reaction for sulfur dioxide and butadiene shown in eq. (1) (see following page).

It is known that the cyclic monosulfones from sulfur dioxide and conjugated dienes decomposed into the original unsaturated hydrocarbons and sulfur dioxide at elevated temperatures. Butadiene sulfone (II) is a colorless crystal and its melting point is 64.5°C. It undergoes addition reactions at the double bond. These include the addition of halogens and halogenated compounds,[9,10] addition of amines,[11,12] addition of mercaptans,[13,14] hydroxylation,[8,15] and hydrogenation,[15,16] but there is no report on its polymerization. It would be of interest to know if it polymerizes,



(1)

whether the polymerization proceeds by the double bond or by ring-opening polymerization.

We have studied the polymerization of butadiene sulfone ($BdSO_2$). The polymerization of $BdSO_2$ was carried out by using azobisisobutyronitrile, (AIBN), butyllithium (BuLi), boron trifluoride etherate ($BF_3 \cdot OEt_2$), tri-*n*-butylboron ($(n\text{-}Bu)_3B$), and Ziegler type catalyst; γ-radiation was also used for the initiation. No polymer was obtained with BuLi, $BF_3 \cdot OEt_2$, $(n\text{-}Bu)_3B$, Ziegler type catalysts, or γ-rays below room temperature. Polymers were prepared in the radical polymerization with AIBN or $(n\text{-}Bu)_3B$ at temperatures above 70°C. The polymers contained the sulfonyl group, and the sulfur content of the polymer decreased as the reaction temperature increased.

It was found that butadiene and sulfur dioxide formed by the thermal decomposition of $BdSO_2$, copolymerized. Polymerization of this type was named decomposition polymerization.

EXPERIMENTAL

Preparation of Butadiene Sulfone

In preparation of butadiene sulfone,[17] butadiene and sulfur dioxide (molar ratio, 1/2) were allowed to react at 100°C. for 12 hr. in a steel bomb together with 1% hydroquinone with respect to the butadiene. The crude sulfone was purified by recrystallization from methanol, m.p. 64.5–65.5°C.

ANAL. Calc. for $C_4H_5SO_2$: C, 40.7%; H, 5.1%; S, 27.1%. Found: C, 40.8%; H, 5.0%; S, 27.2%.

Catalysts

Azobisisobutyronitrile was purified by recrystallization from anhydrous methanol. Boron trifluoride etherate was distilled under nitrogen atmosphere. The fraction boiling in the range 125–126°C. was collected. Butyllithium was used as a solution in *n*-heptane, and its concentration was 1.2 mole/l. Tri-*n*-butylboron was prepared by the following method.[18]

A Grignard reagent was obtained by dropwise addition of *n*-butyl bromide on the magnesium ribbon in ether; then boron trifluoride etherate was also added dropwise. The reaction mixture then was refluxed for 2 hr., and distilled under nitrogen pressure of 25 mm. Hg, and the fraction boiling in the range 110–117°C. was collected.

Polymerization Procedure

The homopolymerizations of $BdSO_2$ with AIBN, BuLi, and $(n\text{-Bu})_3B$ were carried out in benzene in sealed tubes. The solution of $BdSO_2$ and catalyst was in the reaction tubes and the mixture was degassed by three freeze–thaw cycles under nitrogen, then the tubes were sealed under reduced pressure. In the radical polymerization of $BdSO_2$ at high temperatures, because of the high monomer concentrations, the monomer was not completely soluble in benzene at room temperature. $BdSO_2$ was placed in the reaction tubes directly, and then benzene and the benzene solution of AIBN were added. The tubes were sealed by the same procedure as above. The sealed tubes were allowed to stand at the required temperatures. After the polymerization, the contents were poured into methanol to terminate the reaction and to precipitate the polymer.

The polymerizations of $BdSO_2$ by Ziegler catalysts, e.g., $Et_3Al\text{–}TiCl_3$ and $Et_3Al\text{–}TiCl_3$ were carried out in *n*-heptane under a nitrogen atmosphere at room temperature. Et_3Al was added first to *n*-heptane and mixed thoroughly, and $TiCl_4$ or $TiCl_3$ was then added. A brown solid was formed. After 10 min. standing, the *n*-heptane solution of $BdSO_2$ was added. The polymerization was stopped by adding of 2 ml. methanol and 0.3 ml. of concentrated hydrochloric acid and then pouring the reaction mixture into methanol.

The γ-ray irradiation of $BdSO_2$ was carried out in water, tetrahydrofuran, and benzene solution, and also in bulk at room temperature. The radiation source was ^{60}Co.

Analysis of Sulfur in Polymer

The sulfur content of the polymer was determined by Schöniger method.[19]

RESULTS AND DISCUSSION

Polymerizability of $BdSO_2$

Many kinds of catalysts (BuLi, $BF_3\cdot OEt_2$, AIBN, Ziegler catalysts, and γ-rays) have been used for the polymerization of $BdSO_2$. The results are shown in Table I. In the polymerization with BuLi, $BF_3\cdot OEt_2$, $(n\text{-Bu})_3B$, Ziegler catalysts, and γ-rays at below room temperature, no polymer was obtained. When AIBN was used as an initiator, traces of polymer were obtained at 50°C. and 0.0395 g. (1.3 wt.-%) at 70°C. $(n\text{-Bu})_3B$ also gave 0.0301 g. (1.5 wt.-%) of polymer at 80°C. Elemental analysis of the polymer prepared by AIBN at 70°C. gave C, 48.6%; H, 6.1%; S, 21.9%.

TABLE I
Polymerizability of $BdSO_2$

Catalyst	Catalyst concn., mole/l.	$BdSO_2$ concn., mole/l.	Temp., °C.	Time, hr.	Solvent	Polymer yield, g.
AIBN	5.0×10^{-2}	1.69	50	144	Benzene	Trace
AIBN	5.0×10^{-2}	2.54	70	187	Benzene	0.0395
$(n\text{-Bu})_3B$	2.75×10^{-1}	1.69	Room temp.	100	Benzene	0
$(n\text{-Bu})_3B$	2.75×10^{-1}	1.69	80	140	Benzene	0.0301
BuLi	6.0×10^{-2}	1.69	Room temp.	100	Benzene THF	0
BF_3OEt_2	3.96×10^{-1}	1.69	Room temp.	100	Benzene	0
$AlEt_3$–$TiCl_4$[a]	5.93×10^{-2}	0.282	30	5	n-Heptane	0
$AlEt_3$–$TiCl_3$[b]	5.30×10^{-2}	0.423	30	5	n-Heptane	0
γ-Radiation	[c]	1.69	20	25	Water	0
"	[c]	1.69	20	25	Benzene	0
"	[c]	1.69	20	25	THF	0
"	[c]	Bulk	20	25	None	0

[a] Al/Ti = 2.0. Catalyst concentration given as moles Ti/l.

[b] Al/Ti = 3.4. Catalyst concn.

[c] Dose rate 5.08×10^4 r/hr.

From these values, the polymer composition was $(C_4H_6)_{1.48}(SO_2)_1$. This indicates that the reaction mechanism involves formation of butadiene and sulfur dioxide by the thermal decomposition of $BdSO_2$, followed by their copolymerization.

Radical Polymerization of $BdSO_2$ at High Temperature

Polymerizations of $BdSO_2$ were carried out in sealed tubes at 80, 100, 120, and 140°C. by AIBN. The concentrations of $BdSO_2$ and AIBN were 3.02 and 3.57×10^{-2} mole/l., respectively. In this case, $BdSO_2$ was not completely soluble in benzene at room temperature, so $BdSO_2$ was placed in the reaction tube directly, and then benzene and the benzene solution of AIBN were added. The monomer concentration was determined from the total volume at 80°C. The results of the polymerization and the analyses of the polymers are shown in Table II. Plots of conversion against time are given in Figure 1. Polymers precipitated during the reaction. They were rubberlike materials, and the polymer prepared at 140°C. became hard drying. All polymers were white, but when left to stand in air for several days, they became brown and harder.

The polymers were insoluble in organic solvents and decomposed before softening at 150°C. on heating.

Plots of the sulfur content of polymer against the reaction time from Table II, are shown in Figure 2. It indicates that the sulfur content in polymer is independent of the reaction time.

TABLE II
Polymerization of $BdSO_2$ at High Temperature[a]

Temp., °C.	Polymerization time, hr.	Polymer yield, g.	Conversion, %	Analysis		
				C, %	H, %	S, %
80	150	0.0482	1.0	50.24	6.82	21.76
	250	0.0645	1.3	—	—	21.39
	300	0.0560	1.1	—	—	21.62
100	150	0.0790	1.6	54.20	6.85	19.72
	250	0.1465	2.9	—	—	20.15
	300	0.1351	2.7	—	—	19.98
120	106	0.2292	4.6	—	—	16.79
	200	0.2976	6.0	57.17	7.72	16.48
	253	0.2661	5.3	—	—	16.85
140	80	0.3237	6.5	64.06	8.35	13.69
	140	0.3834	7.7	—	—	13.50
	210	0.3606	7.2	64.20	8.56	13.87

[a] Polymerization conditions: $[BdSO_2] = 3.02$ mole/l., $[AIBN] = 3.57 \times 10^{-2}$ mole/l., in benzene.

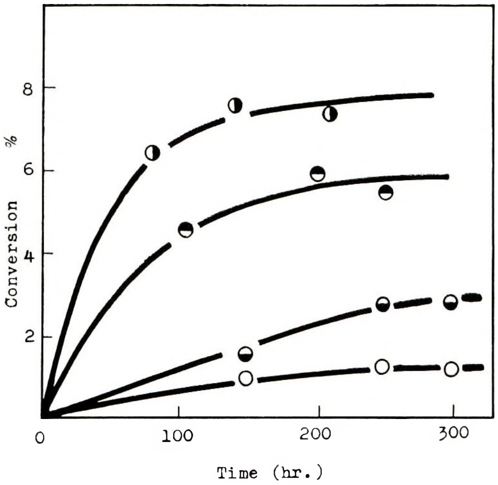


Fig. 1. Time-conversion curves for polymerization of $BdSO_2$ in benzene at various temperatures: (○) 80°C.; (◒) 100°C.; (◓) 120°C.; (◑) 140°C. $[BdSO_2] = 3.02$ mole/l.; $[AIBN] = 3.57 \times 10^{-2}$ mole/l.

Infrared Spectra of Polymers

In Figure 3, infrared spectra of $BdSO_2$ and the polymers prepared at 70, 100, and 140°C. are shown. All the spectra have strong absorption bands due to sulfone at 1110 and 1300 cm.$^{-1}$. The spectrum of the polymer prepared at 70°C. has absorption bands due to the C=C double bond at 1670, 1640, 980, and 730 cm.$^{-1}$. The absorption bands at 730 and 970 cm.$^{-1}$ are characteristic absorptions of *cis* and *trans* double bonds, respectively.

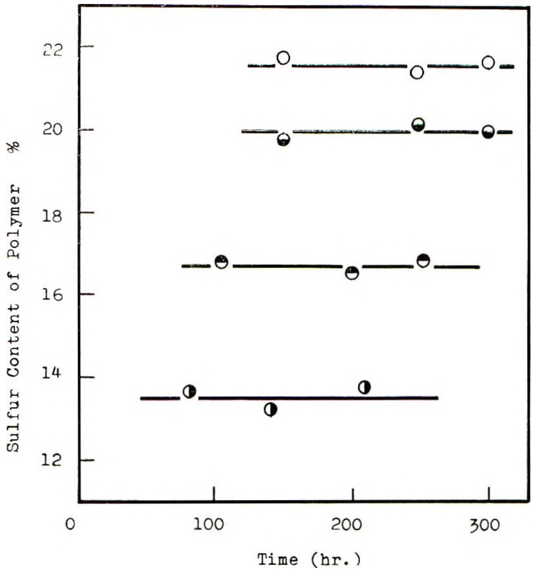


Fig. 2. Effect of polymerization time on sulfur content of polymer: (○) 80°C.; (◒) 100°C.; (◓) 120°C.; (◑) 140°C.

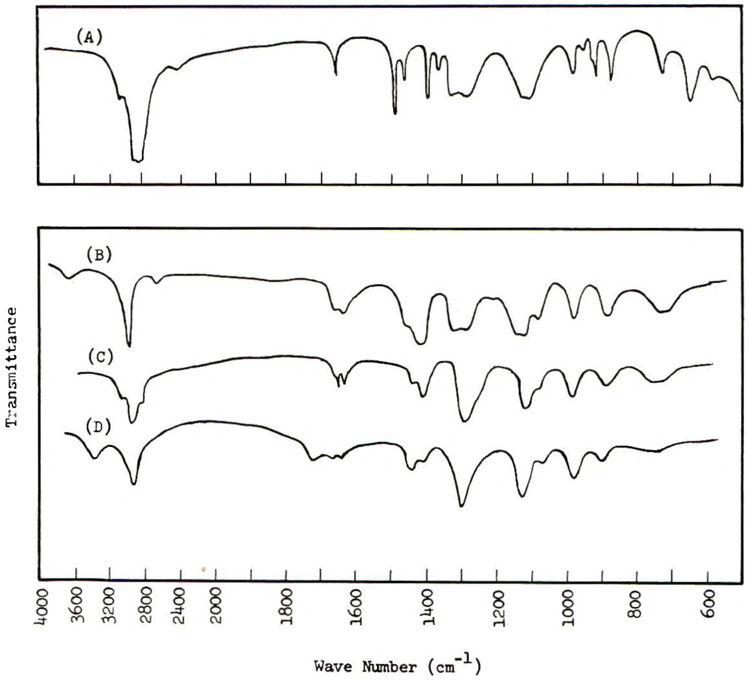


Fig. 3. Infrared spectra of (*A*) $BdSO_2$ and polymers obtained at various temperatures: (*B*) 70°C.; (*C*) 100°C.; (*D*) 140°C.

The spectra of the polymers obtained at 100 and 140°C. also have the bands due to C=C double bond, and both *cis* and *trans* double bonds are present. But in the spectrum of the 140°C. polymer (Fig. 3*D*), the band due to the *cis* double bond at 730 cm.$^{-1}$ is very weak. The band at 1640 cm.$^{-1}$ is probably attributable to the pendent double bond. All the spectra have absorptions at 1640 cm.$^{-1}$ However, the absorption due to $=CH_2$ at 3030 cm.$^{-1}$ is not clear, and it is not certain whether the pendent double bond is present.

The presence of the C=C double bond in the polymer shows that the polymerization by the double bond of $BdSO_2$ did not occur. If $BdSO_2$ was polymerized by ring opening, the ratio of butadiene and sulfur dioxide in the polymer should be unity, but the sulfone content in polymer decreased with increasing reaction temperature. If sulfur dioxide were eliminated from the polymer of $BdSO_2$, $—C_4H_6SO_2—_n$ formed by the ring opening, the sulfur content in the polymer would decrease with increasing reaction time. Therefore, this hypothesis is excluded. It is concluded, therefore, that the ring-opening polymerization did not occur.

It is known that butadiene and sulfur dioxide are formed by the thermal decomposition of $BdSO_2$.[20] A suitable mechanism would thus be the formation of butadiene and sulfur dioxide are by the thermal decomposition of $BdSO_2$ and subsequent copolymerization.

Sulfur Content of the Polymer

Effect of Monomer Concentration. The polymerization of $BdSO_2$ was carried out in benzene at 80°C. at an AIBN concentration of 3.57×10^{-2} mole/l. and various $BdSO_2$ concentrations: 1.21, 1.81, 2.42, and 3.02 mole/l. The results are shown in Table III. The sulfur content is independent of $BdSO_2$ concentration, but the rate of polymerization increases with increasing $BdSO_2$ concentration.

Effect of AIBN Concentration. The polymerization of $BdSO_2$ was carried out at 100°C. at a $BdSO_2$ concentration of 3.02 mole/l. and various AIBN concentrations: 1.79×10^{-2}, 3.57×10^{-2}, 5.36×10^{-2}, and 7.14×10^{-2} mole/l. The results are shown in Table IV. The sulfur

TABLE III

Effect of $BdSO_2$ Concentration on Polymerization Rate and Sulfur Content in Polymer[a]

$BdSO_2$, mole/l.	Polymer yield, g.[b]	Conversion, %[b]	R_p, g./l.-hr. $\times 10^2$	Sulfur content in polymer, %
1.12	0.0129	0.65	0.971	21.71
1.81	0.0214	0.71	1.607	21.32
2.42	0.0334	0.84	2.514	21.04
3.02	0.0329	0.66	2.471	21.85

[a] Polymerization conditions: [AIBN] = 3.57×10^{-2} mole/l., in benzene, 80°C.

[b] Obtained at 96 hr.

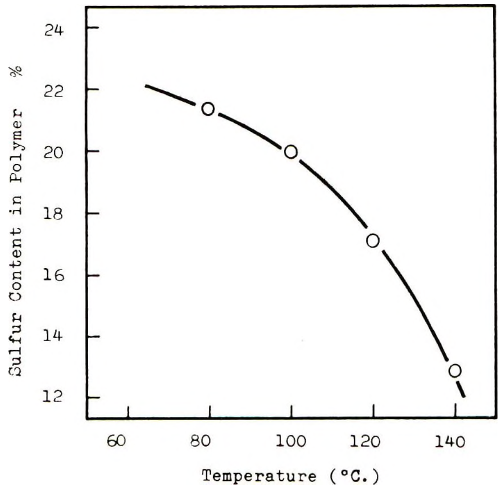


Fig. 4. Effect of polymerization temperature on sulfur content of polymer. $[BdSO_2]$ = 3.02 mole/l., [AIBN] = 3.57 × 10^{-2} mole/l.

content of polymer is also independent of AIBN concentration, and the rate of polymerization increases with increasing AIBN concentration.

Effect of Reaction Temperature. Figure 4 shows the relation between the sulfur content in polymer and reaction temperature. The sulfur content decreases with increasing reaction temperature.

TABLE IV

Effect of AIBN Concentration on Polymerization Rate and Polymer Composition

[AIBN], mole/l. × 10^2	Polymer yield, g.[b]	Conversion, %[b]	R_p, g./l.-hr. × 10^2	Analysis		
				C, %	H, %	S, %
1.79	0.0938	1.88	4.464	54.38	6.85	19.76
3.57	0.1235	2.47	5.857	54.11	6.15	19.62
5.36	0.1544	3.09	7.350	54.13	6.72	19.87
7.14	0.1971	3.96	9.386	54.40	6.64	19.90

[a] Polymerization conditions: $[BdSO_2]$ = 3.02 mole/l., in benzene, 100°C.

[b] Obtained at 150 hr.

TABLE V

Effect of Temperature on Polymer Composition

Temp., °C.	Polymer composition	Calculated			Found		
		C, %	H, %	S, %	C, %	H, %	S, %
80	$(C_4H_6)_{1.55}(SO_2)_1$	50.41	6.29	21.65	50.24	6.82	21.59
100	$(C_4H_6)_{1.83}(SO_2)_1$	53.96	6.74	19.64	54.20	6.85	19.95
120	$(C_4H_6)_{2.30}(SO_2)_1$	58.66	7.33	17.00	57.15	7.72	16.70
140	$(C_4H_6)_{3.14}(SO_2)_1$	64.55	8.05	13.70	64.06	8.35	13.54

Thus, the sulfur content in polymer is independent of the reaction time and the monomer and AIBN concentrations and is dependent on only reaction temperature.

The results of analysis of the polymers give the polymer compositions at each temperature shown in Table V. The polymer compositions are; $(C_4H_6)_{1.55}\ (SO_2)_1$ at 80°C., $(C_4H_6)_{1.83}\ (SO_2)_1$ at 100°C., $(C_4H_6)_{2.30}\ (SO_2)_1$ at 120°C., and $(C_4H_6)_{3.14}\ (SO_2)_1$ at 140°C.

Activation Energy of Polymerization

Arrhenius plots of initial polymerization rate against the reciprocal of temperature are shown in Figure 5. The slope of the line shows the overall activation energy of the polymerization to be 15.5 kcal./mole.

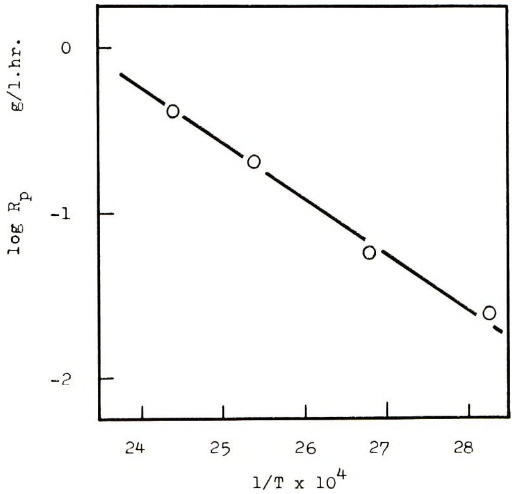


Fig. 5. Relation between logarithm of polymerization rate R_p and reciprocal temperature $[BdSO_2] = 3.02$ mole/l., $[AIBN] = 3.57 \times 10^{-2}$ mole/l.

Polymerization Rate Equation

From the data of Table IV, the effect of initiator concentration on the polymerization rate at 100°C. is shown in Figure 6, and the experimental points are well represented by a straight line of slope 1/2.

The effect of monomer concentration on the polymerization rate is shown in Figure 7, and the slope of the straight line is 1.

From the above results, the polymerization rate is shown to follow eq. (2):

$$R = k[AIBN]^{1/2}[BdSO_2] \tag{2}$$

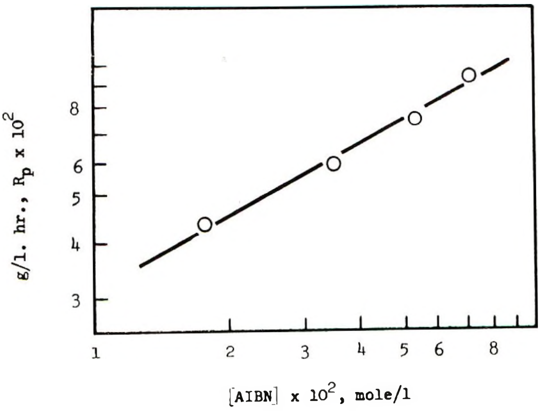


Fig. 6. Polymerization rate at 100°C. vs. concentration of AIBN at constant monomer concentration of 3.02 mole/l.

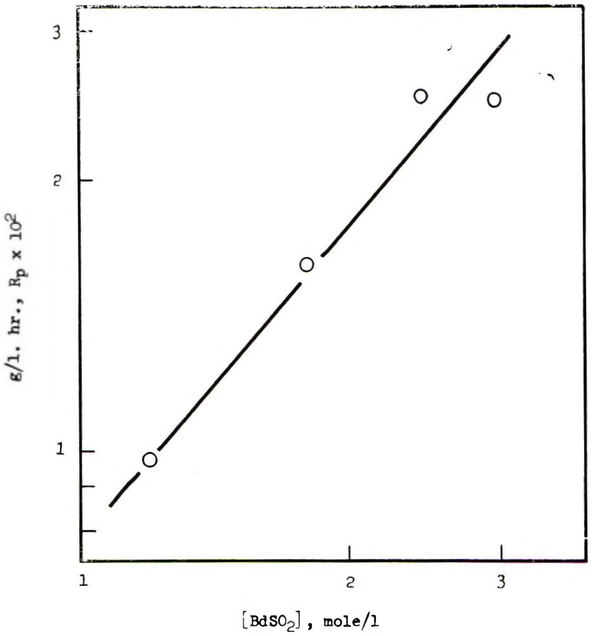


Fig. 7. Polymerization rate at 80°C. vs. concentration of $BdSO_2$ at constant AIBN concentration of 3.57×10^{-2} mole/l.

Thermal Decomposition of $BdSO_2$

The formation of butadiene and sulfur dioxide by the thermal decomposition of $BdSO_2$ has already been reported.[20] The decomposition rates were determined as follows.

$BdSO_2$ and benzene were placed in sealed tubes by the same procedure as in the polymerization of $BdSO_2$ without catalyst. The sealed tubes were allowed to stand at the required temperatures. Then the contents

TABLE VI
Thermal Decomposition of $BdSO_2$

Temp., °C.	[$BdSO_2$], mole/l.	Heating time, hr.	Decomposition weight	
			g.	wt.-%
80	3.02	0	0.1137	2.27
	3.02	2	0.1610	3.22
	3.02	5	0.4412	8.82
	3.02	19	0.8286	16.57
	3.02	50	1.2363	24.73
	3.02	100	1.6960	33.92
	1.21	19	0.4851	24.25
	1.81	19	0.5723	18.75
	2.42	19	0.7021	17.55
100	3.02	2	1.1048	22.09
	3.02	5	1.9081	38.16
120	3.02	2/3	1.2805	25.61
	3.02	2	3.1203	62.40
	3.02	5	3.3800	67.60

were poured into methanol to show the formation of polymers. No polymer formed at 80°C., and traces of polymeric materials were obtained at 100 and 120°C.; however, the quantity was so small that the thermal polymerization is negligible.

After removing benzene and methanol, the weight loss of $BdSO_2$ was measured from the amounts decomposed. The results are shown in Table VI.

The result obtained without heating, shown in Table VI, indicated that a weight loss took place without heating. This weight loss might be due

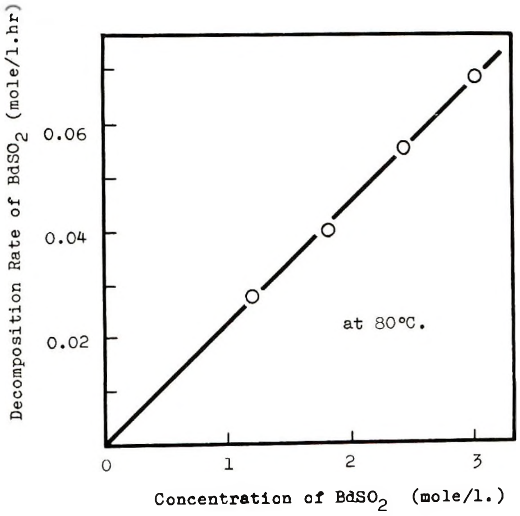


Fig. 8. Decomposition rate vs. concentration of $BdSO_2$.

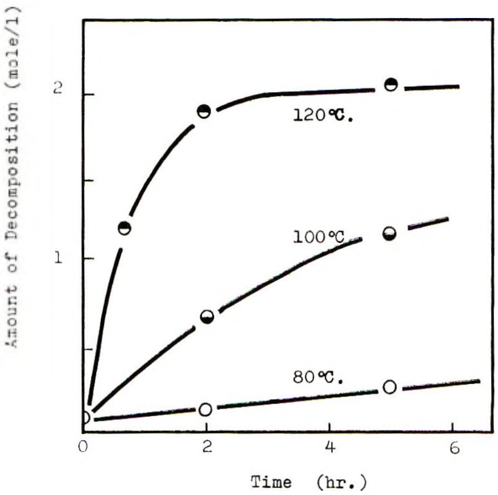


Fig. 9. Time–decomposition curves of $BdSO_2$ in benzene at various temperatures. $[BdSO_2] = 3.02$ mole/l.

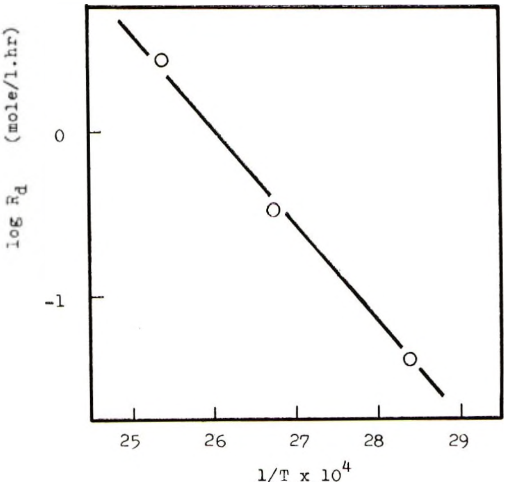


Fig. 10. Relation between logarithm of decomposition rate R_d and reciprocal temperature.

to experimental errors. The relationship between the $BdSO_2$ concentration and the decomposition rate at 80°C. is shown in Figure 8.

The decomposition rate is proportional to the $BdSO_2$ concentration. The plots of the decomposition rate of $BdSO_2$ at various temperatures: 80, 100, and 120°C., are shown in Figure 9. The plots of the initial decomposition rate at each temperature against the reciprocal of temperature are shown in Figure 10. The slope of the straight line shows the activation energy of decomposition of $BdSO_2$ to be 15.3 kcal./mole.

Mechanism of Polymerization of $BdSO_2$

The decomposition polymerization scheme is shown in eqs. (3)–(13).

Initiation:

$$BdSO_2 \rightleftharpoons B + S \tag{3}$$

$$AIBN \rightarrow 2R\cdot \tag{4}$$

$$R\cdot + S \rightarrow S\cdot \tag{5}$$

$$R\cdot + B \rightarrow B\cdot \tag{6}$$

Propagation:

$$B\cdot + B \xrightarrow{k_{11}} B\cdot \tag{7}$$

$$B\cdot + S \xrightarrow{k_{12}} S\cdot \tag{8}$$

$$S\cdot + B \xrightarrow{k_{21}} B\cdot \tag{9}$$

$$S\cdot + S \xrightarrow{k_{22}} S\cdot \tag{10}$$

Termination:

$$B\cdot + B\cdot \rightarrow P \tag{11}$$

$$B\cdot + S\cdot \rightarrow P \tag{12}$$

$$S\cdot + S\cdot \rightarrow P \tag{13}$$

Here B, S, and P represent butadiene, sulfur dioxide, and polymer, respectively, and B· and S· are propagating chain ends having the butadiene and sulfonyl radicals, respectively. The addition of sulfur dioxide to the sulfonyl radical is negligible, therefore k_{22} may be regarded as zero.

The monomer reactivity ratios r_1, r_2 are defined as $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$. The equation for copolymer composition in the copolymerization is given by eq. (14).

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1([M_1]/[M_2]) + 1}{([M_1]/[M_2]) + r_2} \tag{14}$$

Because k_{22} is zero, r_2 is zero. Butadiene and sulfur dioxide are produced by the thermal decomposition of $BdSO_2$, so the initial concentrations of butadiene and sulfur dioxide are equal; therefore, $[M_1]/[M_2] = 1$. From eq. (14),

$$d[M_1]/d[M_2] = 1 + r_1$$

From the polymer composition shown in Table VI, we can obtain the apparent reactivity ratio, r_1.

At 80°C., $(C_4H_6)_{1.55}(SO_2)_1$:

$$d[M_1]/d[M_2] = 1.55 = 1 + r_1$$

$$r_1 = 0.55$$

At 100°C., $(C_4H_6)_{1.83}(SO_2)_1$:

$$1 + r_1 = 1.83$$
$$r_1 = 0.83$$

At 120°C., $(C_4H_6)_{2.28}(SO_2)_1$:

$$1 + r_1 = 2.28$$
$$r_1 = 1.28$$

At 140°C., $(C_4H_6)_{3.14}(SO_2)_1$:

$$1 + r_1 = 3.14$$
$$r_1 = 2.14$$

The reactivity ratio r_1 increases with the temperature rise. This is probably due to the difference in the temperature dependencies of the rates of additions of butadine and of sulfur dioxide to the butadiene radical of the growing chain end, i.e., the difference in the energies of activation of the addition reaction. In other words, with increasing temperature, the increase in the rate of addition of butadiene to the butadiene radical, is probably greater than that of sulfur dioxide.

Therefore, with decreasing temperature, the rate of the alternating propagation increases relatively. Finally, r_2 approaches zero. In this case, an alternating copolymer is obtained. In fact, copolymerization of butadiene with sulfur dioxide at low temperatures have given alternating. copolymers.[8,21] Now, r_1 is k_{11}/k_{12}, so $\ln r_1 = \ln (k_{11}/k_{12}) = \ln k_{11} - \ln k_{12}$. k_{11} and k_{12} are represented as follows:

$$k_{12} = A_{12}e^{-E_{12}/RT}$$

$$\text{Therefore } \ln r_1 = \ln k_{11} - \ln k_{12}$$
$$= \ln (A_{11}/A_{12}) - (E_{11} - E_{12})/RT$$

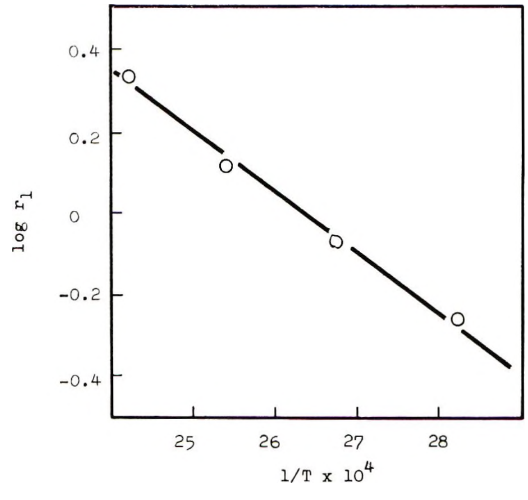


Fig. 11. Relation between log r_1 and reciprocal temperature.

Here, E_{11} and E_{12} are the activation energies of the addition of butadiene and sulfur dioxide to the butadiene radical of propagating chain end, respectively.

Figure 11 shows the plots of logarithm of r_1 against the reciprocal of temperature. The slope of the straight line shows the difference of activation energy E_{11} and E_{12}:

$$E_{11} - E_{12} = 6.8 \text{ kcal./mole}$$

It can be concluded in radical polymerization of $BdSO_2$ at high temperatures that butadiene and sulfur dioxide are formed by the thermal decomposition of $BdSO_2$, and then that this decomposition is followed by copolymerization of the products. The polymer compositions are independent of the reaction times and the concentrations of monomer and initiator, and are dependent on only the polymerization temperature. The polymer compositions are determined by the ratio of addition rate of butadiene and sulfur dioxide to the butadiene radical of growing chain end, and this ratio is dependent on the reaction temperature. The concentrations of monomer and initiator influence the polymerization rates, but not the polymer compositions.

We wish to thank Dr. A. Kogure and T. Suminoe of Japan Synthetic Rubber Co., Ltd. for their support in the preparation of $BdSO_2$.

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Résumé

La polymérisation de butadiène-sulfone (BdSO$_2$) en présence de différents catalyseurs a été étudiée. L'azobisisobutyronitrile (AIBN), le butyllithium, le bore- tri-*n*-butyle (n-Bu)$_3$B, le complexe etheré du trifluorure de bore, les catalyseurs de Ziegler et les rayons-γ ont été utilisés comme catalyseurs. La butadiène-sulfone ne polymérise pas par ces catalyseurs à basse température c.à.d. en-dessous de 60°C. Toutefois, des polymères ont été obtenus à des températures plus élevées en présence de AIBN ou de tributyl-bore. La polymérisation de BdSO$_2$ initiée par AIBN dans le benzène à 80–140°C a été étudiée en detail. Les polymères obtenus sont des matériaux caoutchouteux blancs insolubles dans les solvants organiques. La composition du polymère est indépendante des concentrations en monomère, initiateur et de la durée de réaction. La teneur en soufre du polymère décroît avec une température croissante de polymérisation. Les polymères préparés à 80°C et à 140°C étaient composés de $(C_4H_6)_{1.55}(SO_2)$ et $(C_4H_6)_{3.14}(SO_2)$ respectivement et présentent des doubles liaisons. Ces polymères ne sont pas des copolymères alternant de butadiène et de dioxyde de soufre. Le mécanisme de polymérisation a été discuté au départ des vitesses de polymérisation, de la composition du polymère et de la vitesse de décomposition de BdSO$_2$. Au départ de ces résultats on admet une polymérisation dénommée polymérisation par décomposition, c.à.d. que le butadiène et le dioxyde de soufre produit par décomposition thermique de la butadiène sulfone copolymérisent ultérieurement.

Zusammenfassung

Die Polymerisation von Butadiensulfon (BdSO$_2$) durch verschiedene Katalysatoren wyrde untersucht. Azobisisobutyronitril (AIBN), Butyllithium, Tri-*n*-butylbor (n-Bu)$_3$B, Bortrifluoridätherat, Zieglerkatalysatoren und Gammastrahlen wurden als Katalysatoren verivendet. Butadiensulfon polymerisierte mit diesen Katalysatoren bei niedrigen Temperaturen (unterhalb 60°C) nicht. Nur mit AIBN oder (n-Bu)$_3$B wurden bei höherer Temperatur Polymere erhalten. Die mit AIBN gestartete Polymerisation von BdSO$_2$ in Benzol wurde bei 80–140°C genau untersucht. Die erhaltenen Polymeren bildeten weisse kautschukartige und in organischen Lösungsmitteln unlösliche Stoffe. Die Polymerzusammensetzung war von Monomer-und Starterkonzentration sowie von der Reaktionsdauer unabhängig. Der Schwefelgehalt des polymeren nahm mit steigender Polymerisationstemperatur ab. Die bei 80 und 140°C dargestellten Polymeren entsprachen der Zusammensetzung $(C_4H_6)_{1,55}(SO_2)$ bzw. $(C_4H_6)_{3.14}\cdot(SO_2)$ und besassen Doppelbindungen. Sie waren keine alternierenden Copolymeren aus Butadien und Schwefeldioxyd. Der Polymerisationsmechanismus wurde auf Grund der Polymerisationsgeschwindigkeit, der Polymerzusammensetzung und de Zersetzungsgeschwindigkeit von BdSO$_2$ diskutiert. Die Ergebnisse lassen die Polymerisation als eine "Zersetzungspolymerisation" erscheinen, d.h. das durch die thermische Zersetzung von BdSO$_2$ gebildete Butadien und Schwefeldioxyd kopolymerisieren.

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Acid–Base Properties of Ion-Exchange Resins. Dissociation and Swelling of Resin Copolymers of Methacrylic Acid, Methyl Methacrylate, Divinylbenzene, and Ethylvinylbenzene

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Synopsis

The dissociation, capacity, swelling, and water content of crosslinked methacrylic acid–methyl methacrylate resins have been measured. Resins were prepared with different degrees of crosslinking for the same carboxylate content, and vice versa. The ionic strength of the external solution was also varied, and the behavior of commercial resins compared with that of the laboratory resins. Potentiometric titration curves were obtained, and curves were also obtained by back-titration of the salt form of the resins with acid. The capacities showed that almost all carboxyl groups are accessible in resins containing 2.5% or 4.0% divinylbenzene, but not in those containing 8% or 12%. For these highly crosslinked resins the back-titration curves differed from the forward curves. Apparent dissociation constants $pK'_a = \text{pH} + n \log [(1 - \alpha)/\alpha]$ decreased with increased ionic strength, increased with increased crosslinking, and showed no trend with carboxylate content. Swelling is decreased by increased salt concentration, particularly for lightly crosslinked resins. Maximum swelling is achieved at about 80% dissociation. The reciprocal of the swollen volume is proportional to the per cent of divinylbenzene. Commercial resins showed much lower swelling than laboratory prepared resins ostensibly having the same composition. The Gibbs-Donnan theory of resin dissociation was applied to calculate the intrinsic dissociation constant ($\text{p}K'_0$). Assuming a model of randomly kinked chains dissolved in the sorbed solution, good agreement with the expected value of 4.85 was found (calcd. $\text{p}K'_0 = 4.81 \pm 0.14$), except for the most highly crosslinked resins. For polyampholyte resins, agreement was found by using a model having a uniform potential distribution throughout the resin ($\text{p}K'_0 = 4.9$).

INTRODUCTION

This paper describes an experimental study of the acid–base titration, together with determinations of capacity, swelling, and water content, of several different types of resin all based on methacrylic acid. The intention was to obtain these data on a number of groups of resins, keeping constant within each group all the factors save one which influence the properties of the resin. The factors studied were: (*1*) degree of crosslinking;

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(*2*) carboxylate content; (*3*) ionic strength of the solution; (*4*) source of the resin.

Much of the work published on the acid–base properties of weakly acidic ion-exchange resins is either qualitative in nature or has been restricted to resins with different degrees of crosslinking, in which the carboxylate content was allowed to vary also. Gregor and co-workers[1–6] investigated the titration, capacity, and swelling of a series of acrylate and methacrylate resins having different degrees of crosslinking, in the presence of different monovalent cations. The absorptive capacities and the apparent ionization constants K'_a decreased, and the specific volumes increased, with increased size of the cation (excluding hydration shells). The acid strength of the resins was found to decrease with increased crosslinking and to increase with increased ionic strength. Fisher and Kunin[7] obtained similar results and observed that the nature of the crosslinking agent and its monovinyl diluent has little if any effect. Using two very lightly crosslinked methacrylate gels, Michaeli and Katchalsky[8] made a detailed study of the effect of the external pH on the swelling, electrolyte absorption and degree of ionization, and interpreted the results using polyelectrolyte theory. Kuhn et al.[9] applied this theory to their results on polyacrylate gels, although Howe and Kitchener[10] had found the statistical theory of polyelectrolyte gels inapplicable to their more highly crosslinked methacrylate resins. Chatterjee and Marinsky[11] have recently been more successful in the use of polyelectrolyte theory to interpet their results on two commercial methacrylate resins. Gustafson[12] has recently reported results on the uptake of sodium chloride by a methacrylate resin.

The results described here amplify and extend the existing data, and together with results on polyampholyte resins reported in an earlier article,[13] are used to examine, for the dissociation of these resins, the polyelectrolyte theory which has already had some success here[11,12] and in the case of the dissociation of certain polyampholyte fibers.[14]

EXPERIMENTAL

Preparation, Purification, and Conditioning of the Resins

Nine different resins were employed, of which seven were specially prepared by copolymerization, designated C–I, and two were commercial resins, designated A and B. Resins having different degrees of crosslinking and different carboxylate contents were prepared by copolymerizing methacrylic acid, methyl methacrylate, divinylbenzene, and ethylvinylbenzene in different proportions. Copolymerizations were carried out, under nitrogen, in a closed stainless steel reaction vessel at 60°C. for 24 hr. A 100-g. portion of the appropriate monomer mixture was introduced into the reaction vessel which was immersed in a thermostat at 60°C., and 1 g. of benzoyl peroxide in 100 g. of methanol was added. Oxygen-free nitrogen was bubbled through the mixture, the vessel sealed, and stirring carried out mechanically at a constant rate. Turbidity usually appeared after about 30–40 min., and stirring had to be stopped

TABLE I
Specifications of the Resins

	Monomer content, wt.-%				Moisture regain, % of dry wt. (at 65% R.H., 22.2°C.)	Specific volume of dry resin, ml./g.
Sample	Methacrylic acid	Methyl methacrylate	Divinylbenzene	Ethylvinylbenzene		
A	92–97.5	0	2.5	?	13.95	0.810
B	90–95.5	0	4.5	?	15.57	0.808
C	76.0	0	8.0	16.0	9.70	—
D	64.0	0	12.0	24.0	9.09	0.897
E_1	64.0	28.5	2.5	5.0	13.20	0.859
E_2	64.0	28.5	2.5	5.0	58.12	0.682
F_1	64.0	22.5	4.5	9.0	12.09	0.858
F_2	64.0	22.5	4.5	9.0	55.10	0.702
G_1	64.0	12.0	8.0	16.0	12.43	0.873
G_2	64.0	12.0	8.0	16.0	60.66	0.676
H_1	90.0	2.5	2.5	5.0	17.20	0.826
H_2	90.0	2.5	2.5	5.0	94.51	0.616
I_1	76.0	16.5	2.5	5.0	17.16	0.774
I_2	76.0	16.5	2.5	5.0	77.43	0.601

after 3–4 hr. as the mass became too viscous. After 24 hr. the vessel was opened and the resin scraped out and dried in air.

The air-dried resins were ground in a mill and extracted with methanol to remove excess catalyst. Small samples of each resin were then extracted with water and with toluene. Analysis of the extracts showed that unreacted monomer and uncrosslinked polymer were present only in negligible proportions. Combined with yields of resin of virtually 100% this showed that the overall compositions of the resins could be taken as being the same as those of the monomer mixture used.

After the methanol extraction the resins were washed several times with distilled water. The resins were then conditioned by being subjected to alternate treatments with 1.0*M* potassium hydroxide and 1.0*M* hydrochloric acid, over several days, each treatment lasting 12 hr. Resins C and D were then converted to the acid form with 1.0*M* hydrochloric acid and were subjected to prolonged washing in distilled water until the pH of washings was between 5 and 6.5. Resins E, F, G, H, and I were divided into two parts. One part of each (E_1–I_1) was converted to the acid form and washed free of hydrochloric acid as for resins C and D. The other part of each (E_2–I_2) was given two successive treatments with 1.0*M* potassium hydroxide to convert it to the salt form, then washed with the minimum amount of 0.1*M* potassium hydroxide and centrifuged till dry. All the resins were transferred to flat dishes and stored at 22°C. and 65% relative humidity for several weeks before being used.

The commercial resins A and B were Zeo-Karb resins supplied by the Permutit Co. Ltd. They were washed with distilled water and stored at

22°C. and 65% R.H. The specifications of the resins, together with some of their properties, are given in Table I.

Moisture Regain of the Resins

About 1 g. of each resin, after conditioning at 22°C. and 65% relative humidity, was dried over phosphorus pentoxide under vacuum for several weeks until constant weight was achieved. Determinations were made in triplicate. Moisture content is expressed as a percentage of the dry weight.

Rate of Uptake of Acid and Base by the Resins

These determinations were made to ensure that the acid–base binding capacities of the resins were measured at equilibrium. A measured excess of $0.05M$ hydrochloric acid or potassium hydroxide was added to the resin, rapid stirring begun and the concentration of acid or base in solution determined periodically. Polyethylene vessels were used for experiments with base, and carbon dioxide-free nitrogen filled the reaction vessels, which were thermostatted at 22.5°C. Equilibrium times for base uptake varied from 48 hr. for resins containing 2.5% divinylbenzene to 10 days for resins with 12% divinylbenzene. For acid uptake the time to reach equilibrium was always the shorter. For potentiometric titration experiments, at least 1.5 times the determined equilibrium time was allowed.

Potentiometric Titrations

A discontinuous method was used. Different amounts of aqueous potassium hydroxide were added to samples of the conditioned resins in their acid forms in 100-ml. polyethylene bottles. The solid–liquid ratio was kept about the same, for each determination, at 50 ml. solution to about 0.15 g. resin. Carbon dioxide-free nitrogen was bubbled through the solutions and the bottles sealed and kept in a thermostat at 22.5°C. with intermittent shaking. When equilibrium had been reached the bottles were opened while nitrogen was passed over the surface of the solution, nitrogen bubbling recommenced for a short time, then the pH of the solutions determined by using a Cambridge pH meter with a standard or Alki glass electrode and a calomel electrode. The electrodes were calibrated with $0.05M$ potassium hydrogen phthalate and $0.05M$ sodium borate buffers and stored in carbon dioxide-free water. Individual pH measurements were generally accurate to ±0.005 pH, except in the neutral range pH 6–8, where it was reduced to ±0.03 pH or better. Two parallel series of experiments were carried out in which the external solution used was $0.01M$ and $0.10M$, respectively, with respect to potassium chloride. These titrations will be referred to as "forward titrations."

"Back titration," in which the salt forms of the resins were titrated with acid, were also carried out. Samples of the acid resins were converted to the salt form by treatment with excess potassium hydroxide, centrifuged to remove free base, and different amounts of aqueous hydrochloric acid were added to the samples in 100-ml. polyethylene bottles. Also, resins E_2, F_2, G_2, H_2, and I_2, the salt forms of the resins prepared as described, were used directly for back-titration. In some cases, a second forward titration was carried out after back-titration.

Base-Binding Capacity

After equilibrating the acid resin with excess potassium hydroxide solution, the resin phase was freed from external solution by centrifuging in Terylene cloth baskets (sift size 65 μ) which retained all the particles and its total base content determined by adding excess of standard hydrochloric acid and back-titrating. Sufficient time was allowed to ensure complete elution of the base by the acid. This method was preferred to the more usual one of finding the difference in concentration between control and experimental solutions because it was easier to deal with the acid than the base, and because the resins swell on going from the acid to the salt form, absorbing water and so concentrating the external solution.

Specific Resin Volumes

The specific swollen volumes of the resins V_e (i.e., the volume of resin containing 1 g. polymer) were determined pycnometrically at different external pH values. The equilibrium solution was used as the pycnometric liquid. The wet weights of the resins were determined after centrifuging at 800*g* for 5 min. using baskets of Terylene cloth (65 μ). Dry specific volumes were also determined pycnometrically by using freshly distilled *n*-heptane as pycnometric liquid after the resins had been dried over phosphorus pentoxide as already described. Occluded air in the resins was removed by subjecting the pycnometers to reduced pressure, but this operation proved to be unnecessary in the case of highly swollen resins.

Materials

Methacrylic acid (stabilized with hydroquinone) was fractionated under reduced pressure and the best fraction subjected to fractional crystallization. Methyl methacrylate was purified by fractionation under reduced pressure. The crosslinking agent was a mixture of 33.3% divinylbenzene and 66.7% ethylvinylbenzene and was used in this condition. Benzoyl peroxide was also used without further purification. Carbonate-free potassium hydroxide was made from concentrated solutions of Analar potassium hydroxide by precipitating the carbonate as barium carbonate. Hydrochloric acid and potassium chloride were of Analar grade and glass-distilled water was rendered carbon dioxide-free.

RESULTS AND DISCUSSION

Specifications of the Resins

Table 1 shows the specification of the resins. All the titration curves (Fig. 1) show plateaus of maximum uptake of KOH around pH 12, cor-

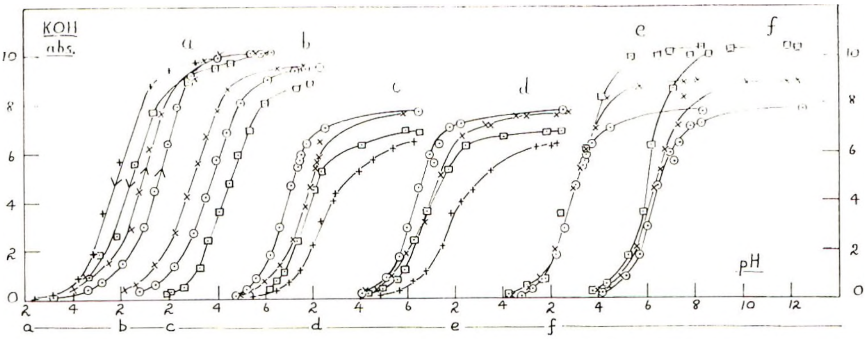

Fig. 1. Titration curves of the resins. KOH absorbed in mmoles per gram dry resin vs. pH of solution. Shown as six groups of curves labelled *a–f* with the pH scales displaced as indicated. (*a*) Forward and backward curves for commercial resin A, $0.1M$ KCl, (⊙) forward and (⊡) backward; resin A, $0.10M$ KCl, (×) forward and (+) backward. (*b*) Commercial resin B, forward only, (⊡) no added salt, (⊙) $0.01M$ KCl, (×) $0.10M$ KCl. (*c*) Resins containing 64% methacrylic acid with different degrees of crosslinking in $0.01M$ KCl, forward only, (⊙) resin E, 2.5% DVB; (×) resin F, 4.5% DVB; (⊡) resin G, 8.0% DVB; (+) resin D, 12.0% DVB. (*d*) Resins containing 64% methacrylic acid with different degrees of crosslinking, in $0.10M$ KCl, forward only, (⊙) resin E, 2.5% DVB; (×) resin F, 4.5% DVB; (⊡) resin G, 8.0% DVB; (+) resin D, 12.0% DVB. (*e*) Resins containing 2.5% DVB with different methacrylic acid contents in $0.01M$ KCl, forward only, (⊙) resin E, 64% MA; (×) resin I, 76% MA, (⊡) resin H, 90% MA. (*f*) Resins containing 2.5% DVB with different methacrylic acid contents in $0.10M$ KCl, forward only, (⊙) resin E, 64% MA; (×) resin I, 76% MA; (⊡) resin H, 90% MA.

responding to the maximum capacities determined separately. The values for the maximum capacity are close to the theoretical maximum capacities calculated from the composition of the resins; except for the resins C, D, and G, of relatively high degrees of crosslinking (Table II).

Evidently all the carboxyl groups are available for titration by KOH in the lightly crosslinked resins, but not in those with 8 or 12% divinylbenzene.

The specific volumes of the dry resins are appreciably lower for the salt forms than for the acid forms. It may be that coulombic attraction between the negatively charged groups and the potassium cations allows a

TABLE II
Base-Binding Capacity

Resin	Experimental base-binding capacity, meq./g.	Theoretical base-binding capacity, meq./g.
A	10.13	—
B	9.58	—
C	6.72	8.84
D	6.50	7.44
E	7.72	7.44
F	7.62	7.44
G	6.90	7.44
H	10.33	10.47
I	8.92	8.84

more compact structure to form as a result of swelling and deswelling. The values for the salt forms given refer to 1 g. of dry resin in the acid form without the potassium ions.

The moisture regain shows a tendency to decrease with increased degree of crosslinking and with decreased methacrylic acid content, but this is by no means uniform, as comparison of the results for resins F and G, and H and I, shows. The most striking effect is the much greater values found for the resins in the salt form than for those in the acid form. This is probably related to their much greater ability to swell, but no direct relation to the swelling volumes could be established. The presence of the potassium and carboxylate ions might also contribute to the increased regain of the salt form.

Potentiometric Titration Curves

A selection of these are shown on Figure 1, mainly as forward curves. Figure 1 (*a* and *b*) shows the results for the commercial resins A and B. Figure 1*b* shows the effect of added salt on the forward titration of resin B, the added salt moving the curve to lower pH regions, i.e., decreasing the apparent pK (pK'_a) due to the suppression of the electrostatic effect by counterion shielding of the fixed charges. Figure 1*a* shows clearly the difference between the forward and backward curves for resin A at two concentrations of added salt, only due in part to the build-up of the salt concentration which occurs on back-titration (at pH 4.370 for $0.1M$ added KCl, the salt concentration on back titration is $0.132M$ and at pH 4.780 for $0.01M$ added KCl, the salt concentration on back titration is $0.042M$; on forward titration the salt concentrations remain sensibly constant at $0.10M$ and $0.01M$, respectively).

Figure 1 (*c* and *d*) shows the forward titration curves of four resins, all containing 64% methacrylic acid, but having different degrees of crosslinking, for two salt concentrations. With increasing degree of crosslinking the slopes of the curves decrease, the curves shift to regions of higher pH, and the maximum base-binding capacity decreases. This increased degree of crosslinking makes the resins into weaker acids with higher values of pK'_a.

Figure 1 (*e* and *f*) shows forward titration curves, at two salt concentrations for three resins all containing 2.5% DVB, but having different methacrylic acid contents. With increased methacrylic acid content, the titration curves show only a slight shift to regions of lower pH.

Titrations were also made for all the resins with no salt added, and for resin C, and backward titration curves, details of which are not reported, but will be referred to for their values of pK'_a and V_e.

Apparent Dissociation Constants pK_a

By making use of eq. (1), where α is the degree of dissociation, values

$$pH = pK'_a - n \log [(1 - \alpha)/\alpha] \qquad (1)$$

TABLE III
Apparent Dissociation Constants pK'_a at $\alpha = 0.5$

	Forward titration			Backward titration	
Resin	No added salt	$0.01M$ ($I = 0.01$)	$0.10M$ ($I = 0.10$)	$0.01M$ $I = 0.022$–0.027	$0.10M$ $I = 0.11$
A	8.32	7.62	6.97	6.47	5.83
B	8.50	7.70	6.98	6.82	6.57
C	9.42	9.17	8.60	—	—
D	9.32	8.41	7.77	7.83	7.42
E	7.98	6.92	6.18	6.52	6.02
F	8.05	7.70	6.95	6.83	6.42
G	8.22	7.63	6.53	7.33	6.87
H	7.67	7.08	5.98	6.37	6.02
I	7.72	7.02	6.27	6.50	6.12

of the apparent dissociation constant pK'_a may be found for the different resins for $\alpha = 0.5$ at the different salt concentrations, and these are shown in Table III. This equation gives an empirical description of the results, but n is not a constant. The pH is that of external solution, while pK'_a includes a term for the transference of hydrogen ion from resin to solution, as well as the dissociation constant of the resin. Changes in pK'_a at $\alpha = 0.5$ with resin composition and salt concentration will now be examined. Theoretical calculation of the intrinsic dissociation constant pK'_0 will also be made here, but a more detailed interpretation of the shapes of the titration curves and the variation of pK'_a and n with α will be made in a subsequent paper.

The effect of salt is to decrease the value of pK'_a, while increased DVB content increases it. This is shown in Figure 2 where straight lines have been drawn through the points, although for the forward titrations there is considerable scatter. These results are in line with those reported pre-

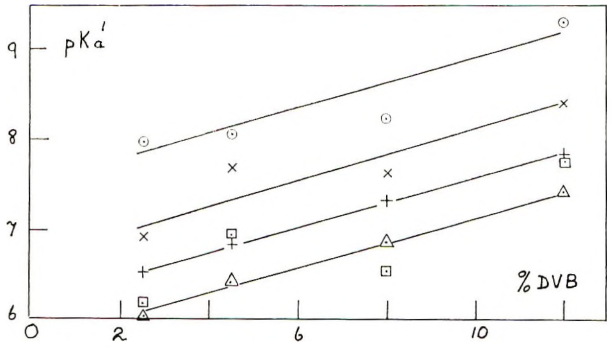

Fig. 2. Effect of crosslinking on the apparent dissociation constants pK'_a: forward titration, (⊙) no added salt, (×) $0.01M$ KCl (⊡) $0.10M$ KCl; backward titration, (+) $0.01M$ KCl, (△) $0.10M$ KCl.

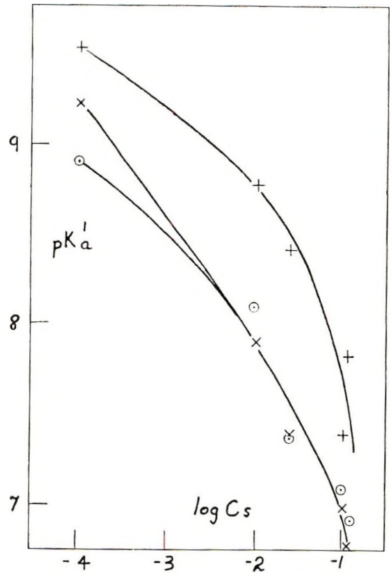

Fig. 3. Effect of salt on the apparent dissociation constants pK'_a. pK'_a vs. logarithm of the salt concentration in the external solution: (×) resin E; (⊙) resin I, (+) resin G.

viously.[1,2] The effect of the carboxylate content on the pK'_a values is very slight over the range investigated, as can be seen by examination of the values for resins E, H, and I. No trend of pK'_a with carboxylate content has been found for resins with 2.5% DVB.

Generally the pK'_a values are somewhat lower on backward titration than on forward titration. (Fig. 2). For resins E, H, and I this can be explained completely by the increased salt concentration present on backward titration due to neutralization, which gives a total external salt concentration of about 0.020–0.027 at $\alpha = 0.5$ for $0.01M$ added salt, and 0.11 for $0.10M$. Figure 3 shows that, within experimental error, values of pK'_a for forward and backward titration fall on smooth curves when plotted against the logarithm of the salt concentration actually present for resins E, I, and G. The shift of the titration curves, and the pK'_a values, to lower pH values at higher salt concentrations is due to the effect of salt in reducing the negative electrostatic potential on the polymer chains. This potential results in a greater attraction for hydrogen ion and so a higher pK for the carboxyl groups here than in a simple acid.

For the other resins, the pH values found on backward titration are somewhat lower than can be explained by the build-up of salt concentration. There is evidently some difference in the environment of the titrating groups on backward titration, which will be examined in a subsequent paper.

Specific Volumes of the Resins

Figures 4–6 show the specific volumes of the resins plotted against the KOH absorbed (equivalents per gram dry resin). The specific volumes increase steadily with the number of groups titrated, but maximum swelling is generally achieved when about 80% of the carboxyl groups are titrated. Further dissociation of carboxyl groups either has no effect on the swelling, or in some cases actually produces a decrease in the swelling.

The effect of salt is demonstrated most clearly in Figure 5*a*, increased salt concentration leading to decreased swelling as is to be expected. This effect of salt is most marked for the more lightly crosslinked resins, for the most highly crosslinked resin D the salt has very little effect on the swelling. Swelling is always less on backward than on forward titration, but this can be explained by the greater salt concentration present on backward titration.

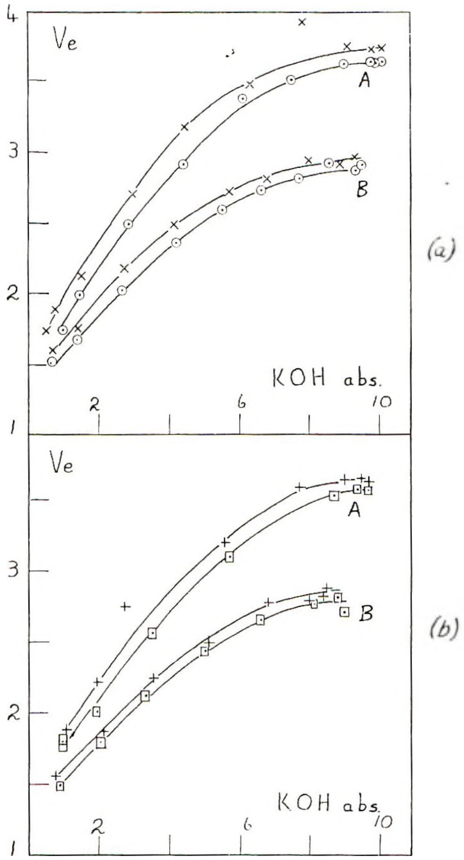

Fig. 4. Specific volumes (V_e) for the commercial resins A and B: (*a*) forward titration, (×) 0.01*M* KCl, (⊙) 0.10*M* KCl; (*b*) backward titration: (×) 0.01*M* KCl; (⊙) 0.10 *M* KCl.

Increased degree of crosslinking produces a marked decrease in the swelling. This illustrated in Figure 7, where the reciprocal of the specific volume at 90–100% dissociation, is plotted against per cent DVB. The S-shaped curve probably results from the interaction of opposing factors.

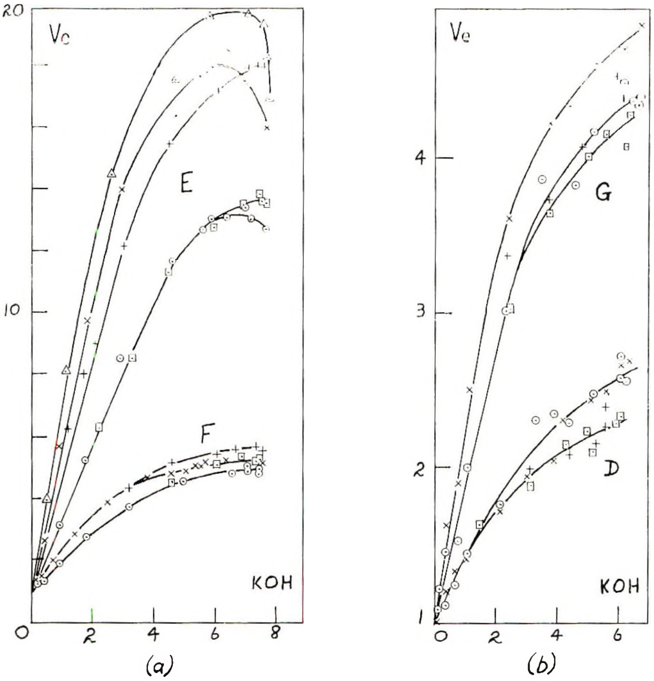

Fig. 5. Specific volumes (V_e) for resins with different degrees of crosslinking, 64% MA in resins, (*a*) resins E (2.5% DVB) and F (4.5% DVB), (*b*) resins G (8.0% DVB) and D (12% DVB): forward titration, (△) no added salt, (×) 0.01*M* KCl, (⊙) 0.10*M* KCl; backward titration, (+) 0.01*M* KCl, (⊡) 0.10*M* KCl.

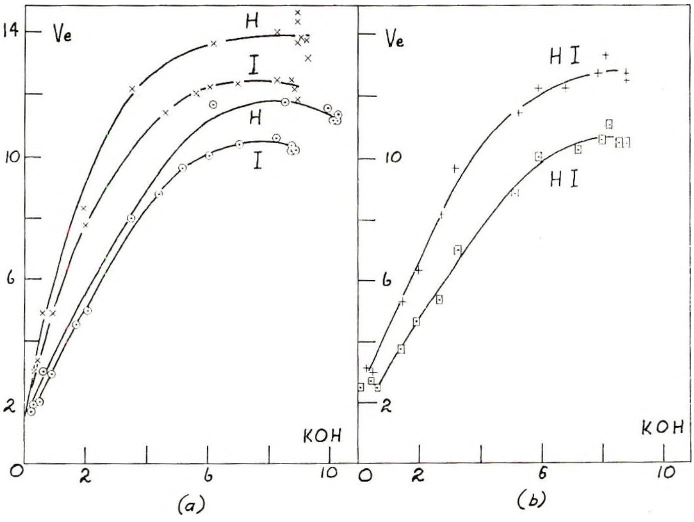

Fig. 6. Specific volumes (V_e) for resins with different methacrylic acid contents, resins H (90% MA) and I (76% MA), 2.5% DVB in resins: (*a*) forward titration, (×) 0.01*M* KCl, (⊙) 0.10*M* KCl; (*b*) backward titration, (+) 0.01*M* KCl, (⊡) 0.10*M* KCl.

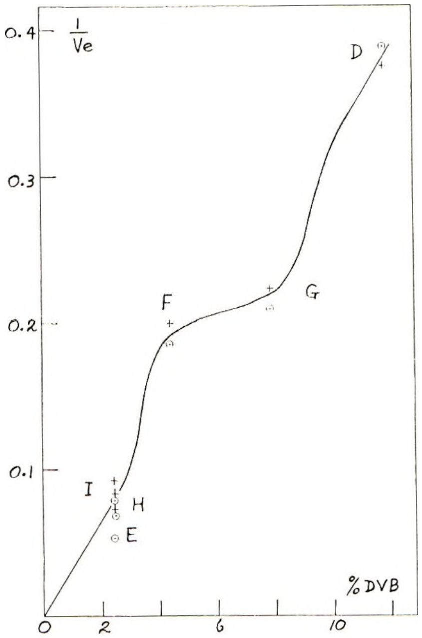

Fig. 7. Effect of crosslinking on the reciprocal resin specific volume ($1/V_e$) at $\alpha = 0.9$–1.0: (⊙) $0.01M$ KCl; (+) $0.10M$ KCl.

Comparison of Laboratory and Commercial Resins

The commercial resins A and B may be compared with the resins H and F, respectively, prepared in the laboratory. Some of their properties were quite different. Resin A had a much lower moisture regain than H, its moisture regain being closer to that of E which has far fewer carboxyl groups. The specific volumes of the dry resins compared reasonably, but on swelling in KOH the laboratory resins swelled more than three times as much as the commercial resins. The values of pK'_a for the commercial resins were consistently higher. Different methods of preparation leading to different internal distributions of crosslinks could explain these discrepancies, though Gustafson[12] has shown that the mean molal activity coefficient of sodium chloride in poly(methacrylic acid) resins is not affected by resin heterogeneity, and Moseley and Freeman[15] that different size particles of the same resin have essentially the same absorptive capacity, for poly(styrene sulfonate) resins. If the commercial resins contain some additives designed to inhibit swelling this could have had a serious effect on results of pK'_a and specific volumes obtained for commercial resins.

The Gibbs-Donnan Theory of Resin Dissociation

The Dissociation Equation. Chatterjee and Marinsky,[11] Gustafson,[16] and Mathieson and Whewell[14] have recently successfully applied the Gibbs-Donnan treatment to the dissociation of solid polyelectrolytes. In the first two applications, the sorbed solution within the resin was regarded as being effectively at the same electrical potential as the solution outside, while in the latter the sorbed solution was considered to be at the same potential as the polymer chains. These two assumptions represent limiting cases, the first for highly swollen resins and the second for resins and fibers which swell little.

In general, if χ_P and χ_{RS} represent the potential on the chains and the sorbed solution, respectively (each assumed uniform), dissociation of a group within the resin involves the hydrogen ion in an initial change of potential of $(\chi_P - \chi_{RS})$. The intrinsic acid dissociation constant is

$$K'_0 = [\alpha/(1 - \alpha)]a_{H1} \exp \{(\chi_P - \chi_{RS})F/RT\} \qquad (2)$$

where α is the degree of dissociation, a_{H1} the hydrogen ion activity in the sorbed solution, F the faraday. For equilibrium between the resin and the external solution whose pH is measured, the Gibbs-Donnan equations show that

$$RT \ln \frac{a_{H1}a_{M2}}{a_{H2}a_{M1}} = -\pi(\bar{V}_H - \bar{V}_M) - (\Delta\mu_H{}^0 - \Delta\mu_M{}^0) \qquad (3)$$

where M refers to a univalent metallic cation, subscripts 1 and 2 to the resin and the external solution, respectively, and π, $\bar{V}$, and $\Delta\mu^0$ represent osmotic pressure, partial molar volume, and change of standard chemical potential between resin and external solution. Only a single simple anion is present, and the $\bar{V}$'s are assumed independent of pressure. Combining these equations gives, for the pH of the external solution,

$$\mathrm{pH}_2 = \mathrm{p}K_0 - \log \frac{1 - \alpha}{\alpha} + \log \frac{a_{M1}}{a_{M2}} + \frac{0.4343}{RT} [(\chi_P - \chi_{RS})F - \pi (\bar{V}_H - \bar{V}_M) + \Delta\mu_M{}^0 - \Delta\mu_H{}^0] \qquad (4)$$

For a swollen resin for which $\chi_P \gg \chi_{RS}$ the equation reduces to that used by Chatterjee and Marinsky.[11] Where there is little swelling, χ_{RS} will approximate χ_P, and eq. (4) reduces to that used by Mathieson and Whewell,[14] since

$$\log (a_{M1}/a_{M2}) = -\chi_P F - \pi \bar{V}_M - \Delta\mu_M{}^0 \qquad (5)$$

To apply these equations we need information on χ_P, $\Delta\mu^0$, π and a_{M1}. In these systems it is reasonable to regard $\Delta\mu^0$ as zero. π can be calculated from water absorption data, and the term in π has been shown to be negligible.[11,14] To calculate χ_P for swollen resins, Chatterjee and Marinsky[11] and Gustafson[16] regarded the polymer chains of the resin as if they were randomly kinked chains dissolved in the sorbed solution, and applied the theory of Katchalsky, Shavit, and Eisenberg.[17] For fibers showing little swelling, Mathieson and Whewell[14] regarded the potential as uniform and calculated it from the Boltzmann equations. The metal ion activity in the resin phase was calculated by Chatterjee and Marinsky using the equations of Lifson and Katchalsky[18] to calculate the osmotic coefficient of the hypothetical unstrained resin and equating it to the activity coefficient of the metal ion.[19] This activity coefficient was calculated directly by Gustafson[16] from measurements of cation and anion concentrations in the resin. The activity term does not appear in the form of the equation used by Mathieson and Whewell.[14]

Calculation of the Dissociation Constant Assuming Randomly Kinked Chains. Equation (4) written for a swelling resin, neglecting terms in π and $\Delta\mu^0$, i.e.,

$$\mathrm{pH}_2 = \mathrm{p}K'_0 - \log\left[(1-\alpha)/\alpha\right] + \log\left(a_{K1}/a_{K2}\right) + \left(0.4343\chi_P F/RT\right) \quad (6)$$

was used to calculate $\mathrm{p}K'_0$. The value of a_{K1} was calculated by the method used by Chatterjee and Marinsky[11] already mentioned, and χ_P was determined by using the equation of Katchalsky and Lifson[18] for randomly kinked noninteracting chains. For resin F the values of log a_{K1}/a_{K2} were compared with values obtained by Gustafson[16] for a comparable system. Table IV shows that, except for $\alpha = 0.10$, the difference between the two sets of values is small and would make no significant change in the values of $\mathrm{p}K'_0$ in relation to the experimental and the other theoretical uncertainties involved. Values of the osmotic pressure term were calculated from the water absorption measurements and shown to be negligible in the expression for $\mathrm{p}K'_0$.

The results of the calculations of $\mathrm{p}K'_0$ are shown in Table V, in which the rows are divided into four blocks. The first block gives the values for the laboratory resins on forward titration, judged to be in reasonable agreement with the value to be expected for a carboxylic acid, i.e., 4.85. The overall average for these resins, and for the commercial resins which also give agreement and are shown in the second block, is 4.78. If the somewhat low figure for resin H, $0.10M$, is excluded, the average is 4.81 ± 0.14, in very good agreement with the expected value. However, the values of $\mathrm{p}K'_0$ averaged for the laboratory resins at fixed values of α show a trend of $\mathrm{p}K'_0$ with α such that $\mathrm{p}K'_0$ falls to a minimum at about $\alpha = 0.7$

TABLE IV
Comparison of log (a_{K1}/a_{K2}) calculated by Different Methods
(Resin F, $0.10M$)

α	Difference $\log\left(\frac{a_{K1}}{a_{K1}}\right)_{\text{calc.}} - \log\left(\frac{a_{K1}}{a_{K2}}\right)_{\text{Gustafson}}$
0.1	0.25
0.2	0.13
0.3	0.08
0.4	0.05
0.5	0.04
0.6	0.00
0.7	−0.03
0.8	−0.04
0.9	−0.05

TABLE V
Calculated Intrinsic Dissociation Constants
pK'_0 Assuming Randomly Kinked Chains

Resin and external soln.	pK'_0									Average for the resin
	$\alpha =$ 0.1	$\alpha =$ 0.2	$\alpha =$ 0.3	$\alpha =$ 0.4	$\alpha =$ 0.5	$\alpha =$ 0.6	$\alpha =$ 0.7	$\alpha =$ 0.8	$\alpha =$ 0.9	
Forward titrations										
E, 0.10M	5.06	5.10	5.04	4.94	4.86	4.82	4.80	4.89	4.93	4.93
E, 0.01M	5.11	4.99	4.97	4.91	4.84	4.67	4.65	4.60	4.83	4.85
G, 0.10M	5.15	5.00	4.78	4.64	4.54	4.45	4.45	4.46	4.77	4.69
G, 0.01M	5.32	5.23	5.04	4.63	4.74	4.62	4.55	4.61	5.19	4.89
H, 0.10M	4.59	4.64	4.63	4.52	4.34	4.13	3.98	4.30	4.47	4.41
H, 0.01M	4.84	4.63	4.56	4.55	4.58	4.61	4.66	4.68	4.73	4.65
I, 0.10M	4.94	4.87	4.80	4.77	4.75	4.66	4.64	4.62	4.57	4.74
I, 0.01M	4.95	4.87	4.77	4.71	4.68	4.62	4.64	4.56	4.50	4.71
D, 0.01M	5.54	5.29	5.00	4.76	4.57	4.62	4.59	4.92	5.17	4.95
Average for the α	5.06	4.96	4.84	4.71	4.66	4.58	4.55	4.63	4.80	4.76
A, 0.10M	4.58	4.88	5.03	4.90	4.77	4.69	4.72	4.81	4.86	4.80
A, 0.01M	5.03	5.16	5.14	5.00	4.92	4.89	4.82	4.72	4.62	4.92
B, 0.10M	4.56	4.60	4.73	4.70	4.72	4.80	4.71	4.82	4.86	4.72
B, 0.01M	5.00	5.00	5.06	5.04	4.92	4.82	4.89	4.86	—	4.95
D, 0.10M	5.56	5.52	5.40	5.19	5.00	4.87	5.20	5.31	5.67	5.31
F, 0.10M	4.90	5.00	5.13	5.26	5.30	5.30	5.24	5.25	5.55	5.21
F, 0.01M	5.12	5.16	5.22	5.22	5.20	5.17	5.05	4.84	5.05	5.12
Backward titrations										
A, 0.10M	4.01	3.89	3.77	3.70	3.65	3.62	3.56	3.70	4.07	3.78
A, 0.01M	4.11	3.80	3.73	3.74	3.77	3.78	3.74	3.82	—	3.81
B, 0.10M	4.45	4.20	4.27	4.26	4.30	4.37	4.44	4.42	—	4.34
B, 0.01M	4.20	3.95	3.98	4.09	4.10	3.94	3.85	4.26	—	4.05
D, 0.10M	4.99	4.77	4.62	4.58	4.65	4.67	4.73	4.87	5.07	4.77
D, 0.01M	4.51	4.29	4.18	4.07	3.99	3.97	4.09	4.42	—	4.19

and then rises slightly. The difference between the two methods of calculating the activity term (Table IV) shows the same trend, but it is not large enough to remove the trend of pK'_0 with α, although the use of Gustafson's method would have reduced the magnitude of the effect. The commercial resins A and B do not show this trend clearly, and the overall accuracy does not permit any conclusions to be based on it.

The third and fourth blocks in Table V show results judged to be in disagreement with the expected value. When all the results for forward titrations are considered there is evidence of a trend of pK'_0 values upwards as resin swelling volumes diminish, and this gives high values for resins D and F. Here, interchain interactions will be the greatest, and it is not surprising that the theory begins to fail. The backward titration for these resins for which this is significantly different from the forward titration, also give disagreement except in one case. Evidently the assumptions made in the treatment do not correctly describe the resin on back-titration.

Calculation of the Dissociation Constant Assuming Uniform Potential. Equation (4) written for a resin showing little swelling, i.e.,

$$\mathrm{pH}_2 = \mathrm{p}K'_0 - \log\,[(1 - \alpha)/\alpha] + 0.4343\chi_P F/RT \qquad (7)$$

with terms in π and $\Delta\mu^0$ again neglected, was also used to calculate pK'_0 for the resins, with χ_P computed assuming a uniform potential distribution.[14] Some of the results are shown in Table VI, in which the rows are divided into three blocks. In the first block are shown results for backward titrations, where good agreement with the expected value is found for three of the commercial resins, but not for the laboratory resins. All the resins on forward titration gave results which were too high, the less the swelling the higher, and two examples only are shown in the second block. In general, this treatment is not valid for the resins, and the agreement for resins A and B on back titration could be fortuitous. This treatment was successful, however, with polyampholyte fibers, so it was applied to the results on the polyampholyte resins J and K, crosslinked copolymers of methacrylic acid and dimethylaminoethyl methacrylate, which were reported in an earlier article.[13] This is shown in the third block of the table. The treatment applies quite well to resin K, which contains excess

TABLE VI
Calculated Intrinsic Dissociation Constants
Assuming Uniform Potential Distribution

Resin and external soln.	pK'_0									Average for resin
	α = 0.1	α = 0.2	α = 0.3	α = 0.4	α = 0.5	α = 0.6	α = 0.7	α = 0.8	α = 0.9	
Backward titrations										
A, 0.10M	4.67	4.74	4.71	4.68	4.70	4.73	4.74	4.92	5.34	4.80
A, 0.01M	4.63	4.50	4.52	4.59	4.70	4.80	4.84	4.96	4.89	4.69
B, 0.10M	5.04	5.03	5.16	5.21	5.34	5.46	5.56	5.58	—	5.29
B, 0.01M	4.69	4.61	4.73	4.91	4.96	4.92	4.88	5.30	—	4.87
D, 0.10M	5.94	5.92	5.92	6.04	6.24	6.46	6.62	7.00	—	—
D, 0.01M	5.80	5.79	5.86	5.90	5.97	6.09	6.29	6.76	—	—
F, 0.10M	5.27	5.43	5.49	5.54	5.51	5.52	5.51	5.52	5.55	—
F, 0.01M	5.27	5.34	5.37	5.31	5.25	5.20	5.19	5.14	5.12	—
Forward titrations										
E, 0.01M	5.38	5.42	5.48	5.51	5.52	5.45	5.51	5.55	5.85	5.52
D, 0.01M	6.24	6.26	6.21	6.18	6.19	6.45	6.60	7.13	7.57	6.54
Ampholyte resins										
K, 0.10M	4.64	4.65	4.69	4.78	4.88	4.98	5.18	5.40	—	4.90
K, 0.01M	4.55	4.49	4.58	4.76	4.89	5.05	5.30	5.60	—	4.90
J, 0.10M	4.32	4.79	5.60	5.61	5.61	5.60	5.59	5.58	5.54	—
J, 0.01M	4.38	4.92	5.56	5.59	5.54	5.51	5.51	5.43	5.30	—

amino groups so that the carboxyl groups all titrate on one side of the isoelectric point and the chains have an overall positive potential. Resin J has excess carboxyl groups and so the titration encompasses the isoelectric point at about $\alpha = 0.23$. Below this point the overall potential on the chains is positive, and reasonable agreement is found. Some further values for J are, for $\alpha = 0.05$, 4.35, and 4.62; $\alpha = 0.15$, 4.52, and 4.63. Above the isoelectric point the values rise to somewhere near those for resin E. It seems that this treatment is valid only where the overall potential has the opposite sign to that of the dissociated group, as in the fibers[14] and the ampholyte resins.

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Résumé

On a mesuré la dissociation, la capacité, le gonflement et la teneur en eau de résines pontées d'acide méthacrylique et de méthacrylate de méthyle. Les résines ont été préparées à différents degrés de pontage pour une même teneur en ions carboxylates et vice-versa. La force ionique de la solution externe a également été variée et le comportement de résines comerciales comparé avec celui de résines de laboratoires. Les courbes de titration potentiométrique ont été obtenues et les courbes de titrage en retour des sels formés au départ de ces résines avec des acides. Les capacités montrent que presque tous les groupes carboxyliques étaient accessibles dans les résines contenant 2,5 à 4% de divinylbenzène mais non pas celles contenant de 8 à 12% de ce dérivé. Pour des résines hautement pontées la titration en retour était différente des courbes de titration directe. Les constantes de dissociation apparente $pK_a = pH + n \log [(1 - \alpha)/\alpha]$ décroissent avec une force ionique croissante, croissent avec un pontage croissant et ne varient pas avec la teneur en carboxylate. Le gonflement décroissait par augmentation de la concentration en sel particulièrement dans les résines faiblement pontées. Un gonflement maximum a été obtenu pour une dissociation d'environ 80%. L'inverse du volume de gonflement est proportionnel au pourcentage du divinylbenzène. Les résines commerciales manifestent un gonflement beaucoup plus faible que les résines préparées en laboratoire bien qu'elles aient la même composition. La théorie de Gibbs-Donnan de la dissociation de la résine a été appliquée pour calculer la constante de dissociation intrinsèque (pK'_0). Admettant un modèle de chaîne statistiquement enroulée, dissoute dans la solution absorbée, on obtient un accord avec les valeurs attendues de 4,85 (valeurs calculées de $pK_0 = 4.81 \pm 0.14$), sauf pour les résines les plus fortement pontées. Pour les résines polyampholytes, un accord a été trouvé sur la base d'un modèle présentant une distribution de potentiel uniforme le long de la résine ($pK_0 = 4{,}9$).

Zusammenfassung

Dissoziation, Kapazität, Quellung und Wassergehalt von vernetzten Methacrylsäuremethylmethacrylatharzen wurde gemessen. Harze mit verschiedenem Vernetzungsgrad bei gleichem Carboxylgruppengehalt und umgekehrt wurden hergestellt. Weiters wurde die Ionenstärke der äusseren Lösung variiert und das Verhalten handelsüblicher Harze mit demjenigen der laboratoriumsmässig hergestellten verglichen. Potentiometrische Titrationskurven wurden erhalten und ebenso "rückwärts"-Kurven durch Titration der Salzform der Harze mit Säure. Die Kapazitäten zeigen, dass bei Harzen mit 2,5% oder 4,0% Divinylbenzol alle Carboxylgruppen zur Verfügung stehen, nicht aber bei Harzen mit 8% oder 12%. Bei diesen hochvernetzten Harzen unterscheiden sich die Rücktitrationskurven von den Titrationskurven. Die scheinbaren Dissoziationskonstanten $pK'_a = pH + n \log (1 - \alpha)/\alpha$ nahmen mit steigender Ionenstärke ab, mit steigender Vernetzung zu und zeigten keinen Gang mit dem Carboxylgruppengehalt. Die Quellung wird, besonders bei schwach vernetzten Harzen, durch höhere Salzkonzentration herabgesetzt. Die stärkste Quellung wird bei etwa 80% Dissoziation erreicht. Der Reziprokwert des Quellungsvolumens ist dem Prozentgehalt an Divinylbenzol proportional. Käufliche Harze zeigen bei offenbar gleicher Zusammensetzung eine viel geringere Quellung als die im Labor hergestellten. Zur Berechnung der wahren Dissoziationskonstanten (pK'_0) wurde die Gibbs-Donnan-Theorie der Harzdissoziation angewendet. Mit einem Modell statistisch verknäuelter, in der sorbierten Lösung gelöster Ketten wurde mit Ausnahme der am stärksten vernetzten Harze eine gute Übereinstimmung mit dem Erwartungswert von 4,85 (ber. $pK'_0 = 4{,}81 \pm 0{,}14$) erhalten. Bei Polyampholytharzen wurdemit einem Modell mit gleichförmiger Potentialverteilung im Harz Übereinstimmung ($pK'_0 = 4{,}9$) erzielt.

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Study of Hydrocarbon-Soluble Organometallic Catalysts. III. Investigations on the Activity and Electric Conductivity of $Al(C_2H_5)_3$–$M(C_5H_7O_2)_n$ Catalysts Employed in the Synthesis of Stereoregular Polyacetylene

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Synopsis

The aim of the present work is to establish some correlations between the catalytic activity of several organometallic hydrocarbon-soluble complex systems and the electric conductivity, as a method which expresses the ionization degree of these catalyst types. The following systems were studied: $Al(C_2H_5)_3$–$VO(C_5H_7O_2)_2$; $Al(C_2H_5)_3$–$Cr(C_5H_7O_2)_3$, $Al(C_2H_5)_3$–$Co(C_5H_7O_2)_3$. The catalytic activity was determined at various molar ratios of $AlEt_3/M(C_5H_7O_2)_n$ in the stereoregular polymerization reaction of acetylene, where M is a metal. The visible and ultraviolet absorption spectra of the catalysts, as well as the variation of extinctions at various $AlEt_3/M(C_5H_7O_2)_n$ molar ratios were also determined. The systems with an optimal catalytic activity also show maximum values of electric conductivity and extinctions. The composition, degree of ionization of the catalyst, and the way in which this influences the catalytic activity are also discussed.

INTRODUCTION

In previous studies[1,2] we referred to the investigation of the correlation between the ionic state of the soluble catalytic complex $Al(C_2H_5)_3$–$Ti(OC_4H_9)_4$ and its catalytic activity in the polymerization of acetylene. The ionized state of the catalytic system was evaluated by means of electric conductivity measurements at various Al/Ti molar ratios of the catalytic components.

It was deemed interesting to continue these investigations, attempting both a generalization of the working method and development of criteria for evaluating of the catalytic activity of hydrocarbon-soluble organometallic complexes used as catalysts in stereoregular polymerizations. To this end we studied the hydrocarbon-soluble catalytic complexes formed by the interaction of $Al(C_2H_5)_3$ with $VO(C_5H_7O_2)_2$, $Cr(C_5H_7O_2)_3$, or $Co(C_5H_7O_2)_3$. In this series of investigations we noted the influence of the transitional metal of the complexing component on the ionization of the catalytic and parallel complex, and the activity of this in the reaction test for the synthesis of stereoregular polyacetylene.

This study was of interest also because there are few published data on the correlation between electric conductivity or other physical and chemical properties of the catalytic complexes and their real activity.[3-7] The methods of Shilov and co-workers were used, as well as other physical investigation methods and the method of electric conductivity determination, to establish the optimal molar ratio of the $Al(C_2H_5)_3$–$Ti(OC_4H_9)_4$ catalytic complex formation, on basis of conductivity data.[8]

Shilov et al. consider that in a reactant medium the catalytic complex is dissociated to ions having an independent kinetic existence.

In our works we observed that it is difficult to conceive of the existence of free ions under conditions of nonpolarized solvents. The catalyst should rather be imagined to be in the form of a complex in an ionized state, protected by the nonpolarized solvent in which it is present in a dissolved state. A similar opinion was previously given in a series of works referring to the alkylation reaction of the aromatic nucleus, using catalysts based on aluminum halides or organometallic complexes.[9,10] Both the ionized state of the complex and the solvent influence it, according to Overberger and Jarovitzky.[11]

In our work, we also used the spectrophotometric method to evaluate the optimal complexing ratio of the catalytic components. The investigated catalytic systems were characterized by the wavelength of maximum visible and ultraviolet absorption, as well as by the variation of extinctions as a function of the $AlEt_3/M(C_5H_7O_2)_n$ molar ratio, according to Jobb's method of equimolecular series.

EXPERIMENTAL METHODS

The catalytic activity of the systems was studied for different $AlEt_3/Me(C_5H_7O_2)_n$ molar ratios, in the range of 1 to 10, at a constant polymerization temperature of 0°C. Redistilled toluene, dried on sodium and maintained in an argon atmosphere, was used as sovent. Polymerizations were carried out at atmospheric pression with C_2H_2, at constant feeding rates of 120 l./hr. Equal amounts of solvent (150 cc.) and equal amounts of the total catalyst mixture (0.5 g./100 cc. reaction volume) were used in all polymerizations.

At 15 min. after initiation, the polymerization was stopped by addition of 50 cc. methanol with 5% HCl. Solid polyacetylene of a bright black color was separated by filtration, vacuum-dried, and extracted with warm acetone over a period of 8 hr. The catalytic activity was assessed by determining the yield of solid acetone-insoluble polyacetylene, or by determining the whole quantity of reacted C_2H_2.

The electric conductivity of catalytic systems in toluene solution was determined by use of a specially constructed cell with platinum electrodes, permitting introduction of the catalyst solution under an inert atmosphere.

The thermostatting of the cell was achieved with paraffin oil. During the resistivity determinations no secondary electric phenomena were found. Concentrations of catalytic complex solutions were identical with that used in polymerization tests, i.e., 0.5 g. catalyst/100 cc. of reaction volume. We have followed the variation of electric conductivity as a function of the $AlEt_3/M(AcAc)_n$ molar ratio, where AcAc denotes the acetylacetonate. To calculate the activating energy of the conductivity, the relation used was:

$$\ln(\sigma_2/\sigma_1) = (E/2kR)[(1/T_1) - (1/T_2)]$$

For the catalytic complexes, obtained at $AlEt_3/M(AcAc)_n$ molar ratios, which show a maximum catalytic activity, the visible and ultraviolet absorption spectra were determined on a double-beam Beckmann type spectrophotometer. In order to determine the visible absorption spectra; use was made of toluene catalyst solutions, and as a standard, toluene solutions of chromium, cobalt, or vanadyl acetylacetonates, at identical concentrations as those employed in the preparation of catalytic complexes. For the ultraviolet absorption spectra, hexane solutions of the catalyst complexes were used, and as a standard, hexane solutions of $Al(Et)_3$.

Determination of extinction variations, as a function of the $Al(Et_3)/M(C_5H_7O_2)_n$ molar ratio were carried out by mixing equimolecular toluene solutions of individual catalytic components in certain proportions, according to Jobb's method. Extinction readings were made on a Carl Zeiss-Jena spectrophotometer. For the system based on vanadium and chromium, the solution concentration was 0.0374 mole/l., while for that based on cobalt, it was of 0.0050 mole/l. Determinations were effected in an 1.09-mm. quartz cell for the catalyst containing cobalt, and in an 1-cm.^{3} cell for those based on vanadium and chromium. Extinctions were read at wavelengths of 460 mμ for the vanadium system, at 500 mμ for that with chromium, and at 590 mμ for that with cobalt.

RESULTS AND DISCUSSION

Activity of Catalyst Systems

Results of experimental tests of acetylene polymerization are given in Tables I–III and in Figures 1 and 2.

These results indicate that in the catalyst systems investigated, the maximum yield in polyacetylene is given at the $AlEt_3/VO(AcAc)_2 = 2$; $AlEt_3/Cr(AcAc)_3 = 3$; and $AlEt_3/Co(AcAc)_3 = 3$ molar ratios. At these molar ratios there is also the lowest percentage of acetone-extractable products and that this increases with increasing polyacetylene yield, hence in the same direction in which the $AlEt_3/M(AcAc)_n$ ratio increases (Fig. 2).

Catalyst systems with different compositions, as expressed by the $AlEt_3/M(AcAc)_n$ molar ratios, have different activities and selectivities.

Molar ratios above 2 for the catalyst containing vanadium and above 3 for those based on chromium and cobalt lead to the unselective polymer-

TABLE I

$Al(C_2H_5)_3$–$VO(C_5H_7O_2)_2$ Catalyst System

$\frac{Al(C_2H_5)_3}{VO(C_5H_7O_2)_2}$	Wt. total polymer, g.	Wt. acetone-insoluble polyacetylene, g.	Toluene-soluble reaction products, g.	C_2H_2 reacted, mole-% × 10^3	Polyacetylene, g./g. total catalyst	Acetone extract	
						Total, g.	g./100 g. polyacetylene
1	1.204	0.636	0.434	2.34	0.85	0.134	21.0
2	4.336	3.922	0.275	8.46	5.23	0.139	3.5
3	3.861	3.220	0.332	7.12	4.30	0.309	9.6
4	2.711	2.098	0.301	5.38	2.80	0.312	14.9
5	2.136	1.543	0.307	4.27	2.06	0.286	18.5
10	1.662	0.925	0.499	3.22	1.23	0.238	25.7

TABLE II

$Al(C_2H_5)_3$–$Cr(C_5H_7O_2)_3$ Catalyst System

$\frac{Al(C_2H_5)_3}{Cr(C_5H_7O_2)_3}$	Wt. total polymer, g.	Wt. acetone-insoluble polyacetylene, g.	Toluene-soluble reaction products, g.	C_2H_2 reacted, mole-% ×10^3	Polyacetylene, g./g. total catalyst	Acetone extract	
						Total, g.	g./100 g. polyacetylene

1	0.788	0.415	0.252	1.51	0.55	0.121	29.1
2	2.041	1.635	0.157	3.81	2.18	0.219	15.2
3	2.322	2.010	0.198	4.48	2.68	0.114	5.6
4	2.162	1.712	0.253	4.09	2.28	0.197	11.5
5	1.733	1.153	0.323	3.53	1.54	0.257	22.3
10	0.599	0.276	0.196	1.25	0.37	0.127	46.0

TABLE III

$Al(C_2H_5)_3$–$Co(C_5H_7O_2)_3$ Catalyst System

$\frac{Al(C_2H_5)_3}{Co(C_5H_7O_2)_3}$	Wt. total polymer, g.	Wt. acetone-insoluble polyacetylene, g.	Toluene-soluble reaction. products, g.	C_2H_2 reacted, mole-% $\times 10^3$	Polyacetylene, g./g. total catalyst	Acetone extract	
						Total, g.	g./100 g. polyacetylene
1	0.672	0.309	0.239	1.31	0.41	0.124	40.1
2	1.306	0.908	0.202	2.46	1.21	0.196	21.6
3	1.568	1.269	0.166	3.07	1.69	0.133	8.8
4	1.358	0.975	0.213	2.56	1.30	0.170	17.4
5	1.155	0.728	0.241	2.19	0.97	0.186	25.5
10	0.519	0.191	0.210	0.95	0.25	0.118	62.0

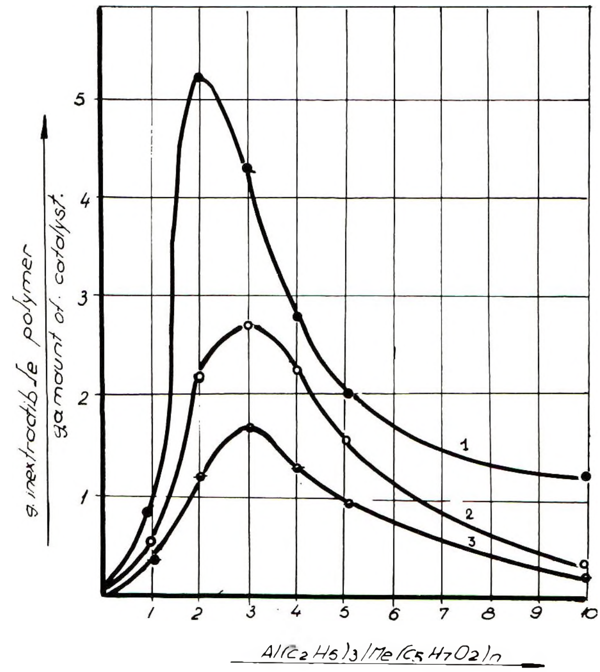

Fig. 1. Variation of yields in polyacetylene nonextractable in acetone as a function of the molar ratio of catalyst components: (*1*) $AlEt_3$–$VO(AcAc)_2$; (*2*) $AlEt_3$–$Cr(AcAc)_3$; (*3*) $AlEt_3$–$Co(AcAc)_3$.

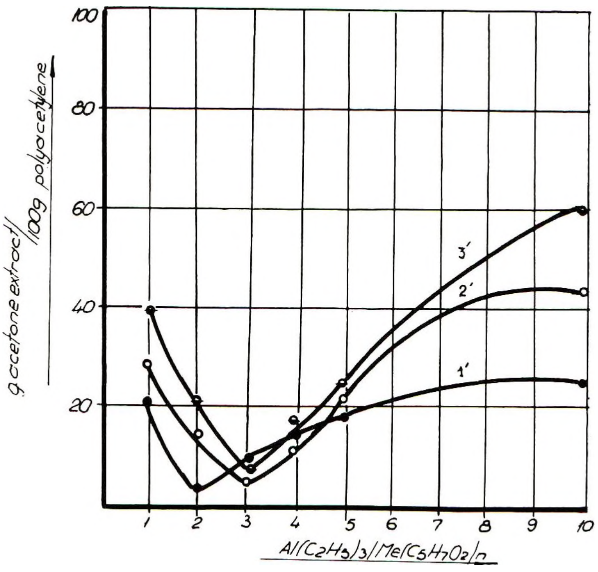

Fig. 2. Variation of yields of acetone-extracable products as a function of the molar ratio of catalyst components: (*1'*) $AlEt_3$–$VO(AcAc)_2$; (*2'*) $AlEt_3$–$Cr(AcAc)_3$; (*3'*) $AlEt_3$–$Co(AcAc)_3$.

ization reactions, the products obtained showing a remarkable dispersion of the degree of polymerization. In these instances, the catalysts favor, approximately to the same extent, both the formation of high molecular

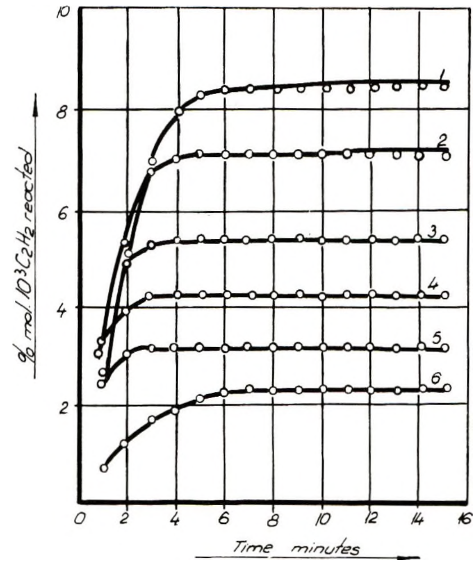

Fig. 3. Overall rate of polymerization of acetylene with $Al(C_2H_5)_3$–$VO(C_5H_7O_2)_2$ catalyst at various molar ratios of catalyst components: (*1*) molar ratio = 2; (*2*) molar ratio = 3; (*3*) molar ratio = 4; (*4*) molar ratio = 5; (*5*) molar ratio = 10; (*6*) molar ratio = 1.

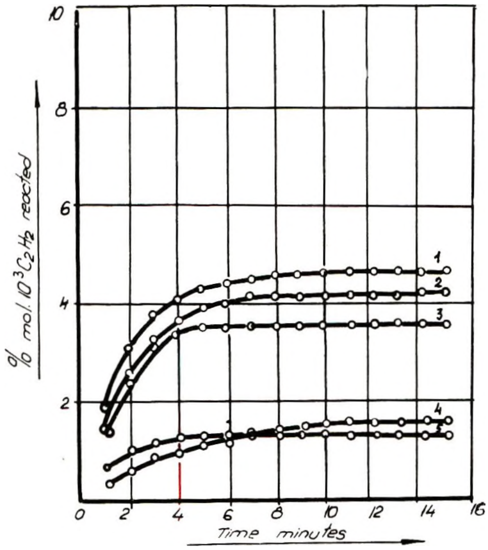

Fig. 4. Overall rate of polymerization of acetylene with $Al(C_2H_5)_3$–$Cr(C_5H_7O_2)_3$ catalyst at various molar ratios of catalyst components: (*1*) molar ratio = 3; (*2*) molar ratio = 4; (*3*) molar ratio = 5; (*4*) molar ratio = 1; (*5*) molar ratio = 10.

weight polyacetylene and the formation of low molecular weight, acetone-extractable by-products. The high yields of extractable products may be due also, to some extent, to the reactions of chain breaks in $Al(C_2H_5)_3$, which is in excess, necessary to obtain the definite kind of catalyst which ensures an optimal activity.

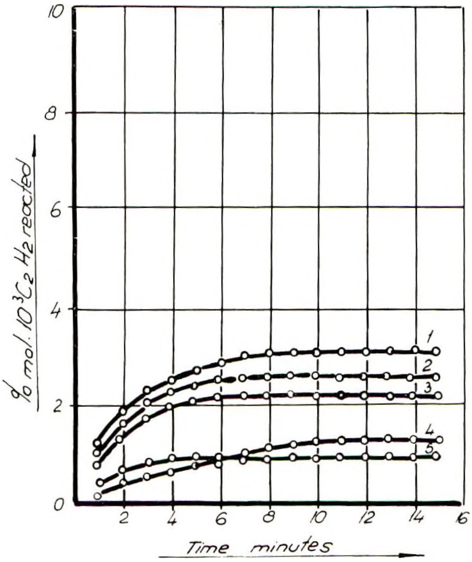

Fig. 5. Overall rate of polymerization of acetylene with $Al(C_2H_5)_3$–$Co(C_5H_7O_2)_3$ catalyst at various molar ratios of catalyst components: (*1*) molar ratio = 3; (*2*) molar ratio = 4; (*3*) molar ratio = 5; (*4*) molar ratio = 10; (*5*) molar ratio = 1.

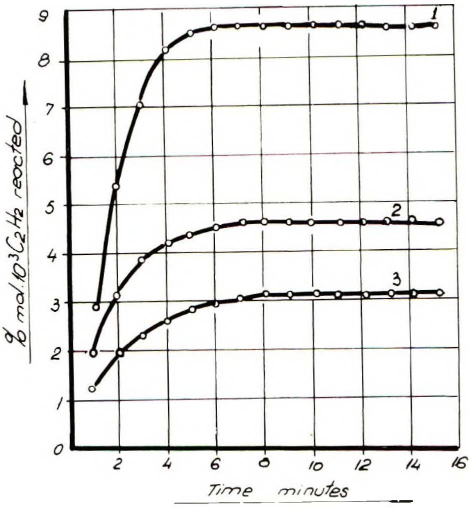

Fig. 6. Comparative absorption–reaction isotherms: (*1*) $AlEt_3/VO(AcAc)_2$ = 2; (*2*) $AlEt_3/Cr(AcAc)_3$ = 3; (*3*) $AlEt_3/Co(AcAc)_3$ = 3.

In the case of high molar ratios, the amount of M(AcAc)$_n$ decreases progressively, increasing that of AlEt$_3$.

It may be assumed, that the amount of catalytic complex, corresponding to the active species—which has a definite stoichiometric composition—will vary also, and thus, influence the yield of polymerization.

A similar explanation may be considered also in the case of low molar ratios, below 2 for V catalyst or 3 for Co and Cr catalysts. From the absorption–reaction isotherms, shown in Figures 3–5, a maximum of acetylene absorption may be established for the catalyst system, formed at AlEt$_3$/VO(AcAc)$_2$ = 2, AlEt$_3$/Cr(AcAc)$_3$ = 3, and AlEt$_3$/Co(AcAc)$_3$ = 3.

The highest absorption velocities of C_2H_2 are obtained for catalysts characterized by AlEt$_3$/M(AcAc)$_n$ molar ratios below 2 or 3, depending on the metal component.

The influence of a particular complexing component on the activity of catalyst having a common Al(C_2H_5)$_3$ base is seen from the absorption–reaction isotherms shown in Figure 6. The catalyst activity for AlEt$_3$/M(AcAc)$_n$ optimal molar ratios falls in the order V > Cr > Co.

The obtained polyacetylenes are stereoregular, having structural characteristics, identical with those obtained by Natta,[12] Hatano,[13] and Angelescu and Gainar.[14] Data on the stereoregular character of the polyacetylenes will be presented in a forthcoming paper.

Spectrophotometric Determinations

A study of visible absorption spectra of the toluene solutions of the catalyst complexes established that all three systems already investigated have a characteristic absorption maximum in the same spectral area. It is worth mentioning that the spectra of the catalyst systems are clearly different from those of pure acetylacetonates.[2]

The ultraviolet spectra shown in Figure 7 are also interesting.

Figure 7 shows that all catalyst systems investigated show an ultraviolet absorption band with a maximum at 294 mμ. This would indicate that interaction of the two catalytic components leads to formation of complexes showing analogous structures.

Obviously, at the interaction of MX$_n$ (where M is a transitional metal atom) with aluminum alkyls, reduction of the transitional metal compound is taking place. The fact that for all the three investigated catalysts systems the maxima appear in the same place in the visible and ultraviolet spectra permits us to assume that the displacement of the absorption bands is not caused only by the appearance of a reduced form of the transitional metal component, but especially by the appearance of some complex combinations between the reduced forms and excess Al(C_2H_5)$_3$.

If only the reduced forms of transitional metal components would cause the displacement of the absorption bands in the spectra, then these should be found in different spectral areas for all three of the investigated catalyst systems. These results support some studies which suggest bimetallic complex structures of the reduced form of the transitional metal compound with aluminum alkyl, for soluble organometallic catalysts.[8,15,16] It may be supposed, that these stoichiometric complexes are formed from an equilibrium of ions in lower valence states. It may even be that at various

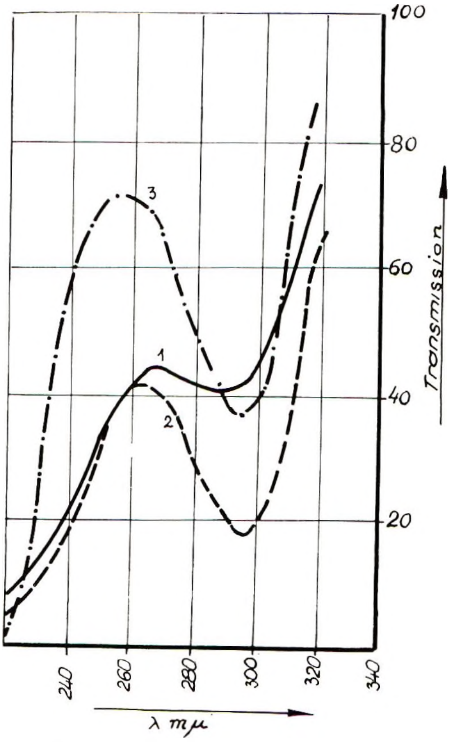

Fig. 7. Ultraviolet absorption spectra of the catalyst systems: (*1*) $AlEt_3$–$VO(AcAc)_2$; (*2*) $AlEt_3$–$Cr(AcAc)_3$; (*3*) $AlEt_3$–$Co(AcAc)_3$.

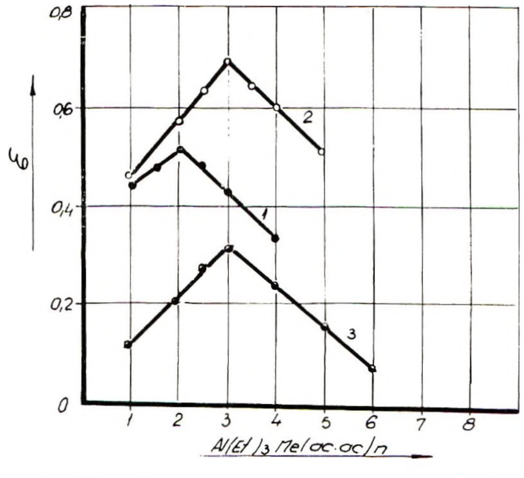

Fig. 8. Variation of extinction as a function of the molar ratio of catalyst components: (*1*) $AlEt_3$–$VO(AcAc)_2$; (*2*) $AlEt_3$–$Cr(AcAc)_3$; (*3*) $AlEt_3$–$Co(AcAc)_3$.

molar ratios of the components, the composition of the complexes formed may differ. However, important from a catalytic viewpoint, is the achievement of that complex concentration of ion groupings, in which the transition metal is found in a valence state corresponding to a maximum activity.

In an attempt to provide support for this idea, we determined the extinctions of various combinations of equimolecular solutions of pure components by Jobb's method.

Depending on the shape of the variation curves of extinction, as a function of the $AlEt_3/M(AcAc)_n$ molar ratio, (Fig. 8) between the molar ratios of 1–6 for all the investigated systems, a characteristic catalytic complex is formed, the structure of which corresponds to 2 g.-mole $AlEt_3$ g.-mole $VO(AcAc)_2$, 3 g./mole $AlEt_3$/g.-mole $Cr(AcAc)_3$; 3 g.-mole $AlEt_3$/g.-mole $Co(AcAc)_3$.

These determinations correlate well with the molar ratios at which the maxima of catalytic activity for the polymerization of acetylene occur.

Study of the Electric Conductivity and its Correlation with the Catalytic Activity

In the present catalyst systems, determinations of the electric conductivity may point out the existence of ion groups or the ionization state of the complex catalyst systems. By these determinations, assessments may be made, as well, on the most favorable stoichiometric molar ratio, which provides the catalytic system a maximum ionizing state.

The extent to which a correlation exists, expressed either by the amount of converted acetylene, or by weight of polyacetylene obtained in the poly-

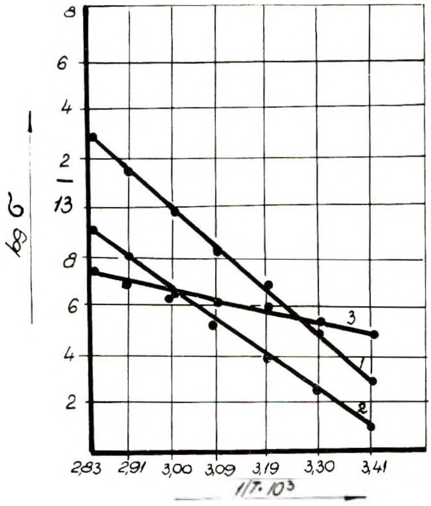

Fig. 9. Variation of electric conductivity with the temperature of toluene solutions: (1) $VO(AcAc)_2$; (2) $Cr(AcAc)_3$; (3) $Co(AcAc)_3$.

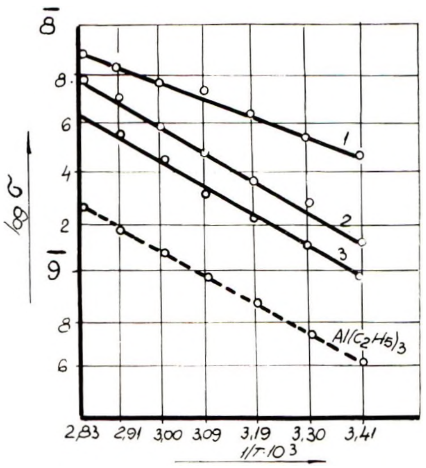

Fig. 10. Variation of electric conductivity with temperature: (*1*) $AlEt_3/VO(AcAc)_2 = 2$; (*2*) $AlEt_3/Cr(AcAc)_3 = 3$; (*3*) $AlEt_3/Co(AcAc)_3 = 3$.

merization reaction, and electric conductivity of the catalytic complexes must be obtained.

Observations may be made also referring to the structure and chemical composition of the catalyst complexes, as well as the intermediate states interfering with the polymerization.

We here present the results obtained for all three of the studied catalytic systems a correlation of these experimental data with the activity and the extinction values, described in the preceding sections.

Figure 9 shows the variation of electric conductivity with the temperature of the toluene–$M(AcAc)_n$ solutions; the $M(AcAc)_n$ concentrations are equal to those at molar ratios of 2 or 3 of the catalytic complexes. The plots cover to the temperature range of 20–80°C. It appears that the electric conductivity values are very low, of the order of magnitude of 10^{-13}

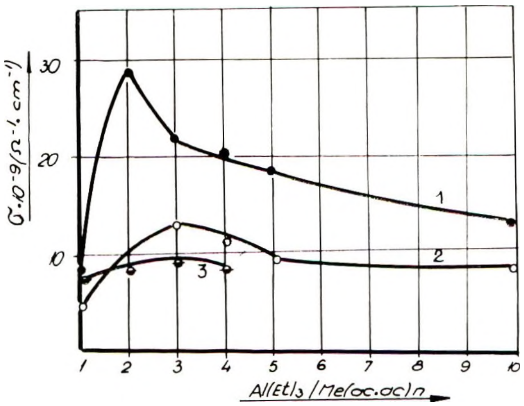

Fig. 11. Variation of electric conductivity at 20°C. as a function of the molar ratio of components: (*1*) $AlEt_3$–$VO(AcAc)_2$; (*2*) $AlEt_3$–$Cr(AcAc)_3$; (*3*) $AlEt_3$–$Co(AcAc)_3$.

$\text{ohm}^{-1}\ \text{cm.}^{-1}$, and rather near to the electric conductivity of the pure solvent.

Figure 10 shows the variation of the electric conductivity with the temperature of a toluene solution which contains $AlEt_3$ in equal concentration with that found in the catalytic complex tests [for an $AlEt_3/M(AcAc)_n$ molar ratio of 2 or 3, depending on the metal] and of the catalytic systems having a composition corresponding to the molar ratios of maximum catalytic activity.

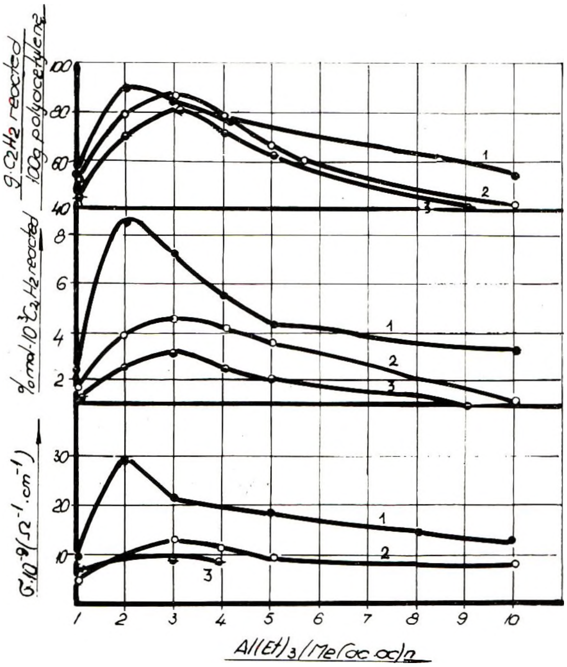

Fig. 12. Conductivity–composition and activity–composition isotherms: (*1*) $AlEt_3$–$VO(AcAc)_2$; (*2*) $AlEt_3$–$Cr(AcAc)_3$; (*3*) $AlEt_3$–$Co(AcAc)_3$.

In all instances, but especially in the case of systems based on vanadium and chromium, an obvious increase of the electric conductivity (of an order of magnitude of 0.5–1) is noticed compared with the electric conductivity values of the $AlEt_3$ solution.

The formation of the ionized catalytic complexes is thus obvious.

The catalytic differentiated activity, expressed by values of the electric conductivity as a function of the molar ratio between the components is shown in Figure 11.

We notice that the investigated catalytic systems show a maximum of conductivity in the $AlEt_3/M(AcAc)_n$ molar ratios of 2 for the vanadium catalyst and 3 for the chromium and cobalt catalysts. The cobalt catalyst system shows some conductivity anomalies for molar ratios higher than 4. This is probably due to the fact that imperfect complexes are formed, or secondary reducing reactions are taking place.

The electric conductivity values decrease in the following order: V > Cr > Co. Correlation with the actual catalytic activity results from the conductivity–composition (Fig. 12, bottom) and activity–composition (Fig. 12, middle and top) isotherms.

The maximum values of the actual catalytic activity correspond with the maximum and minimum values of the electric conductivity.

The $\mathrm{AlEt_3}$–$\mathrm{Co(AcAc)_3}$ system is different, showing a minimum catalytic activity, and also minimum values of conductivity.

In passing, we mention that the samples contain small amounts of catalyst, i.e., proportions corresponding to the quantity of 0.5 g./100 cc. reaction volume.

These experimental results confirm and generalize our previous conclusions, that there is a remarkable correlation between the molar ratio (composition), degree of ionization extinction maximum, and the real activity of the catalytic system ($\mathrm{AlEt_3}$–MR_n, where M = Ti, V, Cr, Co, etc., and R is an ester or acetylacetone grouping). Also, the contribution of conductivity and the fixing of the molar ratio which provides an optimal activity, is specified.

The activation energies of the electric conductivity show small values of about 3000 cal./mole for the $\mathrm{AlEt_3}$–$\mathrm{VO(AcAc)_2}$ system and of about 5000 cal./mole for the chromium and cobalt systems. These results may eventually also be correlated with the catalyst activity.

It may be that in formation of ionized complexes the metal from the ion complex (M–acetylacetone) is reduced by $\mathrm{AlEt_3}$ to a lower valence state, expelling an alkyl radical from the $\mathrm{AlEt_3}$. This has been suggested also in the literature.[8, 17–19]

Products resulting after this reaction are arranged in complex ions, having a central M(II) or M(III) ion and a coordination number of six or four.

Zambelli et al.[7] discussed the reaction between $\mathrm{VCl_4}$ and $\mathrm{AlR_2X}$, showing the formation of some products of the $\mathrm{VCl_2R}$ and $\mathrm{AlRCl_2}$ type.[7]

In the present case, we may consider as a first hypothesis, that the formation of complexes corresponding with an optimal activity, may be of the type:

$$[\mathrm{AcAc}\overset{+3}{\mathrm{V}}\mathrm{OAlEtAcAc}]^+$$

I

In this complex, vanadium has a valance of 3, bonding the V coordinates with the acetylacetone groupings. The vanadium ion is a tetracoordinate. The complex I corresponds with a molar ratio of $\mathrm{AlEt_3/VO(AcAc)_2} = 2$.

The Cr complex may be of the type II, corresponding with an $\mathrm{AlEt_3/M(AcAc)_3} = 3$ molar ratio.

$$[(\mathrm{AcAc})_2\overset{+2}{\mathrm{Cr}}\mathrm{Et_2AlAcAc}]^+$$

II

The chromium ion is bivalent, the main valences being bound with ethyl radicals in the inner and outer coordination area of the complex, while the central ion is tetracoordinated. The cobalt complex is probably analogous.

In addition to these complexes, series of transitions may be formed by addition reactions and substitution of penetration, etc. Complex systems may be formed also, with hexacoordinates of V(IV) or Cr(III).

It may be supposed, that various types of complexes will be found in equilibrium in relation with an excess of components or at various temperatures. The electric conductivity and the catalytic activity, will be determined by the state of equilibrium of the complexes or the associated complex ions which provide: (*a*) maximum concentration in the complex having a certain degree of ionization; (*b*) a certain concentration in the complex, having a central metallic ion at a convenient valence state; (*c*) the existence of some active sites (unpaired electrons), where the monomer molecule may be placed.

We shall return to these problems in a future paper.

Summary

The aim of present paper is to establish some correlations between the catalytic activity in the stereoregular polymerization of acetylene in organometallic systems of the hydrocarbon-soluble types: $Al(C_2H_5)_3$–$VO(C_5H_7O_2)_2$, $Al(C_2H_5)_3$–$Cr(C_5H_7O_2)_3$, and $Al(C_2H_5)_3$–$Co(C_5H_7O_2)_3$, and some physical and chemical properties of these, especially the electric conductivity.

The catalytic activity was determined for all three catalyst systems, depending on the $Al(C_2H_5)_3/M(C_5H_7O_2)_n$ molar ratio, at the polymerization temperature of 0°C. in a toluene solvent, at constant concentrations of the total catalytic mixture. It was found that the catalytic systems formed at molar ratios of $Al(C_2H_5)_3/VO(C_5H_7O_2)_2 = 2$ and $Al(C_2H_5)_3/Cr(C_5H_7O_2)_3$ and $Al(C_2H_5)_3/Co(C_5H_7O_2)_3 = 3$ show maximum catalytic activities and selectivities. The visible and ultraviolet absorption spectra show that the catalytic complexes have identical structures. Variation of extinctions as a function of the $Al(C_2H_5)_3/M(C_5H_7O_2)_n$ relation establishes that the optimal complexing ratio is identical with that of the maximum catalytic activity.

All catalytic complexes in a toluene solution show electric conductivities larger by 0.5–1 orders of magnitude than solutions of $Al(C_2H_5)_3$ at an identical concentration and larger by 4–5 orders than those of $M(C_5H_7O_2)_n$. The maximum conductivity values are found at a molar ratio of 2 for the vanadium complex, and 3 for those with chromium and cobalt.

There is found some correlation between composition, extinction, and electric conductivity, and, on the other hand, the catalytic activity. The degree of dissociation and structure of the studied catalysts were also assessed.

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Résumé

Le présent travail avait pour but d'établir une certaine corrélation entre l'activité catalytique de systèmes complexes de nombreux organométalliques solubles dans les hydrocarbures et la conductivité thermique comme méthode d'expression du degré d'ionisation de ces types de catalyseurs. Les systèmes suivants ont été étudiés: $Al(C_2H_5)_3$–$VO(C_5H_7O_2)_2$; $Al(C_2H_5)_3$–$Cr(C_5H_7O_2)_3$; $Al(C_2H_5)_3$–$Co(C_5H_7O_2)_3$. Leur réactivité catalytiques a été déterminée en fonction du rapport molaire de $AlEt_3/M(C_5H_7O_2)_n$ dans la réaction de polymérisation stéréorégulière de l'acétylène. Les spectres d'absorption dans le visible et l'ultraviolet de ces catalyseurs de même que la variation des extinctions en fonction du rapport molaire $AlEt_3/M(C_5H_7O_2)_n$ ont été également déterminés. On a constaté que les systèmes avec une activité catalytique optimum possèdent également des valeurs maximum de conductivité électrique et des extinctions maximum. On discute de la composition, du degré d'ionisation du catalyseur et de la facon suivant laquelle ceci influence l'activité catalytique.

Zusammenfassung

Die Arbeit hatte die Aufstellung von Korrelationen zwischen der katalytischen Aktivitat einiger metallorganischer, kohlenwasserstofflöslicher Komplexe und der elektrischen Leitfähigkeit, als Mass für den Ionisierungsgrad dieser Katalysatortypen, zum Ziel. Folgende Systeme wurden untersucht: $Al(C_2H_5)_3$–$VO(C_5H_7O_2)_2$: $Al(C_2H_5)_3$–$Cr(C_5H_7O_2)_3$; $Al(C_2H_5)_3$–$Co(C_5H_7O_2)_3$. Ihre katalytische Aktivität wurde in Abhängigkeit vom Molverhältnis $AlEt_3/M(C_5H_7O_2)_n$ bei der stereoregulären Polymerisationsreaktion von Acetylen bestimmt. Weiters wurden die Absorptionnspektren der Katalysatoren im Sichtbaren und im Ultraviolett, sowie die Abhängigkeit der Extinktion vom Molverhältnis $AlEt_3/M(C_5H_7O_2)_n$ bestimmt. Es wurde festgestellt, dass das System mit optimaler katalytischer Aktivität auch die höchsten Werte der elektrischen Leitfähigkeit sowie der Extinktion besitzt. Der Einfluss der Zusammensetzung und des Ionisierungsgrades des Katalysator auf die katalytische Aktivität wird aufgeklärt.

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Alternation Tendency in Copolymerization

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Synopsis

The number fractions of the alternate diads and triads and the average length of the alternate sequence may be used as the indices of the alternation tendency of binary copolymerizations. It is shown that these indices take on maximum values when the monomer feed ratio is such that $[M_1]/[M_2] = (r_2/r_1)^{1/2}$. The physical significance of the customary measure of the alternation tendency r_1r_2 is discussed.

Introduction

It is well known that the kinetics of the competing chain propagations involved in copolymerizations can most conveniently be delineated by referring to the reactivity ratios of the monomers concerned. As a logical extension of this convenience, the tendency of two monomeric units to be linked alternately along a binary copolymer chain has often been estimated from the reciprocal of the product of the two monomer reactivity ratios;

$$r_1r_2 = \frac{k_{11}k_{22}}{k_{12}k_{21}} \tag{1}$$

the tendency being greater the smaller the r_1r_2 value.[1a,2] The validity of this customary method of estimating the alternation tendency is intuitively apparent from the definitions of the reactivity ratios, insofar as it is ascertained that the monomer selection is governed exclusively by the growing chain end.

According to the *Q–e* scheme of Alfrey and Price,[3] the r_1r_2 product is directly related to the difference in polar nature alone:

$$r_1r_2 = \exp\left\{-(e_1 - e_2)^2\right\} \tag{2}$$

This equation would appear to show that the alternation tendency depends only on the polar nature of monomers. On the other hand, it may also be reasonable to assume that the reactivity of monomer governs monomer insertion into the chain and hence controls[5] the alternation or homopolymerization. Yet, it is felt that such an estimation procedure based on the r_1r_2 value has so far received little theoretical assessment in due regard to the characterization of the copolymer structures.

In the present communication, we derive several simple indices of the alternation tendency in conformity with the statistical consideration of the copolymer structure. These indices are compared with the r_1r_2 product. The results reveal the physical significance of, and the condition to be imposed on, the customary measure r_1r_2.

Alternation Indices

As the measures of the alternation tendency of the copolymerization of two monomers, M_1 and M_2, the number fractions of the alternate diads (M_1M_2 and M_2M_1) and triads ($M_1M_2M_1$ and $M_2M_1M_2$) in the copolymer and the average length of the alternate sequence ($M_1M_2M_1M_2$. . .) are adopted.

The probabilities ϕ_1 and ϕ_2 of finding M_1 and M_2 units in an infinitely long copolymer chain are given by[4]

$$\phi_1 = p_{21}/(p_{12} + p_{21}) \tag{3}$$

$$\phi_2 = p_{12}/(p_{12} + p_{21}) \tag{4}$$

where p_{ij} $(i, j = 1, 2)$ is the probability that in the propagation step a growing polymer carrying an end unit M_i selects a monomer M_j. The probability parameters p_{ij} are related with the monomer reactivity ratios in the following manner:[1b]

$$p_{11} = r_1u/(r_1u + 1) \tag{5}$$

$$p_{12} = 1/(r_1u + 1) \tag{6}$$

$$p_{21} = 1/[1 + (r_2/u)] \tag{7}$$

$$p_{22} = (r_2/u)/[1 + (r_2/u)] \tag{8}$$

where u is the molar ratio of the feed monomers:

$$u = [M_1]/[M_2] \tag{9}$$

Let us denote by F_{ij} the number fraction of the diad M_iM_j in a copolymer chain in its stationary limit. Since the F_{ij} is given by

$$F_{ij} = \phi_i p_{ij} \tag{10}$$

the number fraction, $F_{12,21}$, of the alternate diads is written as:

$$F_{12,21} = F_{12} + F_{21} = 2p_{12}p_{21}/(p_{12} + p_{21}) \tag{11}$$

The expression (11) is formally identical with that for the diad syndiotacticity of a polymer formed by a chain propagation which is asymmetric with respect to the selection of the D and L monomer configurations.[5] Insertion of eqs. (6) and (7) into eq. (11) yields:

$$F_{12,21} = 2/[2 + r_1u + (r_2/u)] \tag{12}$$

In a similar fashion, the number fraction, $F_{121,212}$, of the alternate triads can be calculated. The result is:

$$\begin{aligned} F_{121,212} &= p_{12}p_{21} \\ &= 1/[1 + r_1r_2 + r_1u + (r_2/u)] \end{aligned} \tag{13}$$

Next we will calculate the average length of an alternate sequence. We will henceforth refer to the number of diads, i.e., bonds, involved in a sequence of a given type of diads as the sequence length. The average alternate sequence length, $l_{12,21}$, may be calculated by the following simple procedure.

In the first place, the average length l_{ii} of the sequence consisting of M_iM_i diads alone is calculated.

$$\begin{aligned} l_{ii} &= \sum_{n=1}^{\infty} np_{ii}^{n-1}p_{ij} \\ &= 1/p_{ij} \\ i, j &= 1, 2 \qquad i \neq j \end{aligned} \tag{14}$$

The block sequence, whether it consists of M_1 or M_2 units, must necessarily be followed by an alternate sequence. Conversely, any alternate sequence should be linked with either an M_1 or M_2 block at its either end. Consequently, the total number of the alternate sequences in a given chain must be equal to the total sum of the numbers of the M_1 and M_2 block sequences involved in the same chain. These numbers of sequences can be obtained by dividing the numbers of the appropriate diads by their average sequence lengths. Thus we may write the equality:

$$(F_{11}N/l_{11}) + (F_{22}N/l_{22}) = F_{12,21}N/l_{12,21} \tag{15}$$

where N is the total number of the diads which constitute the copolymer chain under question. From eqs. (10), (11), (14), and (15), we finally obtain the average length of the alternate sequence;

$$l_{12,21} = 2/(p_{11} + p_{22}) \tag{16}$$

which tends to infinity as both p_{11} and p_{22} approach zero, indicative of complete alternation. In the limit where $p_{11} = p_{22} = 1$, $l_{12,21}$ becomes unity, implying very little cross-propagation involved. Equation (16) is transformed by the use of eqs. (5) and (8) into:

$$l_{12,21} = 2[1 + r_1r_2 + r_1u + (r_2/u)]/[2r_1r_2 + r_1u + (r_2/u)] \tag{17}$$

All the measures of the alternation tendency thus obtained ($F_{12,21}$, $F_{121,212}$, and $l_{12,21}$) are the functions of the monomer feed ratio u, as well as the monomer reactivity ratios r_1 and r_2.

Alternation Indices at the Monomer Feed for Extreme Alternation

It can be shown by differentiating the alternation indices [eqs. (12), (13), and (17)] with respect to u that they all attain either maximum or

TABLE I
Extreme Values of the Alternation Indices

Alternation index	Maximum	Minimum
$F_{12,21}$	$\dfrac{1}{1+(r_1r_2)^{1/2}}$ at $u = (r_2/r_1)^{1/2}$	0 as u approaches 0 or ∞
$F_{121,212}$	$\dfrac{1}{[1+(r_1r_2)^{1/2}]^2}$ at $u = (r_2/r_1)^{1/2}$	0 as u approaches 0 or ∞
$l_{12,21}$		
for $r_1r_2 < 1$	$1+\dfrac{1}{(r_1r_2)^{1/2}}$ at $u = (r_2/r_1)^{1/2}$	2 as u approaches 0 or ∞
for $r_1r_2 = 1$	2 for any u	
for $r_1r_2 > 1$	2 as u approaches 0 or ∞	$1+\dfrac{1}{(r_1r_2)^{1/2}}$ at $u = (r_2/r_1)^{1/2}$

minimum values when $u = (r_2/r_1)^{1/2}$. These extreme values are given in a tabular form in Table I.

The results given in Table I reveal the quantitative meaning of the product of the monomer reactivity ratios. The product of r_1 and r_2 is directly associated with the maximum attainable values of $F_{12,21}$ and $F_{121,212}$, i.e., the maximum attainable populations of the alternate diads and triads, for

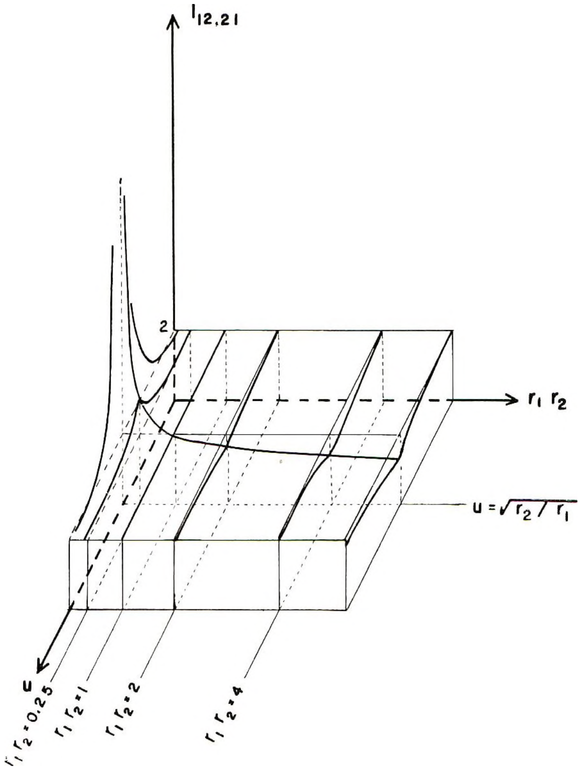

Fig. 1. Variation of $l_{12,21}$ with u and r_1r_2.

the copolymerization of a given pair of comonomers. This maximum is attained when the monomer feed ratio is adjusted in such a way that $u = (r_2/r_1)^{1/2}$. The corresponding copolymer composition is 50:50, as can be calculated from the familiar copolymer composition equation of Lewis and Mayo.[6] The maximum alternation depends only on the copolymerization parameter product, and it increases as the r_1r_2 value decreases.

As for the alternate sequence length, the r_1r_2 value is related to the maximum or minimum length depending whether or not it exceeds unity. Figure 1 shows the variation of $l_{12,21}$ with u and r_1r_2. If $r_1r_2 < 1$, $l_{12,21}$ can attain a maximum value in correspondence to the maximum population of the alternate diads. On the contrary, if $r_1r_2 > 1$, the $l_{12,21}$ approaches a minimum as the monomer feed ratio reaches a value $(r_2/r_1)^{1/2}$, where the population of the alternate diads is maximum. When $r_1r_2 = 1$, a case where the monomer selection conforms to the Bernoullian statistics, the average alternate sequence length is 2, irrespective of the monomer feed ratio.

Comparison of $r_1 + r_2$ with r_1r_2 for the Case of the Equimolar Monomer Feed

In this section we will consider a special case where the monomer feed ratio is kept at unity. In this special case, eqs. (12), (13), and (17) become:

$$F_{12,21}(1) = 2/(2 + r_1 + r_2) \tag{18}$$

$$F_{121,212}(1) = 1/(1 + r_1r_2 + r_1 + r_2) \tag{19}$$

$$l_{12,21}(1) = 2(1 + r_1r_2 + r_1 + r_2)/(2r_1r_2 + r_1 + r_2) \tag{20}$$

These indices should be useful for estimating the extent of alternation tendency on the condition that the copolymerization has been started with an equimolar mixture of two monomers.

$F_{12,21}(1)$ is the function of only the sum of the monomer reactivity ratios, while the other two indices depend on the sum just to the same extent as on the product. Thus it is required to consider the contribution of $r_1 + r_2$ relative to r_1r_2 in this particular case.

According to the Q–e scheme of Alfrey and Price,[3] each r value is related to the ratio of general reactivities (Q) of two monomers and the difference in polar nature (e) between them, while the r_1r_2 product is directly related to the difference in polar nature alone [eq. (2)]. Equation (2) would appear to show that the alternation tendency depends only on the polar nature of monomers, but not on their general reactivity. However, since the u value which leads to the maximum attainable values of the alternation indices depends on both e and Q, viz.,

$$(r_2/r_1)^{1/2} = (Q_2/Q_1) \exp\{(e_1^2 - e_2^2)/2\} \tag{21}$$

it may be said that the difference in general reactivity, if any, has already been taken into account by the adjustment of the monomer feed ratio.

By use of the experimental data for r_1 and r_2 compiled by Mark et al.[7] and by Yamashita et al.,[8] the relations between $r_1 + r_2$ and r_1r_2 have been examined. Included for this examination are 1182, 100, and 101 cases of the radical, cationic, and anionic vinyl copolymerizations,[7] respectively, and 64 cases of the cationic ring-opening copolymerization of cyclic monomers.[8] The $(r_1 + r_2)$ value depends on both the reactivity and the polar nature of monomers, while the r_1r_2 value depends only on the polar nature.

Plots of the values of $r_1 + r_2$ against the r_1r_2 values gave an $r_1 + r_2$ versus r_1r_2 map with three distinct regions A, B, and C, as shown in Figure 2. In the case of the copolymerization system in region A, the r_1r_2 value roughly parallels the $(r_1 + r_2)$ value. Many cases of radical copolymerization fall in this region. However, in region B the r_1r_2 value does not run parallel to the $(r_1 + r_2)$ value; namely, the monomer reactivity has a great effect on the alternation. Many cases of the ionic copolymerization are in region B. In region C, only a few cases are included, and their plots fall very close to region A.

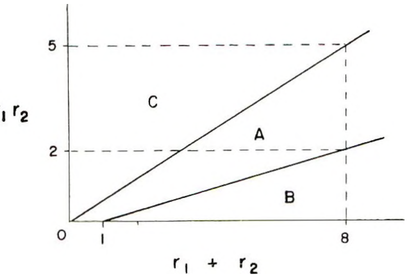

Fig. 2. Plot of r_1r_2 vs. $r_1 - r_2$.

The above situation may imply that the alternation tendency in the different reaction types, radical or ionic, is controlled by different factors. A growing chain end of the radical copolymerization is electrically neutral, and the selection of monomer by the growing chain may in most cases be controlled by the difference in polar nature between monomers and chain end rather than by the monomer reactivity. On the other hand, a growing chain end in ionic copolymerization has an electric charge, and hence the ionic reactivity inherent in isolated monomers may be a predominant factor controlling the competition of monomers to enter into the polymer chain.

Shown in Figure 3 are the percentage populations of the copolymerization systems which are found in various ranges of $(r_1 + r_2)$ values. A good alternation tendency of the radical copolymerization has been observed, i.e., 50.8% of the radical copolymerization has an $(r_1 + r_2)$ value smaller than 2, where the $F_{12,21}$ (1) value is larger than 0.5. On the other hand, only 17% of the cationic, 28.1% of the anionic, and 25.8% of the cationic ring-opening copolymerizations correspond to such a case.

Thus, in the copolymerizations where the alternation tendency is governed primarily by the difference in polar nature between monomers and growing chain end, as in the case of most of radical copolymerizations, two alternation indices, $r_1 + r_2$ and r_1r_2, are roughly parallel to each other. On the other hand, in the copolymerizations where the reactivity of isolated monomer is predominantly effective for the alternation tendency, as in the case of ionic copolymerizations, the index, $r_1 + r_2$, does not bear a simple relation to the index, r_1r_2. This failure of the parallel between r_1r_2 and $r_1 + r_2$ seems to arise when $r_i \cong 0$ and $r_j \gg 1$ $(i, j = 1, 2;\ i \neq j)$, with the r_1r_2 value sufficiently small and yet the $(r_1 + r_2)$ value rather large. Such a case does not lead to the formation of a highly alternating copolymer when the copolymerization is conducted with an equimolar mixture of two monomers. Rather, the resulting copolymer will be close to a homopolymer because, in this case, there is easy alternation of M_i unit to M_j unit and difficult alternation of M_j unit to M_i unit. In such a case, therefore, a choice should be made of the alternation index which is the more pertinent to the copolymerization conditions in regard to the monomer feed ratio.

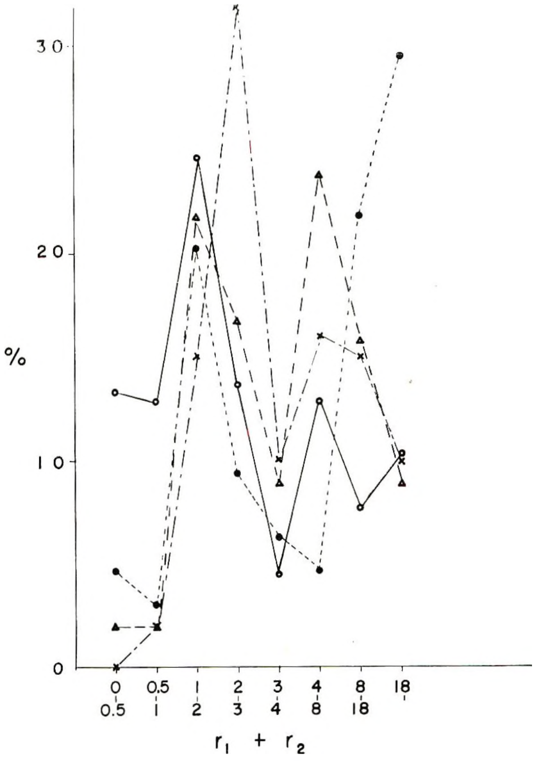

Fig. 3. Population of the copolymerization systems: (○) radical copolymerization of vinyl monomers; (×) cationic copolymerization of vinyl monomers; (△) anionic copolymerization of vinyl monomers; (●) cationic ring-opening copolymerization of cyclic monomers.

Conclusions

The number fractions of the alternate diads and triads and the average length of the alternate sequence can be regarded as the indices of the alternation tendency of binary copolymerizations. These indices take on maximum values when the monomer feed ratio is adjusted in such a way that $[M_1]/[M_2] = (r_2/r_1)^{1/2}$ a ratio which leads to the formation of the 50:50 copolymers. The maxima of these indices are closely related the r_1r_2 product, which has customarily been used as an alternation index.

In the special case where the monomer feed ratio is kept at unity, these three indices depend largely on the value of $r_1 + r_2$. In the case of radical copolymerizations, the $(r_1 + r_2)$ value roughly parallels the r_1r_2 value, whereas in ionic copolymerization, there exists no simple correlation. In the latter case, therefore, a choice should be made between the two quantities according to the monomer feed ratio used.

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Résumé

Les fractions numériques des diades et triades alternes et la longueur moyenne des séquences alternantes peuvent être utilisées comme indice de tendance d'alternance de copolymérisation binaire. On a montré que ces indices présentent des valeurs maximum lorsque le rapport initial du monomère est tel que $[M_1]/[M_2] = (r_2/r_1)^{1/2}$. La signification physique de la mesure habituelle de la tendance d'alternance r_1r_2 est soumise à discussion.

Zusammenfassung

Der Bruchteil an alternierenden Diaden und Triaden sowie die mittlere Länge der alternierenden Sequenzen können als Index für die Alternierungstendenz bei der binären Copolymerisation benützt werden. Es wurde gezeigt, dass dieser Index bei einem Verhältnis im Monomeransatz von $[M_1]/[M_2] = (r_2/r_1)^{1/2}$ Maximalwerte annimmt. Eine Diskussion der physikalischen Bedeutung des üblicherweise als Mass für die Alternierungstendenz benützten Produktes r_1r_2 wird gegeben.

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Aminobutadienes. VI. Polymerization and Copolymerization of 2-Phthalimido-1,3-butadiene*

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Synopsis

2-Phthalimido-1,3-butadiene (2-PB) was polymerized either radically or thermally in bulk and in solution. While the polymer obtained by solution polymerization was soluble in some solvents such as halogenated hydrocarbons, dioxane, and dimethylformamide and had a softening point in the range of 160–170°C., that obtained by polymerization in bulk was insoluble in any solvent and only swollen on being immersed in such solvents as above. The reduced viscosity of the soluble polymer obtained by solution polymerization was approximately 1.0, and this value remained almost unchanged with varying polymerization time. Likewise the cationic polymerization in acetylene tetrachloride or in chloroform at 20°C. with the use of cationic catalysts such as boron trifluoride and stannic chloride was attempted, but no formation of polymer was observed. This monomer preferentially reacted with acrylonitrile, methyl methacrylate, styrene, and *N*-vinylphthalimide to form the respective copolymers; it reacted somewhat less readily with vinyl acetate. The monomer reactivity ratios in the copolymerization with styrene were calculated by the Fineman and Ross method and found to be r_1 (2-PB) = 5.2 and r_2 (styrene) = 0.11, respectively, from which the Q,e parameters were successively evaluated to be $Q = 5.0$ and $e = -0.05$. The fact that e value is close to zero, easily explains why this monomer can copolymerize well both with acrylonitrile, which has a highly positive value of e (1.2) and with styrene, for which e is considerably negative (-0.8).

INTRODUCTION

In the preceding report[2] of this series, we dealt with polymerizations of 1-phthalimido-1,3-butadiene (1-PB) and 1-succinimido-1,3-butadiene (1-SB) and showed that the polymerizations take place easily by a radical process to give high molecular weight polymers and that even cationic reactions take place smoothly and result in formation of polymers, though of somewhat lower molecular weight.[3]

The present paper deals with polymerization and copolymerization of the other isomeric imidobutadiene, 2-phthalimido-1,3-butadiene prepared first by one of the present authors,[1] which was especially chosen here as a typical monomer having a bulky substituent on the C_2 of the butadiene

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* For the preceding papers in this series, see Terada and Takahashi[1] and Terada and Murata.[2]

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chain in order to see how the substitution effect differs from those in the above 1-imidobutadienes as to the polymerizability and polymer properties.

It was also of interest to determine the reactivity of this monomer in copolymerization with several vinyl monomers, the monomer reactivity ratios for the system with styrene, and then the Q and e parameters according to the Alfrey-Price scheme.

EXPERIMENTAL

Materials

2-Phthalimido-1,3-butadiene (2-PB) was prepared as white needles, m.p. 83–85°C., from either ethyl acetoacetate or D-threonine by following the methods reported in a previous paper.[1] Other vinyl monomers, acrylonitrile (AN), methyl methacrylate (MMA), styrene (St), and vinyl acetate (VAc) were supplied commercially and purified just prior to use in to the usual manner.[4] *N*-Vinyl phthalimide (VPI) was prepared by pyrolysis of *N*-β-acetoxyethylphthalimide obtained after condensation of monoethanolamine with phthalic acid and following acetylation; it was obtained as pale yellow needles, m.p. 85–86°C. (from methanol) (lit. m.p.; 86°C.,[5] 85.5–86°C.[6,7]). A commercially obtained benzoyl peroxide (BPO) was purified by repeated precipitation into methanol from chloroform solution and subsequent drying under vacuum, m.p. 104°C. Reagent-grade boron trifluoride etherate and stannic chloride were purified by repeated fractional distillations and used immediately (b.p. 125–126°C. and 113–114°C., respectively).

Acetylene tetrachloride and chloroform were purified by washing with alkali, drying over anhydrous calcium chloride and over phosphorus pentoxide, and by repeatedly fractional distillations under reduced pressure. Dimethylformamide (analytical grade reagent) was repeatedly distilled after dehydration over anhydrous sodium sulfate.

Polymerization Procedure

Given amounts of monomers, initiator, and solvent were weighed into a glass ampule (10 mm. diameter × 100 mm.) cleaned as described previously.[2] The ampule was sealed under nitrogen atmosphere, immersed in a constant temperature bath, and the polymerization was carried out with mechanical shaking.

After the run the contents were added dropwise to a large amount of methanol with vigorous stirring in order to precipitate the formed polymer. The polymer was collected on a glass filter, washed repeatedly with methanol to remove the remaining monomers, and dried over phosphorus pentoxide at 50°C. under vacuum until constant weight was obtained.

The relative viscosity in acetylene tetrachloride was measured at 30 ± 0.01°C. with an Ostwald viscometer.

RESULTS AND DISCUSSION

Bulk Polymerization of 2-Phthalimido-1,3-butadiene

Table I shows the results of the bulk polymerization at 85°C., the melting point of this monomer. This procedure gave, without exception, a transparent mass which was insoluble in any solvent and only swollen on treatment with such solvents as acetylene tetrachloride and ethylene dichloride. In contrast to the case of bulk polymerization of 1-phthalimido-1,3-butadiene or 1-succinimido-1,3-butadiene,[2] this monomer has a strong tendency to give crosslinked polymer.

TABLE I
Bulk Polymerization of 2-Phthalimido-1,3-butadiene

Butadiene monomer	Wt. monomer, mg.	BPO, mole-%	Temperature, °C.	Time, hr.	Yield, %
2-PB	381	0	85	2.5	gel
	500	0.1	85	2.5	gel
	500	0.5	85	2.5	gel
	500	1.0	85	1.0	gel
1-PB[2]	500	0	116	1.0	53.9
	500	0.5	116	5.0	90.5
1-SB[2]	500	0	76	5.0	4.2
	500	0.5	76	5.0	89.5

Solution Polymerization of 2-Phthalimido-1,3-butadiene

Radical Process. To prepare the soluble polymer sample, the polymerization in acetylene tetrachloride was carried out with the use of benzoyl peroxide as a free-radical source, and the desired polymer was obtained in good yield. This solvent for the system was chosen here, since the better solvent for the polymer resulted in the better polymer yield in the polymerization of 1-phthalimido-1,3-butadiene as previously reported.[2] A comparison with the results for 1-phthalimido- and 1-succinimido-1,3-butadienes obtained under the same conditions shows that polymerization of 2-phthalimido-1,3-butadiene proceeds more rapidly than that of such 1-imidobutadienes (Fig. 1). This conclusion seems to agree with that of Carothers obtained in a discussion[8] of the influence of structural variations on the relative rates of various diene polymerizations. The phthalimido group in this monomer is located on the C_2 position on the internal side of the butadiene chain, and therefore gives less steric hindrance to reactive centers of the butadiene chain than in the other isomeric 1-imidobutadienes. Although we should not conclude that this faster rate is attributable solely due to the steric effect, steric hindrance may play some role in the whole explanation, since these imido groups are more bulky than either the butadiene chain itself or than the substituents which Carothers has referred to in his report as alkyls, halogens, and phenyl.

The reduced viscosity of the polymer obtained by solution polymerization

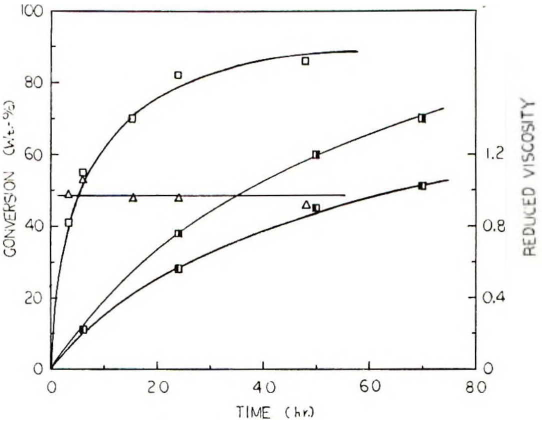

Fig. 1. Solution polymerization of 2-phthalimido-1,3-butadiene at 60°C.: (□) conversion of 2-PB; (◨) conversion of 1-SB; (◧) conversion of 1-PB; (△) reduced viscosity of poly-2-PB (0.50% in acetylene tetrachloride). Monomer, 300 mg.; BPO, 1.0 mole-%; ethylene dichloride, 1.00 ml.

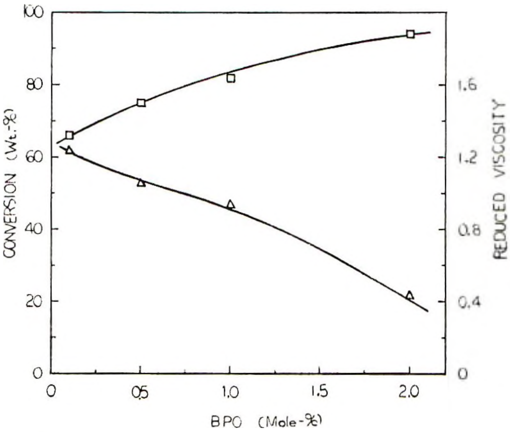

Fig. 2. Solution polymerization of 2-phthalimido-1,3-butadiene at 60°C.: (□) monomer conversion; (△) viscosity (0.50% in acetylene tetrachloride). Monomer, 300 mg.; ethylene dichloride, 1.00 ml.; time, 24 hr.

was found to remain at a virtually constant value close to 1.0 and varied only very slightly with changes of the polymerization time (Fig. 1). This fact shows that the crosslinking could be retarded by the solution process. An analogous retardation to crosslinking was also observed in the copolymerization with various vinyl monomes (Table III), where we obtained soluble polymers even in the bulk processes under conditions giving high monomer conversion. Therefore, it appears possible to avoid gelation of this polymer on polymerization in a slightly diluted system.

Figure 2 shows the relations between the initiator concentration and polymer yield and the reduced viscosity. It is clear that decreasing the initiator concentration decreased the polymer yield and increased the polymer viscosity, as expected before from most results of vinyl and diene polymerizations.

Cationic Process. The cationic polymerization of 2-phthalimido-1,3-butadiene was attempted in acetylene tetrachloride or chloroform solution at 20°C. with boron trifluoride etherate or stannic chloride as the catalyst. However, no formation of poly-2-phthalimido-1,3-butadiene was observed while 1-phthalimido-1,3-butadiene could easily polymerize under such the same conditions[3] (Table II).

TABLE II
Cationic Polymerizations

Butadiene monomer	Wt. monomer, mg.	Catalyst	Catalyst, concn., mole-%	Solvent	Vol. solvent, ml.	Temp., °C.	Time, hr.	Yield, wt.-%
2-PB	200	$SnCl_4$	10	$CHCl_3$	1.33	20	190	0
	271	$BF_3 \cdot Et_2O$	10	$(CHCl_2)_2$	1.18	20	212	Trace
1-PB	300	$SnCl_4$	10	$CHCl_3$	2.00	20	210	80.2
	300	$BF_3 \cdot Et_2O$	10	$CHCl_3$	2.00	20	210	51.5

Polymer Properties. The soluble polymer of 2-phthalimido-1,3-butadiene obtained by radical polymerization in solution is a colorless, transparent resin having a softening point of 160–170°C. and is soluble in acetylene tetrachloride, chloroform, ethylene dichloride, dioxane, dimethylformamide, and nitrobenzene but insoluble in carbon tetrachloride, hydrocarbons, carbinols, and water.

Chemical Structure of the Poly-2-phthalimido-1,3-butadiene

Figure 3 shows the spectra of a sample of the soluble polymer obtained by radical polymerization in solution and of monomer for a comparison of their characteristic absorption bands.

It is concluded that 1,4- or 4,1-addition predominated over 3,4- or 4,3-addition because the vinylidene absorptions in the polymer were less than half of those in the monomer. The possibility of 1,2-addition was eliminated because no vinyl absorptions were detected in the polymer.

Although the infrared data could not be used to decide between 1,4- or 4,1-additions, steric arguments lead us to the conclusion that 4,1-addition was preferred. Similar arguments favor 4,3- over 3,4-additon.

The mode of monomer arrangement in the polymer chains is generally believed to be influenced almost exclusively by resonance stabilization and by steric reasons. However, as shown clearly by the ultraviolet spectroscopic study in the previous paper,[1] the phthalimido group in this monomer is too bulky to conjugate with the adjacent ethylenic double bond of the butadiene chain, and the steric hindrance to the chain will therefore be much stronger both in the polymer and in the polymer radical than in the monomer. Hence, only the ethylenic double bond adjacent to the radical

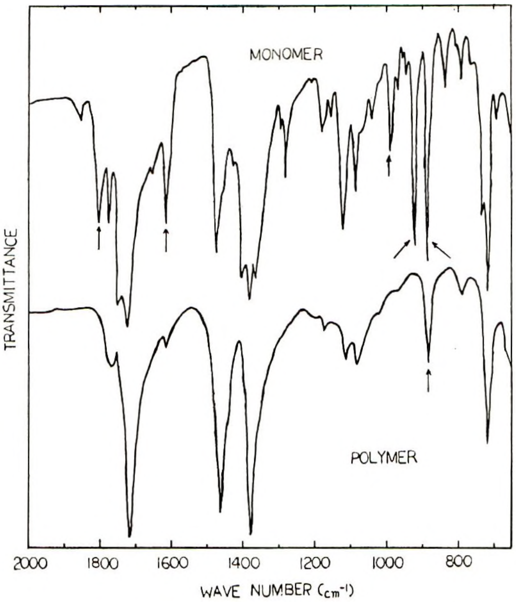

Fig. 3. Infrared spectra of 2-PB and its polymer (Nujol).

center will contribute to and influence the resonance stabilization more than the phthalimido group will. Consequently, we suppose that the effect of resonance stabilization of polymer radicals by an adjacent ethylenic double bond will be virtually the same among the four kinds of the monomer arrangement described above as well as in the case of polymerization of unsubstituted-1,3-butadiene, and that only the steric hindrance by phthalimido group will have a strong influence on details of the polymer growth and will mainly govern the mode of monomer arrangement in the polymer chain; this results in the occurrence of the 4,1-arrangement as the predominant form and the 4,3-arrangement to a lesser extent. In fact, the polymer structure resulting from 1,2-addition polymerization involves such especially strong steric hindrance that it is impossible to build up the molecular model by means of the Stuart models.*

As for the strong tendency to crosslink during the homogeneous bulk polymerization of this monomer, the following explanation is plausible. In this process there is a certain chance for the vinylidene group to remain dangling along the polymer chain as described above. This unsaturated group will have more chances to contribute to further polymerization and network formation than the internal ethylenic double bond in the polymer chain and the pendant 1,2-disubstituted one as such obtained in the vinyl polymerization of 1-phthalimido-1,3-butadiene.[10b] However, this network formation could be completely retarded in dilute systems such as in solution polymerization and in copolymerizations even in bulk state.

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* Flory discussed the fact that the 1,2-arrangement, even in isoprene polymerization, gave a steric hindrance type polymer.[10a]

The fact that 2-phthalimido-1,3-butadiene could not be polymerized cationically may be explained as follows. While in this case cationic polymerization by 1,4- or 1,2-addition should be expected exclusively from the result of the hydrogen chloride addition to this imidobutadiene, this monomer can not accept the polymerization modes other than the 4,1 or 4,3, because of the above-mentioned steric effect; that is, cations can not attack the C_4 positions of this monomer[9] and can not induce the polymerization.

Copolymerizations of 2-Phthalimido-1,3-butadiene

Copolymerizations with acrylonitrile (AN), methyl methacrylate (MMA), styrene (St), vinyl acetate (VAc), and *N*-vinylphthalimide (VPI) were carried out, either in bulk or in solution, and benzoyl peroxide was employed as a free-radical source in a concentration of 1.0 mole-% in each case (Table III).

The infrared spectra of the resulting copolymers (Fig. 4) and the analytical data in Table III show that this imidobutadiene can copolymerize with all of such vinyl monomers, but vinyl acetate enters into the copolymer

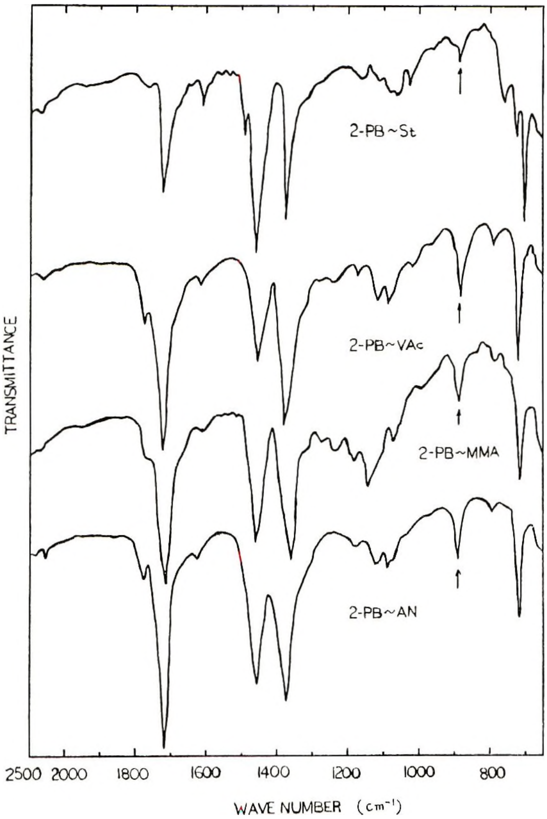


Fig. 4. Infrared spectra of 2-PB copolymers (Nujol).

TABLE III

Radical Copolymerizations of 2-Phthalimido-1,3-butadiene with Various Comonomers

Wt. 2-PB, mg.	Comonomers	Wt. comonomer, mg.	Mole ratio	Solvent	Vol. solvent, ml.	Temp., °C.	Time, hr.	Yield, wt.-%	N, %[a]	2 PB in polymer, mole-%[b]
199	St	936	1:9	—		60	17.0	61.2	2.14, 2.14	18.6
199	VAc	774	1:9	—		60	17.0	19.1	6.20, 6.24	77.6
299	VPI	779	1:3	—		100	3.5	54	7.18, 7.31	77.1
373	VPI	651	1:2	ATC[c]	1.00	100	20.0	87.1	7.22, 7.27	77.1
199	MMA	300	1:3	ATC	0.50	100	2.0	100	—	—
199	MMA	300	1:3	ATC	1.00	60	3.5	27.9	4.88, 4.69	51.8
199	AN	212	1:4	DMF[d]	0.70	60	5.5	46.6	9.76, 9.79	61.7

[a] Determined by the micro Dumas method.

[b] Calculated from the average of nitrogen content.

[c] Acetylene tetrachloride.

[d] Dimethylformamide.

TABLE IV

Copolymerization of 2-Phthalimido-1,3-butadiene (M_1) with Styrene (M_2) at 60°C.[a]

Weight, mg.		Mole × 10^{-4}		DMF, ml.	Time, hr.	Yield, wt.-%		m_1, mole-%	m_2, mole-%
M_1	M_2	M_1	M_2						
99.5	988	5	95	0.50	2.0	6.0	2.97 2.93	26.8	73.2
199	936	10	90	0.50	3.0	10.0	4.34 4.45	46.6	53.4
299	468	15	45	1.00	2.5	8.3	5.71 5.69	69.0	31.0
398	312	20	30	1.00	2.0	7.4	6.18 6.16	78.7	21.3

[a] Benzoyl peroxide (1.0 mole-%) was used in each case.

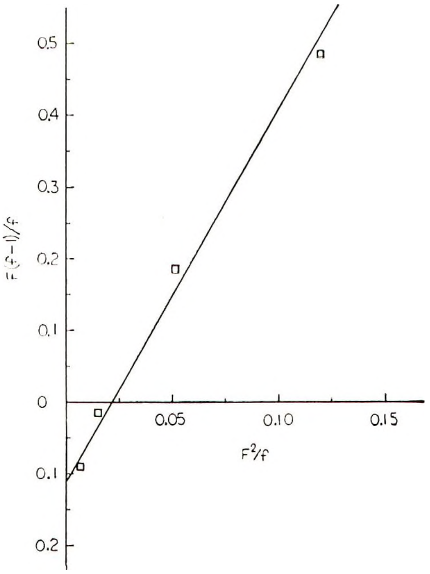


Fig. 5. Fineman-Ross plot for determining reactivity ratios.

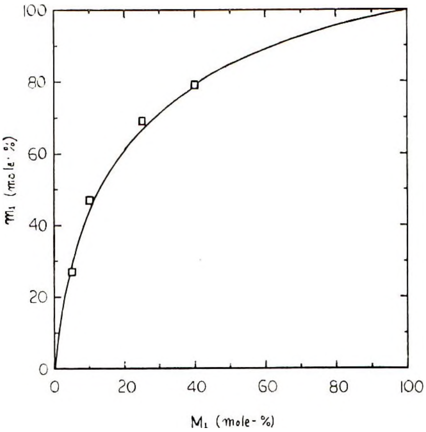


Fig. 6. Composition curve for the copolymerization of 2-PB (M_1) with styrene (M_2).

somewhat less readily than the other comonomers. The infrared spectra also indicate very clearly that all the copolymers contain a certain amount of pendant vinylidene group as found in the case of the soluble homopolymer of 2-phthalimido-1,3-butadiene.

In an attempt to determine the relative reactivity ratios for the system of 2-phthalimido-1,3-butadiene and styrene, the copolymerization by benzoyl peroxide was carried out statically in dimethylformamide at 60°C. All of the procedures were carried out to no further than 10% conversion to determine the beginning stage of each copolymerization. The results are indicated in Table IV, where M_1 and M_2 represent the monomer feeds

(2-phthalimido-1,3-butadiene and styrene, respectively) and m_1 and m_2 are the molar fractions of the monomers in the resulting polymers. Following the Fineman-Ross method,[11]

$$F(f-1)/f = r_1(F^2/f) - r_2$$

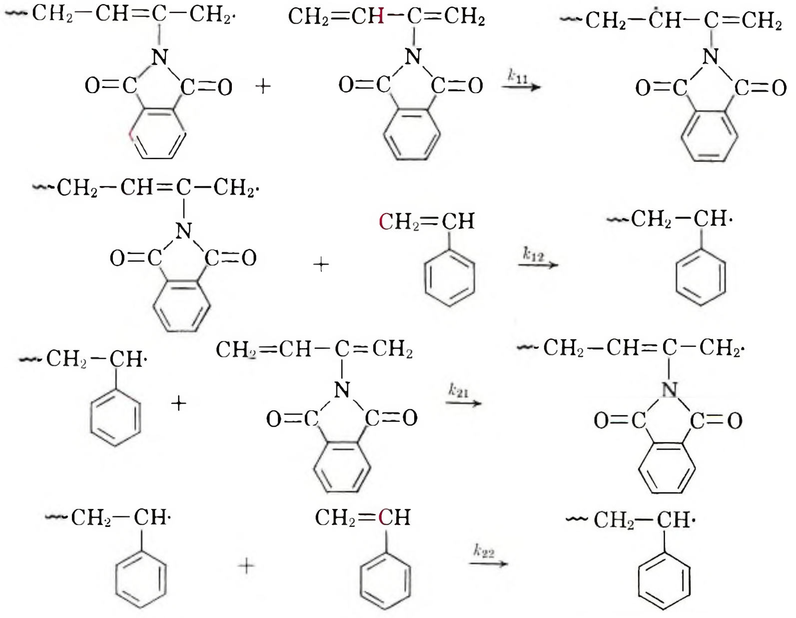
where $F = M_1/M_2$ and $f = m_1/m_2$. The results shown in Table IV followed a straight line, shown as in Figure 5. Thus, we obtained

$$r_1(\text{2-PB}) = 5.2 \pm 0.5 \qquad (1)$$

$$r_2(\text{St}) = 0.11 \pm 0.02 \qquad (2)$$

The copolymer composition curve for this system calculated from the above r_1 and r_2 values, is shown in Figure 6, and gave the best fit to the experimental data.

The reaction scheme of this copolymerization can be illustrated as shown in eqs. (3)–(6).



(3)

(4)

(5)

(6)

Since the definitions of r_1 and r_2 are given by the relations, $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, we estimated

$$k_{11} = 5k_{12} \qquad (7)$$

$$k_{21} = 9k_{22} \qquad (8)$$

Q–e Values of 2-Phthalimido-1,3-butadiene

The Q and e parameters for this monomer were calculated according to the Alfrey-Price method[12] by using the values $Q = 1.0$ and $e = -0.8$ for styrene and the values of eqs. (1) and (2). Thus,

$$Q_1 = 5.0 \tag{9}$$

$$e_1 = -0.05 \tag{10}$$

The fact that the e value, showing an electronic contribution of the substituent to the butadiene chain, is very close to zero, can explain the ability of this monomer to copolymerize with acrylonitrile having a higher e value of 1.2 as well as with styrene having a lower e of -0.8.

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Résumé

Le 2-phthalimido-1,3-butadiène (2-PB) a été polymérisé radicalairement et thermiquement en bloc et en solution. Tandis que le polymère en solution est soluble dans certains solvants tels que des hydrocarbures halogénés, le dioxane et le diméthylformamide, et présente un point de ramollissement entre 160 et 170°C, le polymére obtenu en bloc était insoluble dans n'importe quel solvant et gonflait uniquement par immersion dans des solvants cités ci-dessus. La viscosité réduite du polymère soluble en solution était environ 1.0 et cette valeur restait pratiquement constante tout en changeant la durée de la polymérisation. Similairement la polymérisation cationique dans le tétrachlorure d'acétylène ou dans le chloroforme à 20°C, a été essayée en utilisant un catalyseur cationique tel que le fluorure de bore, le chlorure d'étain, mais on n'a observé aucune formation de polymère. Ce monomère réagit préférentiellement avec l'acrylonitrile, le méthacrylate de méthyle, le styrène, le N-vinyle phthalimide, formant des copolymères, cependant quelque peu plus difficilement avec l'acetate de vinyle. Les rapports de réactivité monomèrique au cours de la copolymérisation avec le styrène ont été calculées par la méthode de Fineman et Ross et trouvés egaux à r_1 (2-PB) $= 5{,}2 \pm 0{,}5$ et r_2 (styrène) $= 0{,}11 \pm 0{,}02$ respectivement, pour lesquels les paramètres Q et e ont été évalués être égaux à $Q = 5{,}0$ et $e = -0{,}05$. Etant donné que cette dernière valeur de e est très voisine de 0, on peut aisément expliquer le fait que ce monomère copolymérise aussi bien avec l'acrylonitrile qui a une valeur aussi positive que e (1,2) et avec le styrène qui a une valeur considérablement négative ($-0{,}8$).

Zusammenfassung

2-Phthalimidobutadien-1,3 (2-PB) wurde radikalisch und thermisch in Substanz und in Lösung polymerisiert. Während das in Lösung erhaltene Polymere in einigen Lösungsmitteln wie gewissen Halogenkohlenwasserstoffen, Dioxan und Dimethylformamid löslich war und einen Erweichungspunkt im Bereich von 160 bis 170°C besass, war das in Substanz erhaltene in allen Lösungsmitteln unlöslich und zeigte in den angeführten Lösungsmitteln nur Quellung. Die reduzierte Viskosität der löslichen, in Lösung erhaltenen Polymeren lag bei 1,0, und dieser Wert war von der Polymerisationsdauer nahezu unabhängig. Versuche zur kationischen Polymerisation in Acetylentetrachlorid oder in Chloroform bei 20°C mit einem kationischen Katalysator wie Bortrifluorid und Zinnchlorid lieferten kein Polymeres. Das Monomere reagierte vornehmlich mit Acrylnitril, Methylmethacrylat, Styrol und *N*-Vinylphthalimid unter Bildung der entsprechenden Copolymeren, jedoch etwas weniger leicht mit Vinylacetat. Die Monomerreaktivitätsverhältnisse für die Copolymerisation wurden nach Fineman und Ross zu r_1 (2-PB) = 5,2 ± 0,5 und r_2 (Styrol) = 0,11 ± 0,02, berechnet. Daraus wurden die Q,e-Parameter zu $Q = 5{,}0$ und $e = -0{,}05$ bestimmt. Da der e-Wert fast Null ist, kann man leicht verstehen, dass dieses Monomere gute Copolymerisation sowohl mit Acrylnitril mit einem hohen positiven e-Wert (1,2), als auch Styrol mit einem beträchtlich negativen (−0,8) zeigt.

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Monomer–Polymer Equilibria of Deuterated α-Methylstyrenes

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Synopsis

The equilibria between α-trideuteromethyl-β,β-dideuterostyrene, α-methyl-2,3,4,5,6-pentadeuterostyrene, and perdeutero-α-methylstyrene and their respective polymeric anions in tetrahydrofuran have been investigated between 253 and 308°K. The heat and entropy changes were both increased by deuteration of the alkyl group. Qualitatively the effect observed appears best explained by the premise that a lowering of steric repulsions occurs with deuterium and hence the effective volume for deuterium is less than that for hydrogen.

INTRODUCTION

Thermodynamic data on polymerization processes are relatively meager, though a great practical need exists for reliable information in this area. Equilibrium studies can give very complete knowledge, provided the system under study has no side reactions and the reactions are readily reversible under experimental conditions. Another very desirable feature is that the system be capable of being quenched, after which the extent of reaction can be leisurely determined. Unfortunately only a few monomer–polymer systems appear to be capable of study in this fashion.

Addition polymerization processes occur, in the main, by the addition of an olefinic monomer M to some active growing species P_i^* where i denotes the number of monomer units in the chain:

$$P_i^* + \mathrm{M} \underset{k_d}{\overset{k_p}{\rightleftharpoons}} P_{i+1}^*$$

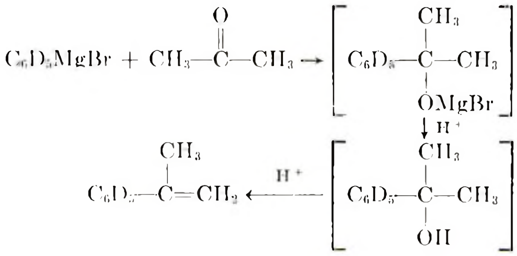
Since i is, in general, large, we consider all P_i's as identical and hence the equilibrium constant is simply the reciprocal of the equilibrium monomer concentration. The active species can in theory[1] be radicals, cations, or anions with no effect upon the position of the equilibrium.

Monomer–polymer equilibria and the related thermodynamic functions for addition polymerizations have been the subject of several investigations.[2–13] Experience has, in general, suggested the occurrence of side reactions with free radicals as active species and transfer reactions and deactivation with cationic systems. However, Szwarc[14–16] demonstrated that anionic polymerization systems actuated by sodium naphthalene can proceed with the absence of transfer and termination reactions. As a result of this development, homogeneous anionic polymerizations involving stable propagation centers have attracted considerable attention over the past several years.

The reaction between α-methylstyrene and aromatic–alkali metal complexes results in the generation of stable polymercarbanions. Hence this system is ideal for the study of the polymerization–depolymerization equilibrium, particularly so since the equilibrium is mobile in the temperaturer ange where the polymercarbanion is stable. This monomer has been studied with good success by several groups of workers.[3,4,6–8] This communication is concerned with the results obtained in an investigation of the chemical equilibria between α-trideuteromethyl-β,β-dideuterostyrene, α-methyl-2,3,4,5,6-pentadeuterostyrene, and perdeutero-α-methylstyrene and their polymeric anions. These measurements were carried out to ascertain the changes arising in the thermodynamic functions of the α-methylstyrene monomer–polymer system when deuterium is incorporated in the above-designated sites. The systems were studied in the solvent tetrahydrofuran (THF). Sodium biphenyl and sodium naphthalene were used to produce the anions.

EXPERIMENTAL

The deuterated α-methylstyrenes were all prepared by the analogous reaction of phenylmagnesium bromide with acetone, except that the appropriately deuterated reagent was substituted depending upon the monomer desired. For example, the preparation of α-methyl-2,3,4,5,6-pentadeuterostyrene was as shown in eq. (1).



$$C_6D_5MgBr + CH_3COCH_3 \rightarrow \left[C_6D_5C(CH_3)_2OMgBr\right] \xrightarrow{H^+} \left[C_6D_5C(CH_3)_2OH\right] \xrightarrow{H^+} C_6D_5C(CH_3){=}CH_2 \qquad (1)$$

Since this reaction produces tertiary alcohols, advantage was taken of the fact that these tertiary alcohols readily dehydrate under acid conditions to yield the olefin directly. Only in the case of perdeutero-α-methylstyrene was the yield of monomer considerably lowered. Apparently, the use of deuterated sulfuric acid in the hydrolysis reaction introduced undesirable side reactions, sulfonation as well as polymerization.[17] Since all the deuterated α-methylstyrenes prepared in this article are heat-sensitive in the presence of acid catalyst, small amounts of acidic by-products may cause the olefin to dimerize under the conditions for distillation and thus lower the yield of monomer.

The impurities in the monomer fraction appear to be condensation products of acetone, such as mesityl oxide and mesitylene. The infrared spectrum of the impure monomer fraction shows a carbonyl band at 1685 cm.$^{-1}$ indicative of α,β-unsaturated ketones.[18] This band is absent in the spectrum of pure deuterated α-methylstyrene.

Pentadeuterobromobenzene

Hexadeuterobenzene and acetone-d_6 (99.5 atom-% D) were purchased from Merck, Sharp and Dohme.

For the preparation of pentadeuterobromobenzene,[19] we used the procedure of Erlenmeyer.[20] From 1 kg. (11.8 mole) of hexadeuterobenzene, 40 g. iron filings and 1.92 kg. (12 mole) of bromine, we obtained 1.44 kg. (75% yield) of pentadeuterobromobenzene, b.p. 155–155.5°C./760 mm. Mass spectrometric analysis for isotopic purity gave 97.8% pentadeuterobromobenzene and 2.2% impurity.

α-Trideuteromethyl-β-β-dideuterostyrene

Into a 3-liter three-necked flask, fitted with a stirrer, 2-liter addition funnel, and reflux condenser, was placed 168 g. (7.0 g.-atom) of magnesium turnings. The flask and magnesium were flamed gently in a nitrogen atmosphere to remove moisture. A solution of 500 ml. of anhydrous ether and 25 ml. of bromobenzene and a small crystal of iodine were added to the flask. The mixture was stirred and after a short induction period, the reaction proceeded satisfactorily. When the initial reaction subsided, the remaining bromobenzene (1 kg., 6.37 mole) in 1 liter of anhydrous ether was added at a rate to maintain a gentle reflux. The addition required 6 hr. The mixture was stirred at room temperature for 15 hr. more.

The Grignard solution was then filtered into a 2-liter addition funnel attached to a 5-liter three-necked flask containing a stirrer and reflux condenser. The flask contained 450 g. (7 mole) of acetone-d_6 in 1 liter of anhydrous ether under a nitrogen atmosphere. The Grignard solution was added dropwise to the stirred solution and the white salt precipitated immediately. The addition was completed in 6 hr., and the mixture was stirred 15 hr. more at 25°C. At the end of this time, the flask was cooled in an ice-water bath and a chilled solution of 600 ml. of concentrated hydrochloric acid in 1400 ml. of water was added dropwise over a 4-hr. period. The salt dissolved, and the other layer changed in color from yellow to deep red. The organic layer was separated and while washing with 1000 ml. (in two portions) of water, the color changed back to yellow. The ether solution was dried (Na_2SO_4) for 48 hr. After removal of the solvent, the α-trideutero-β,β-dideuterostyrene was flash-distilled at 40–45°C./1.5 mm. The crude yield of monomer was 554 g. (71.3%). Vapor-phase chromatography (VPC) showed a 5% impurity of two components before the main monomer peak. These impurities were effectively removed by fractionation at 86.5°C./30 mm. The progress of the fractionation was followed by VPC analysis of the initial fractions. A total of 66 g. of forerun was col-

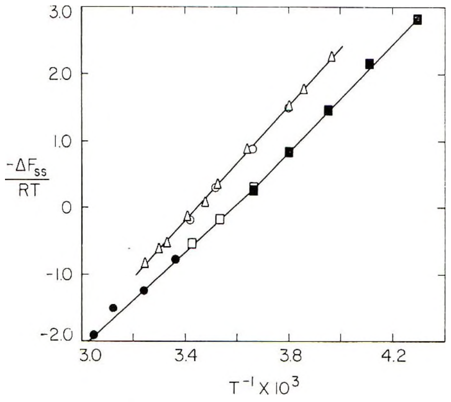


Fig. 1. Polymerization of α-methylstyrenes, free energy function vs. reciprocal temperature: (△) α-trideuteromethyl-β,β-dideuterostyrene; (○) perdeutero-α-methylstyrene; (□) 2,3,4,5,6-pentadeutero-α-methylstyrene; (●) α-methylstyrene, data of McCormick;[3] ■ α-methylstyrene, data of Worsfold and Bywater.[4]

TABLE I
Isotopic Composition of Deuterated Monomers

	$D_2C{=}\overset{CD_3}{\overset{\vert}{C}}{-}C_6H_5$		$H_2C{=}\overset{CH_3}{\overset{\vert}{C}}{-}C_6D_5$		$D_2C{=}\overset{CD_3}{\overset{\vert}{C}}{-}C_6D_5$	
	Preparation I	Preparation II				
d_5	54.7	72.0	d_5	97.7	d_{10}	88.0
d_4	31.9	24.7	d_4	2.3	d_9	10.5
d_3	10.7	3.3			d_8	1.2
d_2	2.3				d_7	0.2
d_1	0.3				d_6	0.1
D in alkenyl group, atom-%	88	92	D in phenyl group; atom-%	99.5	D, atom-%	98.6

lected before the pure α-trideutero-β,β-dideuterostyrene (377 g.) was obtained. The isotopic purity is recorded in Table I.

The residue (110 g.), mainly dimers, b.p. 140–142°C./3 mm., was not investigated further.

α-Methyl-2,3,4,5,6-pentadeuterostyrene

The same technique as described above was used to prepare α-methyl-2,3,4,5,6-pentadeuterostyrene. The Grignard reagent, prepared from 725 g. (4.48 mole) of pentadeuterobromobenzene and 111 g. (4.63 g.-atom) of magnesium turnings in 1.5 liters of anhydrous ether, was added to 255 g. (4.40 mole) of dry acetone in 1 liter of anhydrous ether. The resulting salt was hydrolyzed with a solution of 300 ml. of concentrated hydrochloric acid in 800 ml. of water. After removal of the ether, 365 g. (65.5% yield) of α-methyl-2,3,4,5,6-pentadeuterostyrene was obtained by flash distillation. Fractionation of the monomer was accomplished at 85.5°C./27 mm. Similar impurities as described previously were removed in the first 50 g. of distillate. The results of mass spectrometric analysis of the purified α-methyl-2,3,4,5,6-pentadeuterostyrene (283 g.) are shown in Table I.

Perdeutero-α-methylstyrene

The Grignard reagent, prepared from 725 g. (4.48 mole) of pentadeuterobromobenzene and 111 g. (4.63 g.-atom) magnesium turnings in 1 liter of anhydrous ether, was added to 282 g. (4.40 mole) of acetone-d_6 in 1 liter of anhydrous ether. The resulting salt was hydrolyzed with a solution of D_2SO_4 (prepared from 160 ml. of liquid sulfur trioxide in 320 g. of deuterium oxide). Additional salts were formed and they were filtered from the organic layers. The precipitate was stored in a vacuum desiccator. From the organic filtrate, after removal of the solvent *in vacuo*, only 38 g. of perdeutero-α-methylstyrene was obtained by flash distillation. The main components of this fraction were high-boiling (b.p. >83°C./1 mm.) and evolved a small amount of gas (probably SO_3) on further distillation. An additional monomer fraction (127 g.) was obtained by dissolving the precipitated salts in 200 g. of D_2O and extracting with 500 ml. of anhydrous ether. After drying, the ether was removed *in vacuo*, and the combined monomer samples were fractionated at 79.5–80°C./15 mm. The impurities were concentrated in the first 50 g. of distillate. The results of mass spectrometric analysis of the pure perdeutero-α-methylstyrene (101 g.) is shown in Table I.

A detailed discussion of the techniques and experimental procedures for anionic polymerization is available elsewhere.[4,6,21,22] Experimental manipulations were accomplished with the aid of a high vacuum apparatus, since the exclusion of water, oxygen, and other impurities to which organosodium compounds are sensitive is necessary.

All monomer and solvent purifications, initiator preparations, and polymerization reactions were carried out either directly on the vacuum line or in sealed, evacuated vessels. All reaction vessels and flasks were constructed of Pyrex glass and were thoroughly flamed under high vacuum to remove adsorbed impurities.

Predetermined amounts of monomer, THF, and initiator were mixed in a reaction vessel which was kept at constant temperature until deactivation of the carbanions was accomplished by several drops of water. The time of reaction was 24 hr. This reaction time is in excess[23] of that necessary to permit attainment of the equilibrium between monomer and polymer at a temperature of −40°C. for α-methylstyrene. For this work, under identical conditions, reaction times of 10–12 hr. resulted in equilibrium monomer concentrations identical to those attained with the time limit of 24 hr. Although the equilibrium can be influenced by polymer–solvent interaction,[24] we found no large effect resulting from varying the initial monomer concentration $[\mathrm{M}]_0$ over a limited range. Upon cessation of the reaction, the polymer was isolated in methanol, dried, and its weight determined. Corrections for changes in the specific volume of monomer and solvent were the same as those used elsewhere.[4]

RESULTS

A series of experiments at various monomer concentrations and over a temperature range of −20 to 35°C. were carried out and the equilibrium concentration of monomer, $[\mathrm{M}]_e$, determined. The values for the change in Gibbs free energy for the polymerization–depolymerization equilibria can be obtained from eq. (2)[4,25]

$$-\Delta F_{ss}/RT = \ln 1/[\mathrm{M}]_e \qquad (2)$$

for a standard $1M$ solution. The subscripts in the free energy term denote, respectively, the state of monomer and polymer.[26] The results obtained are shown in Table II and the computed free energy values are presented in Figure 1. Values of ΔH and ΔS calculated from Figure 1 are presented in Table III along with those obtained by McCormick[3] and by Worsfold and Bywater[4] for α-methylstyrene. Results are listed only for α-tri-

TABLE II
Equilibrium Monomer Concentration and Free Energy Data

Monomer	Temp., °K.	$[\mathrm{M}]_0$, mole/l.	$[\mathrm{M}]_e$, mole/l.	$-\Delta F_{ss}/RT$, kcal.
α-Trideuteromethyl-β,β-dideuterostyrene	308.0	3.20	2.27	−0.82
	303.0	2.80	1.80	−0.59
	303.0	3.60	1.85	−0.62
	300.0	2.11	1.71	−0.54
	298.0	2.20	1.21	−0.19
	293.0	2.15	1.13	−0.12
	288.0	1.24	0.94	0.11
	283.0	1.05	0.73	0.32
	283.0	1.07	0.73	0.32
	274.0	1.01	0.41	0.89
	274.0	1.08	0.42	0.86
	263.0	0.58	0.23	1.47
	263.0	1.19	0.23	1.47
	263.0	1.15	0.23	1.47
	259.0	1.01	0.17	1.76
	253.0	1.16	0.10	2.28
α-Methyl-2,3,4,5,6-pentadeuterostyrene	293.0	1.78	1.68	−0.53
	283.0	1.40	1.17	−0.16
	273.0	1.15	0.74	0.30
Perdeutero-α-methylstyrene	292.6	1.73	1.25	−0.22
	284.0	1.33	0.75	0.29
	273.0	0.88	0.41	0.89
	263.0	1.00	0.23	1.47

TABLE III
Heats and Entropies of Polymerization

Monomer	ΔH_{ss}, kcal./mole	ΔS_{ss}, cal./mole-deg.
α-Methylstyrene[a]	−6.96	−24.8
α-Methylstyrene[b]	−8.02	−28.75
α-Trideuteromethyl-β,β-dideuterostyrene	−8.6	−29.6

[a] Data of McCormick.[3]

[b] Data of Worsfold and Bywater.[1]

deuteromethyl-β,β-dideuterostyrene for which the most extensive measurements were made. Statistical evaluation of the data obtained here indicates a maximum error of ±0.2 kcal. in ΔH and ±0.6 e.u. in ΔS. Thus, while the change in ΔF, resulting from deuteration of the alkenyl groups, is indisputable, the amount of the change in either ΔH or ΔS is less certain. For the other two monomers, it is concluded that for the perdeutero-α-methylstyrene the data are indistinguishable from those for the listed deutero monomer and the data for ring-deuterated compound indistinguishable from those for α-methylstyrene.

Good agreement was achieved with the data of Worsfold and Bywater[4] pertaining to the heat and entropy of polymerization of α-methylstyrene when duplicate runs were performed with α-methylstyrene. The effect of the presence of deuterium in the alkenyl group is apparent in a comparison of the respective values of ΔH and ΔS. The presence of deuterium in the phenyl group does not exert any measurable influence on the heat or entropy of the polymerization.

The α-trideuteromethyl-β,β-dideuterostyrene obtained from the second preparation was used for the vast majority of the experiments with that monomer. No detectable difference was uncovered pertaining to the polymerization behavior of the material obtained in the two preparations.

DISCUSSION

With the exception of tetrafluoroethylene ($\Delta H_p \simeq -40$ kcal./mole) heats of polymerization progressively decrease as substitutions of organic groups are made in the ethylenic monomer unit. It is clear that steric repulsion[27] accounts for a large part of this decrease. For poly-α-methylstyrene it has been demonstrated[28] that as the degree of polymerization increases the heat of polymerization decreases and that the decrease is greatest at the low DP of 11 compared to the DP of 46. Our data are essentially for DP's of 200–600.

The changes in both ΔH_p and ΔS_p observed here upon deuteration of the alkenyl group then indicates a decrease of steric repulsions along the polymer chains. This effect of deuterium would be expected in the main to be most pronounced with high polymers and in particular with those like poly-α-methylstyrene, where an extremely low heat of polymerization already indicates a very large steric repulsion. The observation reported here seems to lend considerable support to the suggestions of Bartell[29,30] that nonbonded repulsions can account for many so-called secondary isotope effects. It should be made clear that zero-order energy change occurring with deuterium in the C—D bond is not involved here, since this should be the same for both monomer and polymer. Rather, the averge amplitudes of vibrations are lower with deuterium than with hydrogen, at a given kT, and hence in this dynamic system the volume required by deuterium is smaller than that required by protium.

As with many ring-substituted styrenes, the ring deuteration did not measurably affect the thermodynamic parameters, suggesting that the steric strain is produced more by repulsion involving the methyl and methylene group. Since it would seem feasible that the phenyl ring can twist and relieve strain this appears somewhat acceptable. However, since steric strain is not the only factor determining heats of polymerization, there is the possibility that the lack of change with the ring deuteration is the result of certain compensating factors. At the moment it is clear that more experimental work is indicated, particular an investigation of the thermochemistry of isobutylene deuterated at least in its methyl groups [$CH_2{=}C(CD_3)_2$] and α-trideuteromethylstyrene [$CH_2{=}CCD_3C_5H_6$].

Recalling that in the Fisher-Hirschfelder model the fluorine atom is not especially larger than the hydrogen atom, one is led to speculate that the much greater mass of the fluorine atom makes a substantial contribution to the thermal stability of polytetrafluoroethylene. Thus, one can explain, in part at least, the high heat of polymerization for tetrafluoroethylene on the premise that the polymer is more stable rather than on the premise that the monomer is less stable.[31,32]

The results of this work suggest that deuterated polymers may have measurably greater thermal stabilities. Even though the net results of the changes in ΔH and ΔS observed here do not greatly increase the ceiling temperature, changing from 36 to 47°C. in bulk and from 6 to 17°C. in solution, the effect on the depropagation rate may be more important. Also, when compared to α-methylstyrene perdeuterated α-methylstyrene should be more susceptible to free-radical polymerization.

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Résumé

On a étudié entre 253° et 308°K les équilibres entre l'α-trideuterométhyl-β,β-dideuterostyrène, l'α-méthyl-2,3,4,5,6-pentadeuterostyrène et le perdeutero-α-méthylstyrène et leurs anions polymériques respectifs dans le tétrahydrofurane. Les variations d'entropie et de chaleur croissent toutes deux par deutération du groupe alcoylé. Qualitativement l'effet observé apparaît être le mieux expliqué en admettant qu'il y ait diminution de répulsion stérique avec du deutérium et qu'en conséquence le volume effectif pour le deutérium est inférieur à celui de l'hydrogène.

Zusammenfassung

Das Gleichgewicht zwischen α-Trideuteromethyl-β,β-dideuterostyrol, α-Methyl-2,3,4,5,6-pentadeuterostyrol und Perdeutero-α-methylstyrol und den entsprechenden polymeren Anionen in Tetrahydrofuran wurde zwischen 253 und 308°K untersucht. Enthalpie- und Entropieänderung wurden durch Deuterierung der Alkylgruppe vergrössert. Qualitativ scheint sich der beobachtete Effekt am besten durch die Annahme erklären zu lassen, dass mit Deuterium eine Verringerung der sterischen Abstossung eintritt; das effektive Volumen von Deuterium ist daher kleiner als dasjenige von Wasserstoff.

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Polymerization of Cyclosiloxanes. I. Kinetic Studies on Living Polymer–Octamethylcyclotetrasiloxane Systems*

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Synopsis

The kinetics of the anionic polymerization of octamethylcyclotetrasiloxane (D_4) initiated by α-methylstyrene living polymer in tetrahydrofuran was studied. The following kinetic scheme was postulated:

Initiation:

$$S^- + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M^- \qquad K_1$$

Propagation:

$$M_n^- + M \underset{k_4}{\overset{k_3}{\rightleftharpoons}} M_{n+1}^- \qquad K_2$$

where S^- and M represent the initiator and D_4, respectively. At a living end concentration of 0.0377 mole/l. and a monomer concentration of 1.5 mole/l. in tetrahydrofuran at 25°C. the following kinetic data were obtained: $k_1 = 2.3 \times 10^{-4}$ l./mole-sec., $k_2 < 2.3 \times 10^{-5}$ sec.$^{-1}$, $k_3 = 2.75 \times 10^{-2}$ l./mole-sec. $k_4 \approx 1.17 \times 10^{-2}$ sec.$^{-1}$, $K_1 > 10$ l./mole and $K_2 \approx 2.35$ l./mole. The rate constants k_1 and k_3 were found to be dependent on the concentration of anions. This is attributed to the dissociation of ion pairs to free ions at lower concentration. Under the experimental conditions studied the majority of the anions were present in the form of ion pairs. The reactivity of the free ions is about 100 times greater than that of ion pairs. There is no temperature effect on K_2, indicating zero ΔH and positive ΔS in the propagation reaction.

INTRODUCTION

Application of "living" polymer[1,2] to initiate the polymerization of octamethylcyclotetrasiloxane (D_4) was first demonstrated by Morton and his co-workers[3–5] Both styrene and isoprene dianions have been employed to prepare B–A–B type block polymers, where B and A are D_4 and styrene or isoprene, respectively. They also studied the kinetics of the homopolymerization of D_4 initiated by potassium naphthalene in tetrahydrofuran.[4] The first-order rate plot showed an induction period followed by a linear

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portion, from which the pseudo first-order rate constant was calculated. The experimental data indicated a slow initiation followed by a fast propagation reaction.

Since little is known about the nature of the initiation and propagation reactions in the anionic polymerization of D_4, both reactions were considered in this work. The kinetic scheme employed in the present study is shown in eqs. (1)–(3).

Initiation:

$$S^- + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M_1^- \qquad K_1 \qquad (1)$$

Propagation:

$$M_1^- + M \underset{k_4}{\overset{k_3}{\rightleftharpoons}} M_2^- \qquad K_2 \qquad (2)$$

$$\vdots$$

$$M_n^- + M \underset{k_4}{\overset{k_3}{\rightleftharpoons}} M_{n+1}^- \qquad K_2 \qquad (3)$$

where S^- and M represent α-methylstyrene living polymer and D_4, k_1–k_4 refer to the rate constants of the respective reactions, and K_1 and K_2 to their equilibrium constants.

The above mechanism is similar to that of the water–ε-caprolactam system studied by Tobolsky.[6] The equations to be used for calculating K_1 and K_2 are given in eqs. (4)–(9).

$$P = 1/(1 - K_2[M]_\infty) \qquad (4)$$

$$[S^-]_\infty = [S^-]_0/(1 + K_1[M]_\infty P) \qquad (5a)$$

or

$$[S^-]_\infty = [S^-]_0 - \{([M]_0 - [M]_\infty)/P\} \qquad (5b)$$

$$[S^-]_0 = [S^-]_\infty(1 + K_1 P[M]_\infty) \qquad (6)$$

$$[M]_0 = [M]_\infty(1 + K_1 P^2[S^-]_\infty) \qquad (7)$$

$$K_1 = ([M]_0 - [M]_\infty)/P^2[S^-]_\infty[M]_\infty \qquad (8)$$

$$K_2 = [1 - (1/P)]/[M]_\infty \qquad (9)$$

where $[M]_0$, $[M]_\infty$ are initial and equilibrium concentrations of D_4, respectively; $[S^-]_0$, $[S^-]_\infty$ are initial and equilibrium concentrations of living ends, respectively; P is the number-average degree of polymerization per growing polysiloxanolate. Thus if $[S^-]_0$, $[M]_0$, $[M]_\infty$, and P are experimentally determined, K_1 and K_2 can be calculated. Separate experiments can be carried out under the same experimental conditions to determine k_1 and k_3; k_2 and k_4 may then be calculated.

EXPERIMENTAL

Preparation of Living Polymer

The living polymer was prepared by reacting a dilute solution of α-methylstyrene in tetrahydrofuran (THF) with Na–K alloy. The degree of polymerization of the living polymer thus prepared was found to be about 3 by titration. Flame spectrophotometric analysis showed that the counterions consisted of 24 mole-% Na and 76 mole-% K.

Polymerization of D_4

A 30-ml. portion of living polymer solution in THF and 24 ml. of pure D_4 were mixed in a high vacuum system and divided into three precalibrated ampules, each holding 18 ml. of solution. These ampules were sealed off and were distributed among constant temperature baths at 25, 37.4, and 50.8°C. After 24 hr. each ampule was opened and trimethylchlorosilane was introduced immediately to terminate the reaction. The characteristic color of the living polymer disappeared instantly, indicating the formation of dead polymer. The polymer solution was then transferred to an aluminum cup and dried for 24 hr. under high vacuum at 150°C.

Determination of Number-Average Molecular Weight, $\bar{M}_n$

$\bar{M}_n$ was calculated from the melt viscosity by the use of Barry's equation.[7]

$$\log [\eta] = 1 + 0.0123M^{1/2} \tag{10}$$

The melt viscosity was measured with a Haake Rotovisco and determined by using eq. (11):

$$[\eta] = SUK \tag{11}$$

where S is the scale reading, U is the speed of rotation, and K is a constant.

Determination of k_3

A spectrophotometric method was employed to determine k_1. A 10-ml. portion of very dilute solution of living polymer was mixed with 8 ml. of D_4, and the mixture was immediately transferred into an optical cell. The optical density at 340 mμ was continuously recorded with a Cary spectrophotometer; optical cells having optical path lengths ranging from 0.02 to 1 cm. were used.

Determination of k_3

A polydimethylsiloxanolate was employed for the determination of k_3. Hydroxy-end-blocked polydimethyl siloxamer, was obtained by reacting D_4 with excess NH_4OH. The solution of the diol in THF was then slowly added to Na–K alloy in a high vacuum system to form the corresponding siloxanolates. Flame spectrophotometric analysis showed that the final solution contained 0.439% K and 0.135% Na by weight.

Polydimethylsiloxanolate solution (40 ml.) in THF and 32 ml. of D_4 were mixed in a flask. The mixture was distributed among several precalibrated ampules. All ampules were sealed off under high vacuum and placed in a constant temperature bath (25°C.). A polymerization was terminated by opening the ampule, adding trimethylchlorosilane to the reaction mixture, and then shaking the mixture vigorously. The dead polymer was transferred to an aluminum cup and dried in a vacuum oven overnight at 100°C.

RESULTS AND DISCUSSION

The experiment was carried out at 25, 37.4, and 50.8°C. Four samples at each temperature, with $[S^-]_0$ ranging from 0.0109 to 0.155 mole/kg. were investigated. The concentration was expressed as moles per kilogram to avoid the correction for the change in density of the solution. Since the final percentage conversion of D_4 is very sensitive to variation in the initial concentration of D_4,[4,5] the initial composition of the solution was kept approximately constant, i.e., 10 parts of the THF solution of living polymer and 8 parts of pure D_4 by volume.

Equilibrium Concentration of D_4, $[M]_\infty$

Since the monomers at equilibrium were actually a mixture of D_n, where $n \geq 4$, a statistical molecular weight, M_s, was used for the calculation of $[M]_\infty$. M_s was calculated from eq. (12)

$$M_s = \sum_{n=4}^{\infty} X_n M_n \approx 360 \tag{12}$$

where X_n and M_n represent the mole fraction and molecular weight of the cyclo-n-meric species. The values of X_n were obtained from Carmichael's data,[8] as shown in Table I. The values of $[M]_\infty$ thus calculated are shown in Table II. The value of $[M]_\infty$ is, within experimental error, approximately constant. The average $[M]_\infty$ at 25°C. was found to be 0.455 mole/kg. (±10%).

TABLE I

Species	X_n
D_4	0.47
D_5	0.35
D_6	0.12
D_7	0.03
D_8	0.01
D_9	0.02

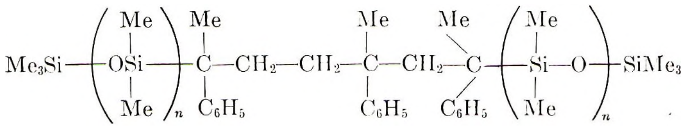
TABLE II
Polymerization of D_4 Initiated by α-Methylstyrene Living Polymer

Temp., °C.	Expt. no.	$[S]_0$, mole/l.	$[M]_0$, mole/kg.	$[M]_\infty$, mole/kg.	P	$[S^-]_\infty$, mole/l.	$K_1 \times 10^2$, kg./mole	K_2, kg./mole
25	1-25	0.115	1.55	0.495	35.0	0.0849	2.05	1.96
	3-25	0.0895	1.54	0.414	49.4	0.0667	1.67	2.37
	4-25	0.0368	1.57	0.447	82.0	0.0230	1.62	2.21
	5-25	0.0109	1.57	0.464	153.3	0.0037	2.74	2.14
37.4	1-37	0.115	1.55	0.525	30.8	0.0817	2.52	1.84
	3-37	0.0895	1.54	0.431	44.4	0.0645	2.01	2.27
	4-37	0.0368	1.57	0.461	77.9	0.0226	1.75	2.14
	5-37	0.0109	1.57	0.461	152.4	0.0037	2.78	2.15
50.8	1-50	0.115	1.55	0.508	28.6	0.0786	3.20	1.90
	3-50	0.0895	1.54	0.439	39.3	0.0615	2.04	2.22
	4-50	0.0368	1.57	0.467	74.4	0.0220	1.93	2.11
	5-50	0.0109	1.57	0.475	157.0	0.0039	2.40	2.09

$[M]_\infty$ is almost independent of temperature. This indicates that the effect of temperature on K_2 is negligible, suggesting that the change in enthalpy on polymerization is zero. Details will be discussed later.

Number-Average Degree of Polymerization, *P*

P was defined as the number-average degree of polymerization per growing polydimethylsiloxanolate anion. Since the polysiloxane chain formed in the present system had the structure I, a correction has to be



I

made to convert $\bar{M}_n$ to P. Thus P was calculated according to eq. (13):

$$P = (\bar{M}_n - 2M_g - \bar{M}_p)/2M_s \tag{13}$$

where $\bar{M}_n$ is the number-average molecular weight of the polymer; $\bar{M}_g$ is the molecular weight of the end group; and $\bar{M}_p$ is the molecular weight of α-methylstyrene living polymer; and M_s is as defined previously.

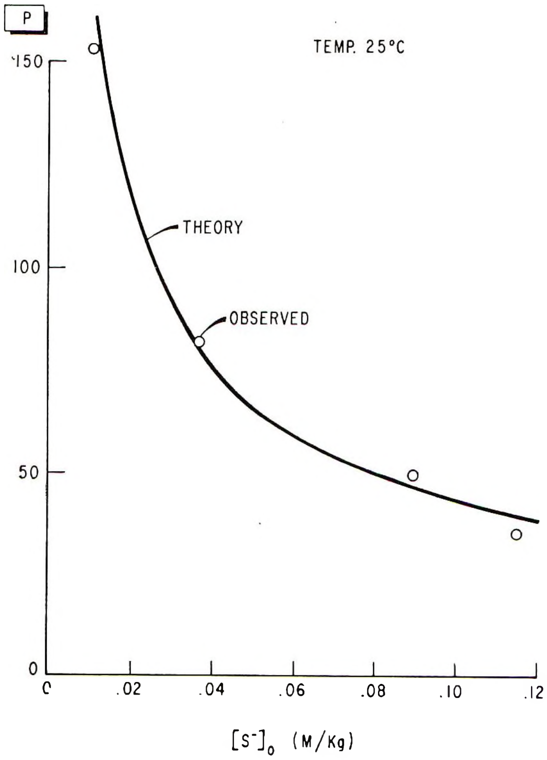


Fig. 1. Plot of P vs. $[S^-]_0$. Temperature 25°C.

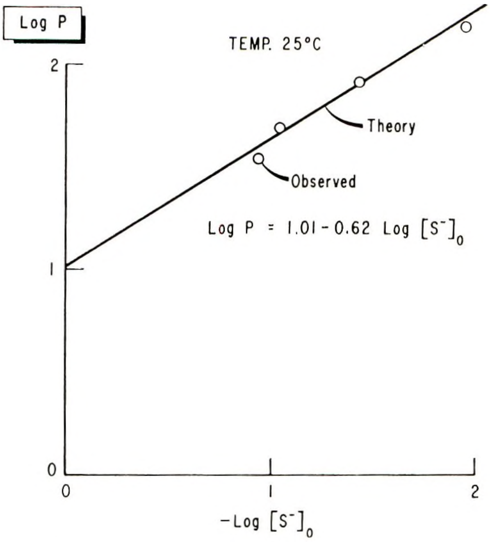


Fig. 2. Plot of log P vs. log $[S^-]_0$. Temperature 25°C.

The calculated values of P are shown in Table II and plotted against $[S^-]_0$ in Figure 1. It is clearly demonstrated that P increases rapidly as $[S^-]_0$ approaches zero. The log P versus log $[S^-]_0$ plot (Fig. 2) is a straight line represented by

$$\log P = 1.01 - 0.62 \log [S^-]_0 \tag{14}$$

The full line curves shown in Figures 1 and 2 were calculated from eqs. (5b), (8), and (9) by using the following data: $[M]_0 = 1.55$ mole/kg., $K_1 = 0.016$ kg./mole, and $K_2 = 2.1$ kg./mole.

Furthermore, since $P = ([M]_0 - [M]_\infty)/([S^-]_0 - [S^-]_\infty)$, a plot of P versus $1/([S^-]_0 - [S^-]_\infty)$ should be a straight line with a slope of $([M]_0 - [M]_\infty)$, 1.1 in the present case. The actual plot (Fig. 3) has a slope of 1 rather than 1.1, a difference which is within the experimental error.

It is interesting that P is slightly dependent on the temperature, i.e., the higher the temperature, the lower the value of P. This indicates that more living ends initiate the polymerization at higher temperature, causing a decrease in P. This is supported by the fact that the characteristic

TABLE III

Temperature, °C.	P	$[S^-]_0$, mole/kg.	$[S^-]_\infty$, mole/kg.
25	35	0.115	0.0849
37.4	30.8	0.115	0.0817
50.8	28.6	0.115	0.0786

color of living polymer in sample 1–50 is appreciably weaker than that in sample 1–25 at equilibrium. The calculated values of $[S^-]_\infty$ shown in Table II confirm this point. These are summarized in Table III. As a consequence of this temperature effect on $[S^-]_\infty$, K_1 varies with temperature.

Equilibrium Constant, K_2

The values of K_2 calculated from eq. (9) are listed in Table II. The average value of K_2 at 25°C. is 2.17 kg./mole (± 10%). These data indicate that K_2 is not dependent on $[S^-]_0$ or temperature. The latter suggests that the enthalpy of polymerization is nearly zero and the entropy of polymerization is positive. This indicates that the activation energy for the polymerization of D_4 is almost equal to the activation energy for the depolymerization to D_4 and the driving force for the polymerization is due to an increase in entropy on polymerization. The entropy of polymerization, ΔS, calculated from $\ln K_2 = \Delta S/R$, was found to be about 1.6 cal./mole-deg.

A positive value of ΔS observed in this system is in opposition to what is usually found in the polymerization of vinyl compounds where ΔS is negative. It must be mentioned that a positive entropy of polymerization is not a characteristic of ring-opening polymerization, since the entropy of polymerization in tetrahydrofuran system has been found to be -17 ± 0.6 cal./mole-deg.[9] Thus, the positive entropy of polymerization in the present system can not be attributed thoroughly to the opening of a ring to a linear chain. The flexibility of the polysiloxane chain must play an important role here and is probably responsible for this unusual behavior. Such a flexibility may arise from unusually large freedom of motion within the chain due to free rotation about the Si—O—Si bonds, and flexing of the readily deformable Si—O—Si angle.[10] Consequently, as the ring molecule of D_4 is opened to give a linear polysiloxane chain, the net effect is a gain in entropy, which constitutes the driving force of the polymerization.

Equilibrium Constant, K_1

K_1 is calculated from eqs. (5b) and (8). Its values are shown in Table II. These are suprisingly lower than one would have expected from the viewpoint of basicity of the respective anions. In order to check this point, K_1 was redetermined by an independent method. $[S^-]_\infty$ was determined directly by spectrophotometric method and K_1 and K_2 were recalculated from the measured $[S^-]_\infty$ by using eqs. (8) and (9). The extinction coefficient of the styryl anions was found to be 1.2×10^7 cm.^{2}/mole in this system. P was calculated from $P = ([M]_0 - [M]_\infty)/([S^-]_0 - [S^-]_\infty)$. The results obtained at 25°C. are shown in Table IV.

TABLE IV

$[S^-]_0 \times 10^2$, mole/l.	$[M]_0$, mole/l.	$[S^-]_\infty \times 10^4$, mole/l.	P	K_2, l./mole	K_1, l./mole
6.12	1.45	6.36	17.2	2.30	13.5
3.64	1.47	2.74	30.6	2.36	10.5
1.08	1.45	0.275	95.8	2.41	9.9

$[S^-]_\infty$ obtained by the spectrophotometric method is significantly lower than those shown in Table II. To judge from the color of the polymer solution at equilibrium, the $[S^-]_\infty$ value obtained by the spectrophotometric method appears to be more reliable. Therefore, the K_1 value obtained by this method is considered to be more accurate. It must be mentioned that K_1 calculated by this method is markedly higher than those presented in Table II, whereas K_2 is of about the same order of magnitude. This is understandable from eqs. (8) and (9) since K_1 is very sensitive to the variation of P, whereas K_2 is not. The value of K_1 appears to be greater than 10.

As mentioned previously, there is a temperature effect on P, indicating a possible dependence of K_1 on temperature. Since the determination of P by the spectrophotometric method at high temperature was rather difficult, quantitative data are not available. However, the data shown in Table II qualitatively indicate a positive change in enthalpy and a positive change in entropy. Probably the same explanation given in the case of K_1 can also be applied here. The solvation of the anion in this case will certainly play an important role in the initiation step.

Rate Constant, k_1

Two methods were used to calculate K_1 from the same experimental data. Both methods gave similar results within experimental error. The equations employed for these two methods are (15) and (16).

Method I:

$$2.3 \log (D_0/D_t) = k_1[M]_0 t \tag{15}$$

Method II:

$$-(dD_t/dt)_{t\rightarrow 0} = k_1 D_0 [M]_0 \tag{16}$$

Where D_0, D_t represent the optical density at 340 mμ initially and at time t, respectively, and $[M]_0$ is the initial D_4 concentration.

The above equations are valid in our present case since $[M]_0/[S^-]_0 \gg 10^3$ and $D_0/D_\infty \geq 100$. A typical example for method I is shown in Figure 4.

Results obtained by these two methods are collected in Table V. These data indicate the dependence of k_1 on $[S^-]_0$, i.e., as $[S^-]_0$ decreases, k_1 increases. Such a phenomenon is a general one in the anionic polymerization of vinyl compounds and has been explained in terms of ionic dissocia-

TABLE V

Initiation Rate Constant, k_1

Expt. no.	$[S^-]_0 \times 10^3$, mole/l.	$[M]_0$, mole/l.	$k_1 \times 10^4$, l./mole-sec.		$[S^-]_0^{-1/2}$
			Method I	Method II	
1	5.18	1.48	2.55	2.28	13.9
6	3.95	1.45	2.36	3.10	15.9
3	0.144	1.42	4.45	4.07	85.5
5	0.130	1.49	4.57	4.76	87.7
4	0.075	1.52	5.60	5.56	115.0

tion.[11] According to the ionic dissociation hypothesis, eq. (17) can be derived:

$$\ln([S^-]_0/[S^-]_t) = \{k_i + k_f (K_d/[S^-]_0)^{1/2}\}[M]_0 t \tag{17}$$

where K_d is the dissociation constant of the ion pairs; k_i and k_f are rate constant of iron pairs and free ions, respectively; and $[S^-]_0$ and $[S^-]_t$ are living end concentrations initially and at time t, respectively. Consequently,

$$k_1 = k_i + k_f (K_d/[S^-]_0)^{1/2} \tag{18}$$

A plot of k_1 versus $[S^-]_0^{-1/2}$ therefore should give a straight line with a slope equal to $k_f k_d^{1/2}$ and an intercept corresponding to k_i. This is shown in Figure 5.

From Figure 5 it can be concluded that the dependence of k_1 on $[S^-]_0$ is undoubtedly due to the dissociation of ion pairs to free ions. The value of k_i was found to be 2.1 × 10^{-4} l./mole sec.$^{-1}$ and that of $k_f k_d^{-1/2}$ was

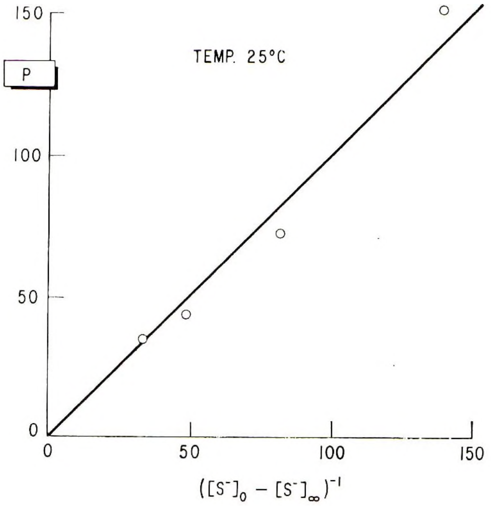


Fig. 3. Plot of P vs. $([S^-]_0 - [S^-]_\infty)^{-1}$. Temperature 25°C.

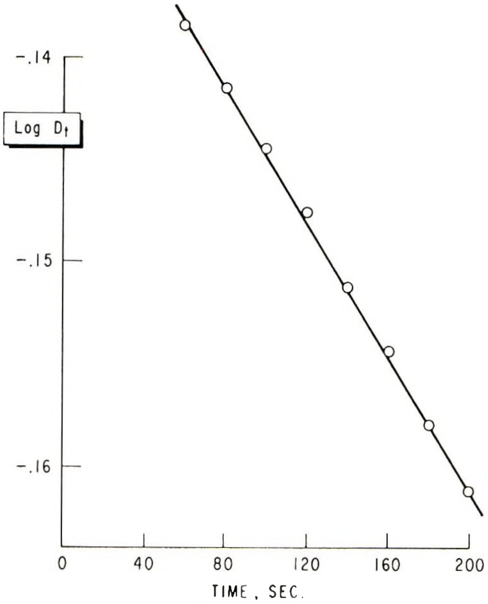


Fig. 4. Determination of k_1 (method I).

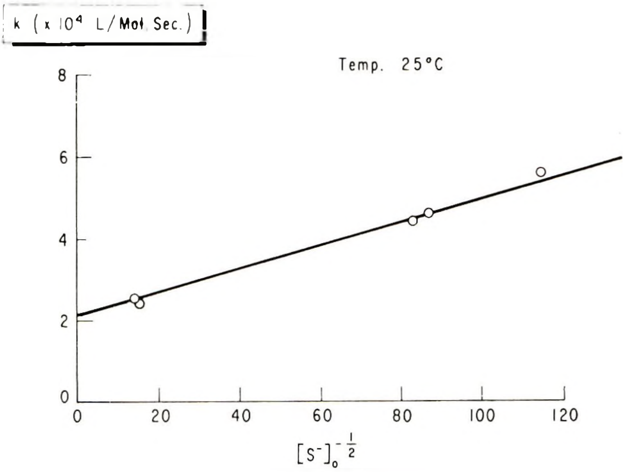


Fig. 5. Plot of k_1 vs. $[S^-]_0^{-1/2}$. Temperature 25°C.

2.9×10^{-6}. If a value of 10^{-8} is assumed for k_d, then k_f would be 2.4×10^{-2}, which is about 100 times greater than k_i. Using these values one also can estimate the fraction X of living ends presented as free ions, from the relation

$$k_1 = k_f X + k_i (1 - X) \tag{19}$$

At a concentration of living ends of 5.18×10^{-3} mole/l., 99.74% of living ends are estimated to be present in the form of ion pairs and only 0.26% as free ions.

Rate Constant, k_3

The k_3 was determined by eq. (20):

$$2.3 \log \{([M]_0 - [M]_\infty)/([M]_t - [M]_\infty)\} = k_3[\equiv SiO^-]t \qquad (20)$$

where $[M]_0$, $[M]_t$, and $[M]_\infty$ represent the concentration of D_4 initially, at time t, and at infinity respectively, and $[\equiv SiO^-]$ is the concentration of polydimethyl siloxanolate, which is assumed to be constant throughout the polymerization.

The results are shown in Table VI.

TABLE VI

$[\equiv SiO^-]$ $\times 10^2$, mole/l.	$[M]_0$, mole/l.	$k_3 \times 10^2$, l./mole sec.
1.43	1.44	2.75
0.782	1.44	3.43

These results show also the similar trend as observed in k_1. This again is probably due to the ionic dissociation of the polydimethyl siloxanolate.

Rate Constants k_2 and k_4

To calculate k_2 and k_4 the unit of concentration used for K_1 and K_2 was converted into liters per mole. Furthermore, since k_1 and k_3 are both dependent on $[S^-]_0$, the calculation of k_2 and k_4 is restricted to the particular concentration at which k_1, k_3, K_1, and K_2 were determined. Thus at 25°C. and $[S^-]_0 = 0.0337$ mole/l., $[M]_0 = 1.51$ mole/l., the following set of kinetic data were obtained:

$$k_1 = 2.3 \times 10^{-4} \text{ l./mole-sec.}$$

$$k_2 < 2.3 \times 10^{-5} \text{ sec.}^{-1}$$

$$k_3 = 2.75 \times 10^{-2} \text{ l./mole-sec.}$$

$$k_4 \approx 1.17 \times 10^{-2} \text{ sec.}^{-1}$$

$$K_1 > 10 \text{ l./mole}$$

$$K_2 \approx 2.35 \text{ l./mole}$$

The relatively low value of k_2 as compared with k_4 is due to not only the steric factor but also the formation of more basic anions.

It must be noted that the kinetic data presented above were obtained from the kinetic scheme postulated in this work. For such a kinetic scheme to be valid, a true equilibrium should be established. The establishment of such equilibrium is rather difficult if the P value is high. As the P value increases, the time required to reach a true equilibrium increases. During this period the slow killing of living ends is inevitable, especially when the reaction is carried out at high temperature. In the present case, the reaction was terminated after 24 hr. Although the equilibrium D_4 concentration at this time reached a constant value in all cases, it is still not clear if a true equilibrium is reached.

Furthermore, the kinetic scheme is also based on another assumption, i.e., M is a single species. This assumption is not true, as mentioned previously. This would mean that there should be a series of rate constants and equilibrium constants associated with D_4, D_5, . . ., etc. The kinetic study of such a system will be extremely difficult. Thus the kinetic data obtained from the simple scheme as proposed in this work are considered to be only approximate.

The author is indebted to Dr. D. R. Weyenberg and Dr. R. H. Baney for their stimulating discussions, Mr. E. G. Gooch for flame spectrophotometric analysis, Mr. L. C. Springer for his friendly assistance in recording the reaction time, and Mr. R. Krager and Mr. R. R. Buch for checking $\bar{M}_n$ values.

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Résumé

Les cinétiques de polymérisation anionique du octaméthylcyclotétrasiloxane (D4) initié par un polymère vivant d'α-méthylstyrène dans le tétrahydrofurane ont été étudiées. Le schéma cinétique suivant a été admis:

Initiation:

$$S^- + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M^- \qquad K_1$$

Propagation:

$$M_n^- + M \underset{k_4}{\overset{k_3}{\rightleftharpoons}} M_{n+1} \qquad K_2$$

où S^- et M représentent l'initiateur et D_4 respectivement. A une concentration en chaînes actives de 0.0377 mole/l. et une concentration en monomère de 1.5 mole/l. dans le tétrahydrofurane à 25°C les données cinétiques suivantes ont été obtenues: $k_1 = 2.3 \times 10^{-4}$ l./mole-sec., $k_2 < 2.3 \times 10^{-5}$ sec^{-1}, $k_3 = 2.75 \times 10^{-2}$ l./mole-sec., k_4 1.17×10^{-2} sec^{-1}, $K_1 > 10$ l./mole et K_2 2.35 l./mole. Les constantes de vitesse k_1 et k_3 sont dépendantes de la concentration en anion. Ceci est attribué à la dissociation de la paire d'ions en ions libres à basse concentration. Dans les conditions expérimentales étudiées, le majorité des anions sont présents sous la forme de paires d'ions. La réactivité d'ions libres est environ 100 fois plus grande que celle des paires d'ions. Il n'y a pas d'effet thermique sur k_2 ce qui indique que ΔH est nul et ΔS positif au cours de la réaction de propagation.

Zusammenfassung

Die Kinetik der anionischen, mit lebenden α-Methylstyrolpolymerem gestarteten Polymerisation von Octamethylcyclotetrasiloxan (D_4) in Tetrahydrofuran wurde untersucht. Folgenes kinetisches Schema wurde aufgestellt. Start, $S^- + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M^-$,

Start:

$$S^- + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M^- \qquad K_1$$

Wachstum:

$$M_n + M \underset{k_4}{\overset{k_3}{\rightleftharpoons}} M_{n+1}, \qquad K_2$$

wo S^- und M den Starter bzw. D_4 bedeuten. Bei einer Konzentration an lebenden Enden von 0,0377 mole/l. und einer Monomerkonzentration von 1,5 mole/l. in Tetrahydrofuran bei 25°C wurden folgende kinetische Daten erhalten: $k_1 = 2{,}3 \times 10^{-3}$ l./mole-sec, $k_2 < 2{,}3 \times 10^{-5}$ sec^{-1}, $k_3 = 2{,}75 \times 10^{-2}$ l./mole-sec, $k_4 \approx 1{,}17 \times 10^{-2}$ sec^{-1}, $K_1 > 10.$ l./mole und $K_2 \approx 2{,}35$ l./mole. Die Geschwindigkeitskonstanten k_1 und k_3 ziegten eine Abhängigkeit von der Anionenkonzentration. Das wird auf die Dissoziation von Ionenpaaren in freie Ionen bei niedrigeren Konzentrationen zurückgeführt. Bei den verwendeten Versuchsbedingungen war die Mehrzahl der Anionen in Form von Ionenpaaren anwesend. Die Reaktionsfähigkeit der freien Ionen ist etwa 100 mal grösser als diejenige der Ionenpaare. Es besteht kein Temperatureinfluss auf K_2, ein Hinweis auf ein ΔH gleich Null und ein positives ΔS bei der Wachstumsreaktion.

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A New, General Synthetic Method for the Preparation of Linear Poly-*p*-xylylenes

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Synopsis

A new, general synthetic route to poly-*p*-xylylene and substituted poly-*p*-xylylenes is described. The key intermediate in the new process is di-*p*-xylylene [(2,2)*p*-cyclophane]. It has been found that di-*p*-xylylene is quantitatively cleaved by vacuum vapor-phase pyrolysis at 600°C. to two molecules of *p*-xylylene. *p*-Xylylene spontaneously polymerizes on condensation to form high molecular weight, linear poly-*p*-xylylene. The conversion of di-*p*-xylylene to poly-*p*-xylylene is quantitative. The process is adaptable to the preparation of a wide variety of substituted poly-*p*-xylylenes by pyrolysis of ring-substituted di-*p*-xylylenes and polymerization of the resultant substituted *p*-xylylenes. Many of these polymers are not attainable by any other route. All are linear and free of crosslinking. Evidence supporting the proposed mechanism of pyrolytic cleavage of every molecule of di-*p*-xylylene to two molecules of *p*-xylylene is presented. Tough, transparent polymeric films are obtained from the process when the polymerization of the *p*-xylylenes is conducted on glass or metal surfaces. Outstanding combinations of physical, electrical, and chemical properties are displayed by poly-*p*-xylylene, polychloro-*p*-xylylene, and other substituted polymers. A comparison of the relative merits of the original Szwarc route and the new di-*p*-xylylene route to poly-p-xylylenes is presented.

RESULTS AND DISCUSSION

A new, general synthetic route to poly-*p*-xylylene and substituted poly-*p*-xylylene has been discovered.[1] The key intermediate in this process is di-*p*-xylylene (I). It has been found that di-*p*-xylylene is quantitatively cleaved by vacuum vapor-phase pyrolysis at 600°C. to form two molecules of the reactive intermediate, *p*-xylylene (II). In systems maintained at less than 1 mm., *p*-xylylene spontaneously polymerizes on surfaces maintained below 30°C. to form high molecular weight, linear poly-*p*-xylylene (III). The overall transformation of I to III is quantitative. Poly-*p*-xylylene prepared in this fashion is linear, completely and rapidly soluble in chlorinated biphenyls at 300°C., and free of low molecular weight byproducts. This reaction sequence, which is termed pyrolytic polymerization, is illustrated in eq. (1).*

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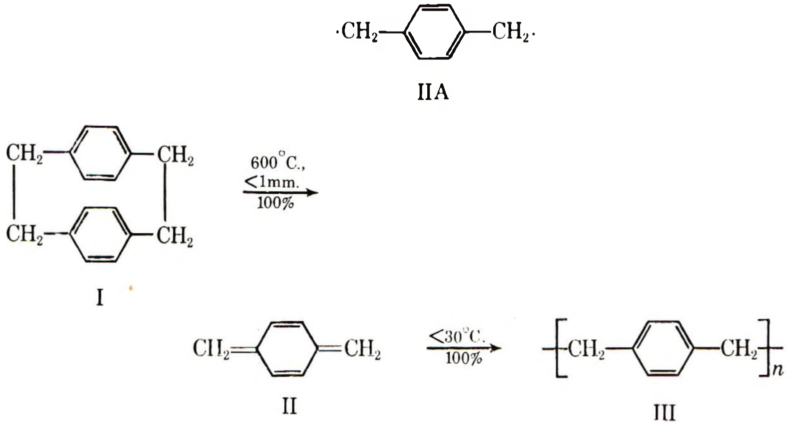
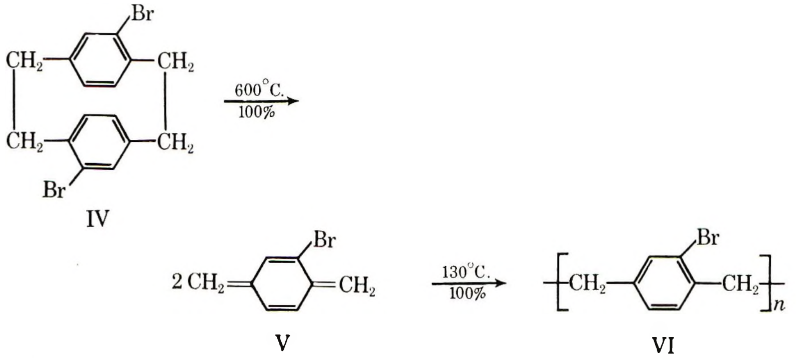
* In this paper *p*-xylylenes are represented by quinonoid structures (such as II). Their high level of chemical reactivity and free radical behavior, however, suggests that diradical structures such as IIA are important in rational explanations of the unique character of these molecules.



(1)

The di-*p*-xylylene route to poly-*p*-xylylene is readily adaptable to the preparation of substituted poly-*p*-xylylenes by pyrolytic polymerization of appropriately substituted di-*p*-xylylenes. Several substituted di-*p*-xylylenes with equivalent substitution in each ring have been prepared, including the dichloro, dibromo, dicyano, dimethyl, diethyl, and tetrachloro derivatives.* The pyrolysis of these ring-substituted dimers proceeds under the same conditions described for di-*p*-xylylene. For example, pyrolysis of dibromodi-*p*-xylylene (IV) at 600°C. results in formation of two molecules of 2-bromo-*p*-xylylene (V). At a system pressure of less than 0.5 mm., the polymerization of (V) will occur on any solid surface maintained below 130°C. to form polybromo-*p*-xylylene (VI).



(2)

In a similar fashion polychloro-*p*-xylylene, polycyano-*p*-xylylene, polymethyl-*p*-xylylene, polyethyl-*p*-xylylene, and polydichloro-*p*-xylylene were prepared by pyrolytic polymerization of the corresponding di-*p*-xylylene derivatives. The chief characteristic which distinguishes the polymerization of the various substituted *p*-xylylenes is the temperature at which the monomer will condense and polymerize. There appears to be a threshold condensation temperature for each species which is related to

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* The synthesis of these compounds will be discussed in a series of forthcoming publications.

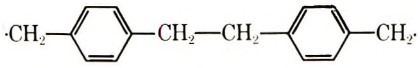
molecular weight and volatility. The threshold condensation temperature refers to the highest temperature of a surface on which the condensation and polymerization will take place at any appreciable rate at the pressure involved. The reactive monomers will not condense and polymerize on any surface maintained above this temperature, and they will condense and polymerize on any surface maintained below this temperature down to at least −180°C. At the normal system pressure ($\cong$100 μ) the threshold condensation temperatures have been determined for several *p*-xylylene monomers (Table I).

TABLE I

Monomer	Condensation temperature, °C.
p-Xylylene	30
2-Methyl-*p*-xylylene	60
2-Ethyl-*p*-xylylene	90
2-Chloro-*p*-xylylene	90
2-Cyano-*p*-xylylene	130
2-Bromo-*p*-xylylene	130
Dichloro-*p*-xylylene	130

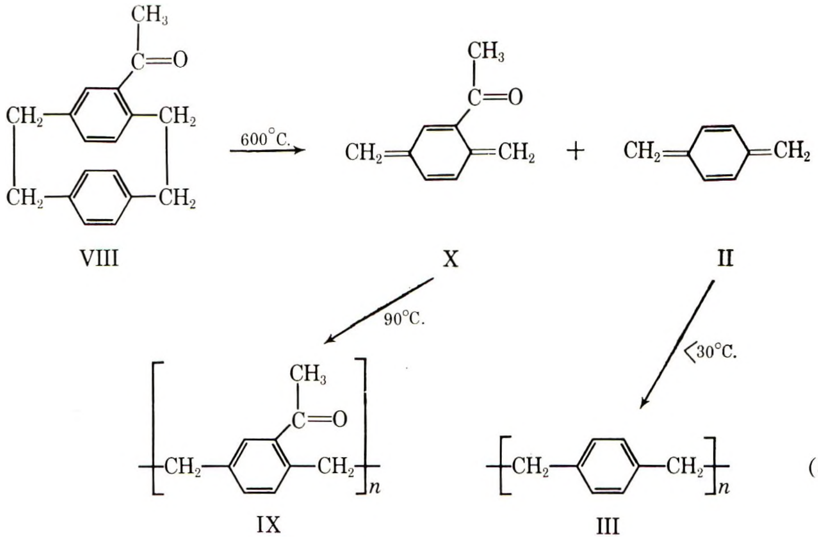
Mechanism of Pyrolytic Cleavage of Di-*p*-xylylene

In the above discussion it has been stated that di-*p*-xylylene and ring-substituted derivatives are pyrolyzed at 600°C. to form two *p*-xylylene molecules. This process would require either the concerted or stepwise cleavage of two carbon–carbon bonds in the dimer. An alternate possibility is that only one carbon–carbon bond is cleaved in the pyrolysis step yielding polymerizable diradical species such as VII.



VII

Conclusive evidence that the final products of pyrolysis under the reported conditions are *p*-xylylenes has been obtained from a study of the pyrolytic polymerization of unsymmetrically substituted di-*p*-xylylenes.[2] Acetyl di-*p*-xylylene (VIII) was pyrolyzed at 600°C. and 0.5 mm. pressure. The pyrolysis vapors were led initially through a 15-in. length of 1-in. i.d. glass tubing maintained at 90°C., and subsequently through a 10-in. length of the same tubing maintained at 20°C. Two entirely distinct polymers were obtained from this reaction. The first polymer was removed from the 90°C. zone at the conclusion of the reaction and was shown to be polyacetyl-*p*-xylylene (IX) on the basis of elemental analysis and the presence of a strong carbonyl band in the infrared spectrum at 5.9 μ. This polymer was soluble in *s*-tetrachloroethane at room temperature, and exhibited a crystalline melting point of 190°C. A second polymer was recovered from the 25°C. polymerization zone. This polymer proved to be poly-*p*-xylylene on the basis of infrared spectrum (identical to that of authentic poly-*p*-xylylene), melting point (400°C.), and lack of solubility in all solvents below 250°C. These results can only be rationalized by the formation of both *p*-xylylene and acetyl-*p*-xylylene (X) species in the pyrolysis step. While this evidence does not shed light on the question of whether both bonds in the dimer are broken simultaneously or sequentially, it is entirely clear that the ultimate pyrolysis products are II and X. The observed fractionation and selective polymerization of the two *p*-xylylene species is readily explainable on the basis of the concept of threshold condensation temperature. The overall process is illustrated in eq. (3).



(3)

This concept was further shown to be general from studies of the pyrolytic polymerization of carbomethoxy di-*p*-xylylene and ethyl di-*p*-xylylene. In each case two distinct polymers were recovered from the 90°C. and 25°C. polymerization zones. In these latter studies polycarbomethoxy-*p*-xylylene and polyethyl-*p*-xylylene were isolated from the 90°C. zone, and poly-*p*-xylylene in each case from the room temperature zone.

Additional evidence regarding the mechanism of pyrolysis of di-*p*-xylylenes was obtained by addition of iodine vapor to the condensation and polymerization zone. *p*-Xylylene diodide was isolated from the products formed, indicating the presence of *p*-xylylene in the pyrolysis gases.

The facile cleavage of di-*p*-xylylene (I) to *p*-xylylene is in all probability due to the high degree of steric strain in the dimeric species, and to the comparatively stable nature of *p*-xylylene. Brown and Farthing[3] have shown that the aromatic rings of di-*p*-xylylene are puckered on the basis of x-ray crystallographic evidence, Cram and Steinberg[4] have attributed the unusual ultraviolet characteristics of I to the interaction of the π electron clouds of the two rings, and Weissman[5] has shown that rapid interchange of the free electron of di-p-xylylene anion occurs between the π orbital systems of the two aromatic rings in electron magnetic resonance studies. Early indications of ring-opening reactions of di-p-xylylene leading to higher molecular weight products were reported by Schaefgen,[6] and by Cram and Allinger.[2]

Effect of Temperature on Pyrolysis of Poly-p-Xylylene

A study of the effect of pyrolysis temperature on the degree of conversion of I to II has been conducted. In these experiments the isolable products are poly-p-xylylene and di-p-xylylene. With a contact time of about 0.1 sec. quantitative conversion of I to III was obtained at pyrolysis temperatures of 550 and 600°C., while at pyrolysis temperatures of 400 and 500°C., III was produced in yields of 6 and 50%, respectively. Higher conversions of I to III in the 400–500°C. range can be obtained by use of longer contact times. Cleavage of I to reactive species can even be obtained at temperatures as low as 300°C. by heating in the melt. The quantitative cleavage of I to III at 600°C. provides, for the first time, a pure source (99%) of p-xylylene free of solvent, unreacted p-xylene, and by-products. Studies on the chemistry and physical properties of this molecule will be the subject of subsequent papers.

Review of Previous Synthetic Methods and Comparison with New Method

Poly-p-xylylene is, of course, not a new polymer. Szwarc[7–9] in the pioneering research in this field discovered that p-xylene is converted to the reactive intermediate p-xylylene in 10–15% yield by vacuum pyrolysis at 900–950°C. Szwarc[7–9] was also the first to report the spontaneous polymerization of p-xylylene on condensation to form poly-p-xylylene. While these extremely fascinating discoveries have aroused considerable interest in research laboratories, the process and the polymers obtained have been found to have a number of practical limitations. It has been shown that: (*1*) yields of p-xylylene of at best of 25% are obtained at the extreme pyrolysis temperature of 1150°C.;[10] (*2*) the preparation of substituted poly-p-xylylenes is limited to those cases in which the substituent group is stable at 900°C.; (*3*) polymers prepared by the Szwarc process are loosely crosslinked;[11–13] (*4*) the vapor-deposited polymeric products are contaminated with 10–20% of low molecular weight by-products.[10,12]

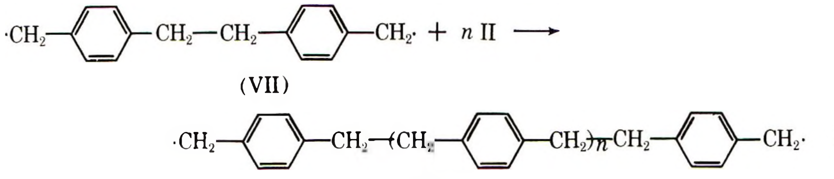
In contrast, the di-p-xylylene route to poly-p-xylylene is a high-yield process and permits the formation of a wide variety of substituted polymers due to the much lower pyrolysis temperature. It also produces linear polymers free of crosslinking and low molecular weight by-products.

Other synthetic routes to poly-p-xylylene have been reported. The conversion of p-xylyltrimethylammonium hydroxide to p-xylylene at 100°C., and the immediate and concurrent polymerization of the monomer produces linear, soluble poly-p-xylylene in high yields.[14] The scope of this synthetic route is limited to those cases in which the substituent groups are not affected by the strongly basic nature of the solution. Furthermore, this process produces polymers in particulate forms which are not easily converted into other usable shapes.

A recent review[13] describes other synthetic routes to poly-*p*-xylylenes. Most of these involve organometallic intermediates and are not of general applicability.

Mechanism of Polymerization of *p*-Xylylene

It has been suggested[13] that the polymerization of *p*-xylylene to poly-*p*-xylylene occurs by a free-radical mechanism in which, as the initial step, two *p*-xylylene molecules condense on a surface and react to form the diradical intermediate (VII). Growth progresses by addition of *p*-xylylene units to each end of the diradical, forming the "living" polymer (XI). Growth is terminated by reaction of the radical end groups with reactive sites in other growing polymer molecules, by reaction with chain transfer agents (e.g., mercaptans), or by the reactive sites becoming buried in the polymer matrix.



(VII)

(XI)

(4)

This mechanism for polymerization of *p*-xylylene suggests that the polymer should exhibit paramagnetic properties. It has been reported[10] that poly-*p*-xylylene prepared by the Szwarc process contains no detectable concentration of free-radical species. On the other hand, poly-*p*-xylylenes prepared from di-*p*-xylylenes are true "living" polymers and exhibit radical concentrations of $5–10 \times 10^{-4}$ moles of free electrons per mole of xylylene. The absence of radicals in Szwarc polymers may be due to the presence in the polymerizing polymer matrix of the 10–20% by-products which would be available for reaction with the radical chain ends. Some of these by-products,[11,12] such as the anthracenes and stilbenes, would be expected to exhibit a high level of reactivity with the growing sites. These by-products are essentially absent in polymer produced from di-*p*-xylylene.

Solubility Characteristics of Poly-*p*-xylylenes

Poly-*p*-xylylenes prepared by the di-*p*-xylylene route are deposited on glass or metal as transparent, colorless, tough, polymer films. A wide range of physical properties is attainable in the poly-*p*-xylylene family via introduction of nuclear substituents. Solubility characteristics in particular are affected by the degree and nature of substitution on the aromatic ring. Poly-*p*-xylylene and polydichloro-*p*-xylylene exhibit comparable solubility characteristics and can only be dissolved in high-boiling solvents such as the chlorinated biphenyls or benzyl benzoate at temperatures above 200°C. Polychloro-*p*-xylylene and polybromo-*p*-xylylene are more soluble and reduced viscosities of these polymers can be measured in α-chloronaphthalene at 150°C. The alkylated poly-*p*-xylylenes are substantially more soluble than the halogenated derivatives. Polymethyl-*p*-xylylene is soluble in hot toluene, polyethyl-*p*-xylylene is soluble in *s*-tetrachloroethane at room temperature, and poly-*n*-butyl-*p*-xylylene is soluble in chloroform at room temperature. All of the polymers produced by the di-*p*-xylylene route are completely soluble in the solvents listed. No trace of crosslinked product has been observed to form in this process. Reduced viscosity measurements have been conducted on the above polymers with the exception of poly-*p*-xylylene and polydichloro-*p*-xylylene. Reduced viscosities of 1.0–2.5 were measured on all polymers, indicating that products of high molecular weight are formed.

Physical Properties of Poly-*p*-xylylenes

The mechanical, thermal, and electrical properties and permeability characteristics of several of the poly-*p*-xylylenes have been measured and interesting trends noted as the nature of the substituent group is varied. The mechanical and thermal properties of several poly-*p*-xylylenes are listed in Table II. As many investigators have reported previously,[7–12] poly-*p*-xylylene and some substituted poly-*p*-xylylenes exhibit a high level of crystallinity. In our own studies it has been established that poly-*p*-xylylene and halogenated derivatives are highly crystalline in nature. Polymethyl-*p*-xylylene and polyethyl-*p*-xylylene are less crystalline, and poly-*n*-butyl-*p*-xylylene is amorphous at room temperature. Glass transition temperatures of 60–90°C. are measured for most of the more highly crystalline polymers. The alkyl-substituted poly-*p*-xylylenes exhibit lower glass transition temperatures with the ethyl and *n*-butyl derivatives possessing a major glass transition of room temperature or below.

The tensile properties of the poly-*p*-xylylenes were measured on 1–2 mil thick film samples stripped from the inside of a glass deposition chamber. High tensile strengths are obtained in the polymers in the as-deposited condition. Most of the poly-*p*-xylylenes are high-modulus materials at room temperature and exhibit tensile moduli above 300,000 psi. Exceptions are polyethyl-*p*-xylylene, which exhibits a room temperature modulus of 175,000 psi, and poly-*n*-butyl-*p*-xylylene, which is elastomeric at ambient temperature. A reasonable level of toughness and extensibility is observed in all of the vapor-deposited poly-*p*-xylylenes. Polychloro-*p*-xylylene, polymethyl-*p*-xylylene, and polyethyl-*p*-xylylene are outstanding in this regard and normally exhibit elongations at break in excess of 200% for 1–2 mil film samples.

The permeability characteristics of several poly-*p*-xylylenes to the permanent gases and to moisture vapor are reported in Table III. Polychloro-*p*-xylylene, polybromo-*p*-xylylene, and polymethyl-*p*-xylylene are outstanding as barriers to the permanent gases and to moisture and are

TABLE II

Mechanical and Thermal Properties of Several Poly-*p*-xylylenes

Properties	Poly-*p*-xylylene	Polychloro-*p*-xylylene	Polybromo-*p*-xylylene	Polydichloro-*p*-xylylene	Polycyano-*p*-xylylene	Polymethyl-*p*-xylylene	Polyethyl-*p*-xylylene
Room temperature tensile properties[a]							
Tensile strength, psi	6,800	10,600	8,000	6,000	8,700	9,500	11,000
Tensile modulus, psi	350,000	460,000	400,000	400,000	435,000	400,000	175,000
Elongation at break, %	10–15	220	30	5–10	7–12	230	275
Thermal properties[b]							
Crystalline melting point, °C.	400	290	270	>300	270	200–210	160–170
Glass transition temperature, °C.	80	80	80	110	90	50–60	25
Tensile modulus at 200°C., psi	25,000	25,000	20,000	25,000	20,000	<1,000	<100

[a] Measured on 1–2 mil films in Instron tensile tester at 10% strain/min.

[b] From secant modulus–temperature curve. Melting points also obtained from x-ray data and from melting behavior in sealed melting point tubes.

TABLE III
Permeability Characteristics of Several Poly-*p*-xylylenes

Polymer	Permeability at 77°F., cm.^{3}(STP)-mil/100 in.^{2}-24 hr. Hydrogen	Carbon dioxide	Oxygen	Nitrogen	Moisture vapor permeability at 77°F. g.-mil/atm.-100 in.^{2}-24 hr.
Poly-*p*-xylylene	250	225	30	9	6.0
Polychloro-*p*-xylylene	200	21	8	1	0.6
Polybromo-*p*-xylylene	75	6	4	0.1	0.6
Polydichloro-*p*-xylylene		130	30	4.5	5.0
Polycyano-*p*-xylylene	295	50	15		30
Polymethyl-*p*-xylylene	166	44	9.5	2.6	1.1
Polyethyl-*p*-xylylene	716	314	83	15	4.1

TABLE IV
Electrical Properties of Several Poly-*p*-xylylenes

Electrical properties	Poly-*p*-xylylene	Polymethyl-*p*-xylylene	Polychloro-*p*-xylylene	Polydichloro-*p*-xylylene
Dielectric constant (1 Kc./sec.)	2.65	2.48	3.2	2.82
Dissipation factor (1 Kc./sec.)	0.0002	0.0025	0.04	0.003
Dielectric strength (1–3 mil films), v./mil	7,000	6,000	5,000	5,000

at least equal to any known organic polymer in this important property. Polycyano-*p*-xylylene is an excellent barrier to the permanent gases but is quite permeable to moisture.

The electrical properties of several poly-*p*-xylylenes are reported in Table IV. Poly-*p*-xylylene exhibits outstanding electrical properties as an insulating film. In particular, it possesses an extremely low dissipation factor, probably due to the highly symmetrical, nonpolar nature of the polymer. Electrically continuous films as thin as 0.5 μ can be prepared.

EXPERIMENTAL

Procedure for Conversion of Di-*p*-Xylylene and Symmetrically Substituted Di-*p*-xylylenes to Poly-*p*-xylylene and Substituted Poly-*p*-xylylenes

The following equipment and procedure were employed for the conversion of di-*p*-xylylenes to parylenes. The pyrolysis reactions were carried out in a 24-in. section of 1-in. i.d. Vycor tubing. The first 6 in. of the tube served as a distillation zone, and the following 18-in. section as the pyrolysis zone. The pyrolysis tube was connected by appropriate glass connections to a glass deposition chamber. Deposition chambers ranging in diameter from 1 to 6 in. and in length from 8 to 20 in. were employed. The end of the chamber was connected by tubing through a Dry Ice trap to a 4 ft.^{3}/min. mechanical pump. A thermocouple or Pirani vacuum gauge probe was placed in the system between the Dry Ice trap and the pump to record pressure and pressure changes.

In each experiment a measured quantity of di-*p*-xylylene or ring-substituted derivative was placed in a porcelain boat and the boat placed in the distillation zone. The system was then closed and evacuated to 1–100 μ, depending on the derivative in question. The di-*p*-xylylene was distilled at the rate of 1 g. every 3 or 4 min. through the pyrolysis zone. To achieve this rate, the distillation zone was maintained at temperatures ranging from 140 to 220°C., depending on the derivative. The pyrolysis zone was heated to 600°C., the temperature being measured by the thermocouple in the middle of the furnace on the outside of the tube. The pyrolysis gases were then led into a deposition chamber. The glass joints leading from the pyrolysis zone to the deposition chamber were maintained at about 200°C. to prevent premature polymerization. The deposition chamber was usually held at room temperature, although with some derivatives it was heated as high as 160°C. to permit deposition of polymer over a fairly broad area.

A pressure rise of 5–100 μ is generally observed during the course of a pyrolytic polymerization. At the end of the run the pressure falls back to the base pressure. The heating jacket on the distillation section of the pyrolysis tube is removed at this point to insure that complete distillation of the charge has occurred. When it is established that the distillation is complete, the vacuum is broken; the equipment dismantled, and the polymeric film recovered from the walls of the deposition chamber. Typical data for the preparation of several poly-*p*-xylylenes are recorded in Table V.

Pyrolytic Polymerization of Monosubstituted Di-*p*-xylylenes

The distillation and pyrolysis steps were conducted as described above for di-*p*-xylylene and substituted di-*p*-xylylenes. The pyrolysis gases were led to immediately in a deposition zone which consisted of a 24-in. section of 1-in. i.d. glass tubing. The initial 15-in. section of this tubing (zone A) was heated to 90–100°C. The final 9-in. section of the tubing (zone B) was maintained at room temperature. The end of the deposition zone was connected via rubber tubing through the Dry Ice trap to the vacuum pump.

Polymerization of Acetyl Di-*p*-xylylene. A 0.8-g. portion of acetyl di-*p*-xylylene (m.p. 110–111°C.) was distilled at a steady rate over a 7-min. period through the pyrolysis zone maintained at 570°C. and at a system pressure of 0.4 mm. Polymer A formed in the initial 9-in. section of zone A, and

TABLE V

Experimental Data on Preparation of Several Poly-*p*-xylylenes

Di-*p*-xylylene (DPX) derivative	Polymer produced	Weight of dimer, g.	Distillation temp., °C.	Pyrolysis temp., °C.	Length of run, min.	Weight of product, g.[a]	Weight of extracted polymer, g.[b]	Conversion, %
Di-*p*-Xylylene	Poly-*p*-xylylene	1.50	175	600	20		1.50	100
"	"	1.00	175	550	20		1.00	100
"	"	1.00	175	500	20		0.50	50
"	"	1.00	175	400	20		0.06	6
Dichloro-DPX	Polychloro-*p*-xylylene[c]	3.00	150–160	600	30	3.00	3.00	100
		2.00	150–160	500	20	1.96	0.29	16
Dibromo-DPX	Polybromo-*p*-xylylene[d]	3.00	165–175	660	18	2.86	2.86	
Dicyano-DPX	Polycyano-*p*-xylylene	4.00	170–180	660	15	3.52	3.52	
Tetrachloro-DPX	Polydichloro-*p*-xylylene	2.00	165–175	660	20		1.82	
Dimethyl-DPX	Polymethyl-*p*-xylylene	2.00	150	660	12	1.5		
Diethyl-DPX	Polyethyl-*p*-xylylene	2.00	160	660	12	1.8		

[a] Stripped from walls of deposition chamber. Remainder of polymer deposited in tubing and traps.

[b] Product extracted with refluxing toluene or carbon tetrachloride for one hour and then dried to constant weight.

[c] An elemental analysis was obtained on the polymer. Calcd. for C_8H_7Cl: C, 69.35%; H, 5.05%; Cl, 25.60%. Found: C, 69.3%; H, 5.1%; Cl, 25.6%.

[d] A bromine analysis was obtained on the polymer. Calcd. for C_8H_7Br: Br, 43.7%. Found: Br, 43.7%.

the remaining 6-in. length of tubing was free of polymer. Polymer B formed in zone B. Crude yields of 0.5 g. of polymer A and 0.3 g. of polymer B were obtained. Polymer A after extraction with ether and drying weighed 0.33 g. This product had a crystalline melting point of 190–195°C., a reduced viscosity of 1.7 in α-chloronaphthalene at 100°C., and was soluble in *s*-tetrachloroethane at room temperature. Tough polymeric fims could be cast from solutions in *s*-tetrachloroethane. The infrared spectrum of the polymer exhibited a strong band at 5.9 μ indicative of a carbonyl group and a band at 11.28 μ indicative of 1,2,4-trisubstituted benzene. An elemental analysis of the polymer was obtained.

ANAL. Calcd. for $C_{10}H_{10}O$: C, 82.20%; H, 6.85%; Found: C, 81.9%; H, 7.1%.

On the basis of this evidence this polymer is considered to be polyacetyl-*p*-xylylene. Polymer B, after extraction with boiling acetone and drying, weighed 0.23 g. This polymer had a melting point above 330°C. and an infrared spectrum identical to that of poly-*p*-xylylene.

Polymerization of Carbomethoxy Di-*p*-xylylene. The experimental procedure and equipment were identical to that reported for acetyl di-*p*-xylylene. Over a period of 5 min. 0.8 g. carbomethoxy di-*p*-xylylene (m.p. 137–138°C.) was distilled through the pyrolysis zone maintained at 580°C. at a system pressure of 0.2 mm. In this run, zone A was heated to 110°C. and zone B maintained at room temperature. Polymer A formed on the inner surface of the initial 6-in. section of zone A. The following 9-in. length of zone A was devoid of polymer. A second polymer, polymer B, formed in zone B. After extraction with ether and drying, a total of 0.31 g. of polymer A was obtained. This polymer exhibited a crystalline melting point of 200–210°C., was soluble in *s*-tetrachloroethane at room temperature, and exhibited a reduced viscosity (at 0.2% concentration) of 3.1 in this solvent at 25°C. Tough polymeric films could be cast from solutions in this solvent. A strong ester carbonyl band was present at 5.8 μ in the infrared spectrum of the polymer. The polymer is assigned the structure polycarbomethoxy-*p*-xylylene. A total of 0.11 g. of polymer B was recovered after mechanical removal, extraction with chloroform, and drying. This polymer had a melting point above 330°C. and an infrared spectrum identical to that of poly-*p*-xylylene.

It is a pleasure to acknowledge the assistance of a number of people, in particular that of Mr. John A. Stenstrom. The physical property data and permeability characteristics were measured by Dr. C. N. Merriam and Mr. J. A. Stenstrom. The data on electrical properties were obtained from Dr. W. E. Loeb. The electron magnetic resonance studies were conducted by Dr. R. G. Shaw.

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Résumé

Une nouvelle méthode synthétique générale pour la fabrication de *p*-polyxylylène et de poly-*p*-xylylène substitué est décrite. L'intermédiaire principal dans ce nouveau procédé est le di-*p*-xylylène [(2,2)-*p*-cyclophane]. On a trouvé que le di-*p*-xylylène est quantitativement rompu par pyrolyse à l'état vapeur sous vide à 600°C en deux molécules de *p*-xylylène. Le *p*-xylylène polymérise spontanément par condensation pour former une substance de poids moléculaire élevé, le poly-*p*-xylylène linéaire. La transformation du di-*p*-xylylène en poly-*p*-xylylène est quantitative. Ce processus peut être adapté à la préparation d'une grande variété de poly-*p*-xylylène substitués par pyrolyse des di-*p*-xylylènes substitués dans le noyau et la polymérisation du *p*-xylylène substitué en résultant. Beaucoup de ces polymères ne sont pas obtenables par une autre voie. Tous sont linéaires et pourvu de pontage. On apporte une évidence du mécanisme proposé en ce qui concerne la rupture pyrolytique de chaque molécule de di-*p*-xylylène en deux molécules de *p*-xylylène. Des films durs et transparents polymériques sont obtenus au départ de ce procédé lorsque la polymérisation du p-xylylène est conduite sur une surface de verre ou de métal. Une combinaison exceptionnelle de proriétés physiques, électriques et chimiques sont présentées par le poly-*p*-xylylène, le polychloro-*p*-xylylène et d'autres polymères substitués. La comparaison des mérites relatifs de la méthode originale de Szwarc et la nouvelle méthode conduisant du di-*p*-xylylène jusqu'au poly-*p*-xylylène est présentée.

Zusammenfassung

Ein neuer allgemeiner Syntheseweg zu Poly-*p*-xylylen und substituiertem Poly-*p*-xylylenen wird beschrieben. Das Schlüsselzwischen-produkt bei dem neuen Prozess ist Di-*p*-xylylen [(2,2)-*p*-cyclophan]. Di-*p*-xylylen kann bei Dampfphasepyrolyse im Vakuum bei 600°C quantitativ in zwei Moleküle *p*-Xylylen gespalten werden. *p*-Xylylen polymerisiert bei der Kondensation spontan unter Bildung von hochmolekularen, linearem Poly-*p*-xylylen. Die Umwandlung von Di-*p*-xylylen zu Poly-*p*-xylylen verläuft quantitativ. Das Verfahren kann für die Darstellung einer grossen Vielfalt substituierter Poly-*p*-xylylene durch Pyrolyse ringsubstituierter Di-*p*-xylylene und Polymerisation der gebildeten substituierten *p*-Xylylene angewendet werden. Viele dieser Polymeren sind auf keinem anderen Weg zugänglich. Alle sind linear und unvernetzt. Versuchsergebnisse zur Stützung des vorgeschlagenen pyrolytischen Spaltungsmechanismus einer jeden Di-*p*-xylylenmolekel in zwei *p*-Xylylenmolekel werden angeführt. Beiausführung der Polymerisation der *p*-Xylylene an Glas- oder Metalloberflächen werden mit diesem Verfahren zähe, transparente Polymerfilme erhalten. Eine aussergewöhnliche Kombination physikalischer, elektrischer und chemischer Eigenschaften zeigen Poly-*p*-xylylen, Polychlor-*p*-xylylen und andere substituierte Polymere. Ein Vergleich der gegenseitigen Vorzüge des ursprünglichen Verfahrens von Szwarc und des neuen Di-*p*-xylylenverfahrens zur Gewinnung von Poly-*p*-xylylen wird durchgeführt.

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Aromatic Polyamides of 2,6-Naphthalenedicarboxylic Acid

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Synopsis

Wholly aromatic polyamides have been prepared by the interfacial polycondensation of 2,6-naphthalenedicarboxylic acid chloride with *m*-phenylenediamine. Also, copolyamides with isophthaloyl or terephthaloyl chlorides and the naphthalene diacid chloride were synthesized. The resultant polyamides were amorphous or slightly crystalline as determined by x-ray diffraction, had tensile properties characteristic of hard, strong materials, and were more thermally stable than aromatic polyamides prepared solely from benzene diacid chlorides.

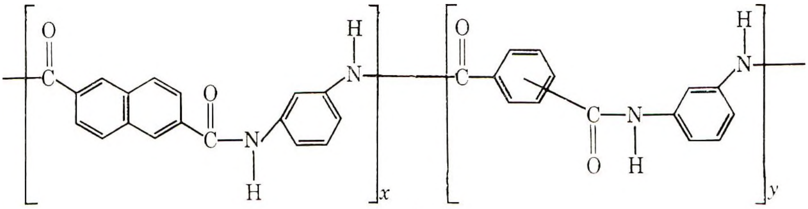
INTRODUCTION

Morgan and co-workers[1] have demonstrated the versatility of the interfacial polycondensation technique for the preparation of polyamides, polyesters, polyurethanes, and polyureas. This technique has been successfully applied to the preparation of aromatic polyamides where rapid, low-temperature, and nonequilibrium reactions are necessary since high molecular weight aromatic polyamides cannot be prepared by conventional melt polycondensation methods. Due to the lower reactivity of aromatic diamines and diacid chlorides, the choice of organic solvent, reactant ratio, concentration, etc., becomes more critical than in aliphatic systems. High yields of high molecular weight polyamides have been achieved with aromatic diamines and isophthaloyl or terephthaloyl chlorides under careful control of the aforementioned conditions.[2–5] We have extended this technique to the preparation of polymers derived from naphthalenedicarboxylic acid derivatives, and the resultant polymers were generally less soluble and more thermally stable than their benzene analogs.

RESULTS AND DISCUSSION

Extensive work was done on optimizing the solvent, reactant ratio, base strength, molarity, and stirring speed necessary to obtain high yields of high molecular weight polyamides. Chlorinated and aromatic hydrocarbons were not successful solvents, and cyclohexanone was the only solvent found which consistently yielded high molecular weight polymers. The reactant ratios were 1:1 diacid chloride to diamine, the HCl acceptor was sodium hydroxide, the concentrations were 0.10 mole/l. diacid chloride and 0.20 mole/l. diamine, and the stirring speed was 1600 rpm. We found that the addition of some cyclohexanone to the aqueous solution of the diamine prior to the addition of the diacid chloride solutions was necessary for the production of high molecular weight polymer in high yields. Since mass transfer of diamine is believed to be important in interfacial polycondensations,[6] addition of cyclohexanone led to the existence of a "polymerization zone" containing diamine, so that the rapid reaction which occurred upon addition of the diacid chloride solution yielded high molecular weight polymer before precipitation occurred. *p*-Phenylenediamine, which is poorly soluble in water and which would transfer to the organic solvent very rapidly, gave low yields (40–50%) of low molecular weight polymer (RSV = 0.2–0.45). Prior addition of organic solvent to the aqueous phase had no effect, and low molecular weight polymer precipitated almost immediately after addition of the diacid chloride solution.

The statistical repeating unit of the polymers prepared in this study has the structure I. Table I lists the various high molecular weight polyamides obtained.



I

The homopolymer was soluble at room temperature in concentrated sulfuric acid, hexamethylphosphoramide, and *N*-methylpyrrolidone, and the copolymers were soluble in the above solvents and slightly soluble in dimethylacetamide. Clear, coherent and light yellow films were cast from 10–15% solutions of the polymers in *N*-methylpyrrolidone.

The polymers were amorphous or slightly crystalline and had tensile properties characteristic of hard, strong[7] materials, as can be seen in Table II.

The homopolymer was slightly crystalline and, as expected, the copolymers were amorphous. The only copolymer which showed some crystallinity after annealing was the one derived from an 80/20 mole-% mixture of 2,6-naphthalenedicarboxylic acid and isophthalic acid with *m*-phenylenediamine. The bulky nature of the aromatic polyamide backbone, which hinders the formation of intramolecular hydrogen bonds possible in crystalline polyamides, is probably responsible for the amorphous nature of these polymers.

We have compared the thermal stability in air of the aromatic polyamides prepared from the 2,6-naphthalenedicarboxylic acid with those prepared from the benzene derivatives, and the results are shown in Figures 1 and 2. These figures indicate that the presence of the naphthalene moiety signifi-

TABLE I
Polymers and Copolymers from the Interfacial Polycondensation of 2,6-Naphthalenedicarboxylic Acid Chloride with Aromatic Diamines with Cyclohexanone as the Organic Solvent

No.	Diacid chloride Compounds	Mole-%	Diamine	Yield of polymer, %	η_{sp}/c[a]
1	2,6-Naphthalenedicarboxylic	100	*m*-Phenylenediamine	96	1.85
2	2,6-Naphthalenedicarboxylic Isophthaloyl	80 20	*m*-Phenylenediamine	92	1.4
3	2,6-Naphthalenedicarboxylic Isophthaloyl	70 30	*m*-Phenylenediamine	95	0.82
4	2,6-Naphthalenedicarboxylic Isophthaloyl	50 50	*m*-Phenylenediamine	88	1.45
5	2,6-Naphthalenedicarboxylic Terephthaloyl	80 20	*m*-Phenylenediamine	94	1.35
6	2,6-Naphthalenedicarboxylic Terephthaloyl	70 30	*m*-Phenylenediamine	96	1.76
7	2,6-Naphthalenedicarboxylic Terephthaloyl	50 50	*m*-Phenylenediamine	94	0.85

[a] Reduced specific viscosity was measured at 25°C. on 0.5% solutions in *N*-methylpyrrolidone.

TABLE II
Physical Properties of Polymers Derived from 2,6-Naphthalenedicarboxylic Acid

Polymer[a]	X-ray crystallinity, %	Average interchain distance, A.	Break strength, psi	Break elongation, %	Tensile modulus, psi × 10^5
1	4	5.00	8300	5–6	2.8
2	0, 4.5[b]	5.5, 4.9[b]	8500	4	2.6
3	0	5.3	7800	4	2.4
4	0	4.9	6000	3	2.2
5	0, 0[b]	5.3, 5.1[b]	7400	5	1.8
6	0	4.9	8000	5	2.2
7	0	5.3	7300	4	2.3

[a] The polymer number refers to the polymer whose composition is described in Table I.

[b] These polymers were annealed in a nitrogen atmosphere at 200°C. for 24 hr.

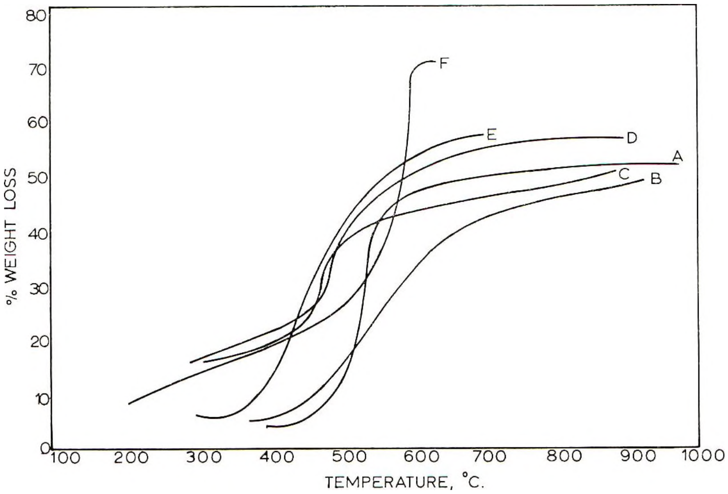


Fig. 1. Relative thermal stability of aromatic polyamides: (*A*)–(*D*) polymers 1–4 given in Table I; (*E*) polymer from isophthaloyl chloride and *m*-phenylenediamine;[5] (*F*) polymer from isophthaloyl chloride and *p*-phenylenediamine.[5]

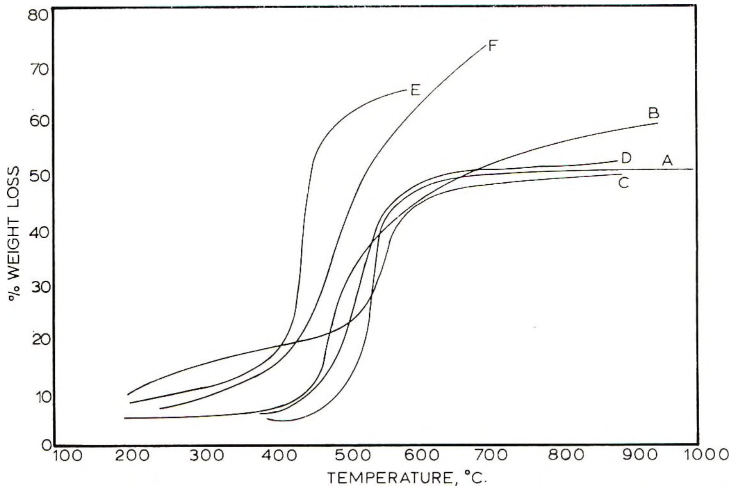


Fig. 2. Relative thermal stability of aromatic polyamides: (*A*)–(*D*) polymers 1 and 5–7 given in Table I; (*E*) polymer from terephthaloyl chloride and *m*-phenylenediamine;[5] (*F*) polymer from terephthaloyl chloride and *p*-phenylenediamine.[5]

cantly increases the thermal stability of wholly aromatic polyamides. At 500°C. the homopolymer has lost 10% of its weight, while at the same temperature, polymers of isophthaloyl or terephthaloyl chloride with *m*-phenylenediamine lose 60 and 35% of their weight, respectively. Dine-Hart and co-workers[5] found that the polymers containing terephthalic acid groups were more thermally stable than those derived from isophthalic acid. However, we only find a slight increase in the thermal stability of the copolymers containing the terephthalic moiety. This is probably due to the presence of the naphthalenedicarboxylic acid group which masks the isomeric effect on thermal stability seen in the benzene analogs.

EXPERIMENTAL

The *m*- and *p*-phenylenediamines used in this work were obtained from Matheson, Coleman and Bell. The *m*-phenylenediamine was purified by vacuum distillation, and pure *p*-phenylenediamine was obtained by vacuum sublimation.

The isophthaloyl and terephthaloyl chlorides were reagent-grade materials obtained from Matheson, Coleman and Bell and were purified by vacuum distillation and recrystallization from 60/40 by volume benzene–heptane mixtures. The thermal analysis of the polymers was performed in air on a du Pont 950 thermogravimetric analyzer.

Preparation of 2,6-Naphthalenedicarboxylic Acid Chloride

To a solution of 253 g. (1 mole) of 2,6-naphthalenedicarboxylic acid, prepared by alkaline hydrolysis of the dimethyl ester obtained from the Sun Oil Co., in 1500 ml. of benzene, was added 4.5 g. of acetamide catalyst and 286 g. of thionyl chloride. The reaction mixture was heated under gentle reflux until the solution became clear. The solution was cooled and the diacid chloride crystallized as yellow needles. Upon recrystallization from a benzene–heptane (60/40) solution, a 95% yield of light yellow needles of 2,6-naphthalenedicarboxylic acid chloride, m.p. 177–178°C., was obtained.

ANAL. Calculated for $C_{12}H_6Cl_2O_2$: C, 57.10%; H, 2.32%. Found: C, 57.42%; H, 2.57%.

Interfacial Polycondensation of 2,6-Naphthalenedicarboxylic Acid Chloride with *m*-Phenylenediamine

A solution of 5.04 g. (0.02 mole) of 2,6-naphthalenedicarboxylic acid chloride in 100 ml. of cyclohexanone was added to a rapidly stirred solution of 2.16 g. (0.02 mole) of *m*-phenylenediamine and 4.24 g. of sodium hydroxide in 50 ml. of water to which 75 ml. of cyclohexanone had been added. The temperature of the reaction mixture rose from 28 to 40°C., and after 8 min. the off-white precipitate was collected, washed with water, and dried in a vacuum oven at 60°C. for 5 hr. The yield was 5.5 g. (96%); RSV of a 0.5% solution of this polymer in *N*-methylpyrrolidone at 25°C. was 1.85.

Interfacial Polycondensation of 2,6-Naphthalenedicarboxylic Acid Chloride, Benzenedicarboxylic Acid Chloride, and *m*-Phenylenediamine

The copolymerizations were all performed by the same general procedure; a typical run is described below.

To a rapidly stirred solution of 4.32 g. (0.04 mole) of *m*-phenylenediamine and 8.4 g. (0.08 mole) of sodium hydroxide in 100 ml. of water and 100 ml. of cyclohexanone was added a mixture of 8.1 g. (0.032 mole) of 2,6-naphthalenedicarboxylic acid chloride and 1.63 g. (0.008 mole) of isophthaloyl chloride in 200 ml. of cyclohexanone. The reaction mixture was stirred for 10 min., during which time the temperature rose from 25 to 40°C. The white solid which precipitated was collected, washed with water, and dried under vacuum at 60°C. for 5 hr. The yield was 10.2 g. (92%); RSV of a 0.5% solution of this polymer in *N*-methylpyrrolidone at 25°C. was 1.40.

The author wishes to thank Drs. H. J. L. Schuurmans and M. E. Mullier for their helpful suggestions and Mr. D. Ditoro for performing the thermogravimetric analysis.

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Résumé

Des polyamides complètement aromatiques ont été préparés par polycondensation interfaciale du chlorure de l'acide 2,6-naphthalènedicarboxylique avec la *m*-phénylènediamine. Des copolyamides avec des chlorures d'isophthaloyle ou de téréphthaloyle et de chlorures de diacides naphthaléniques ont équalement été synthétisés. Les polyamides en résultant étaient amorphes ou légèrement cristallins tel que cela a été déterminé par diffraction aux rayons-X Ils présentaient des propriétés de tractions caractéristiques de matériaux durs et tenaces et étaient thermiquement plus stables que les diamides aromatiques préparées uniquement au départ de chlorure de benzène dicarboxylique.

Zusammenfassung

Vollständig aromatische Polyamide wurden durch Grenzflächenpolykondensation von 2,6-Naphthalindicarbonsäurechlorid mit *m*-Phenylendiamin dargestellt. Auch Copolyamide mit Isophthaloyloder Terephthaloydlchlorid und dem Naphthalindicarbonsäureamid wurden synthetisiert. Die gebildeten Polyamide waren nach dem Röntgendiagramm amorph oder schwach kristallin, hatten für harte, feste Stoffe charakteristische Zugeigenschaften und waren thermisch stabiler als die nur aus Benzoldicarbonsäurechloriden dargestellten Polyamide.

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Mechanism of Polymerization of α-Olefins on Oxide Catalysts

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Synopsis

The polymerization of ethylene on a chromic oxide catalyst with and without a solvent has been studied. It was found that the active catalyst surface is formed exclusively as a result of its interaction with ethylene. This interaction is accompanied by the formation of products which poison the surface of the catalyst when they are sorbed on it in the absence of a solvent. A catalyst which contains no Cr^{+6} atoms as a result of reduction by alcohol is inactive. On the other hand, a catalyst which contains only Cr^{+6} atoms becomes active only after it has been partially reduced. The most probable product of this reduction is trivalent chromium atoms. The results obtained have given grounds for the assumption that the active complex contains Cr^{+6} and Cr^{+3} atoms. A possible mechanism of the reaction is discussed. Owing to the oxidative action of CrO_3 on the ethylene molecules, part of the Cr^{+6} is reduced to Cr^{+3}, and the trivalent chromium becomes alkylated. The monomer molecule is added at the Cr^{+3}—C bond thus formed. A strong Lewis acid, CrO_3, lowers the electron density on the Cr^{+3} atom. This increases the strength of the Cr^{+3}—C bond and the ability of the Cr^{+3} atom to coordinate with the monomer molecule. The monomer molecule enters the chain at the moment when the strength of the Cr^{+3}—C bond is weakened due to coordination of this molecule with the Cr^{+3} atom.

Introduction

The mechanism of polymerization of α-olefins on oxide catalysts has been discussed by many workers;[1-5] however, not all experimental facts can be explained satisfactorily on the basis of the ideas they put forth. In order to elucidate certain questions of the mechanism of this reaction the author investigated the polymerization of ethylene on a chromic oxide catalyst with and without solvent.

Experimental

The chromic oxide catalysts were prepared by impregnating a carrier with a solution of chromic anhydride and subsequently drying first at 105°C. and then at 160°C. for 4 hr. The CrO_3 content was 6.5%. The carrier was commercial alumosilicate (specific surface area 412 $m.^2/g.$, average pore radius 40 A.) with 3% aluminum oxide applied additionally to its surface in the tests with the solvent, and 10% in those without one.

The aluminum oxide was applied to the alumosilicate by impregnating with a solution of aluminum nitrate, drying at 105°C., and roasting at 500°C.

The catalyst was activated in glass ampules at 350°C. and a residual pressure of 10^{-1} mm. Hg for 3 hr. and at a pressure of 10^{-4} mm. Hg for 2 hr., after which the ampules were sealed.

The solvent was heptane purified by passing it at a flow rate of 2 liters/hr. successively through columns with large-pore and small-pore silica gels, bubbling through dry purified nitrogen, and collecting it in a 2.5-liter receiver, where it was kept under an atmosphere of dry purified nitrogen.

The ethylene from a cylinder (99.85% pure) was further purified by passing at a constant rate under a gage pressure of 1.5 atm. through columns of charcoal, Nichrome catalyst, calcium chloride, Ascarite, large-pore and small-pore silica gel and collected in a condenser cooled with liquid nitrogen. From the condenser the ethylene was evaporated into a 3-liter surge tank. The operation was repeated several times until the pressure in the surge tank reached 80–100 atm.

Ethylene polymerization tests were performed in a 300-ml. autoclave with a screened electromagnetic stirrer, a device for breaking catalyst ampules during the test, and a recess for a thermocouple.

After placing the ampule with the catalyst in the autoclave the latter was evacuated with a mechanical pump at 250°C. for 4 hr.

The rate of the reaction was followed by the change in pressure in the autoclave, the pressure being measured with a standard gage calibrated to $^1/_3$ atm. When, in the course of the test, the pressure had dropped by 3 atm., a fresh portion of ethylene was added to the autoclave. Tests without solvent were carried out with 1.5 g. of catalyst, while in those with the solvent 0.5 g. was used. The amount of solvent added was 140 ml.

Triisobutylaluminum as a 20% solution in heptane was placed in the autoclave in a sealed ampule which was broken simultaneously with the catalyst ampule.

The molybdic oxide catalysts were prepared by impregnating commercial alumosilicate with a solution of ammonium molybdate and subsequently drying at 105°C. for 5 hr., and roasting at 500°C. in a stream of dry air for 3 hr. These samples were used only for determining their oxidative capacity.

Reduction of the chromic oxide and molybdic oxide catalysts with the solvent was carried out in metal ampules. A 1-g. portion of the sample was placed in a 25-ml. ampule, flushed with pure nitrogen, and 8 ml. of the solvent was added; then the ampule was closed hermetically and placed in an electrically heated column. After reduction the solvent was decanted, the ampule was immersed in boiling water and evacuated for 20 min. to remove the last traces of solvent. The benzene used for reducing the samples was purified with sulfuric acid, $KMnO_4$ solution, and alkali, washed with water, dried with anhydrous calcium chloride, and distilled twice over a sodium-potassium alloy in a stream of purified nitrogen. The degree of reduction was determined as the ratio between the amount of oxide reduced to its total initial content. Complete reduction of the chromic oxide samples was achieved by treating with ethyl alcohol at 140°C.

For analysis the CrO_3 was extracted from the samples by boiling the sample repeatedly with sulfuric acid (1:50). The MoO_2 content was determined cerimetically.

Results and Discussion

Without solvent the reaction was performed in an autoclave at 80°C. and 10–13 atm. under static conditions with the stirrer shut off. During the initial period extensive takeup of ethylene was observed (Fig. 1), due partly to sorption of the ethylene by the catalyst surface. After the rate of ethylene takeup had decreased and had attained a constant value the system was evacuated and flushed with pure nitrogen (indicated with a cross on the curve), after which the second portion of ethylene was added. The result was a severalfold increase in the rate of the reaction, which remained constant after this.

These data indicate that the interaction of ethylene and chromic anhydride results in the formation of products which are sorbed by the catalyst surface and poison it. Removal of these products with a stream of inert gas restores the activity of the catalyst.

The data also indicate that after the active surface has formed, CrO_3 and ethylene do not interact any longer to form products capable of poisoning the catalyst.

Additional ethylene polymerization tests without solvent in a continuous-stream system were carried out in a glass reactor so that the change in color of the sample could be observed; these showed that no matter how mild the conditions under which the reaction is accomplished, its beginning always coincides with reduction of the catalyst.

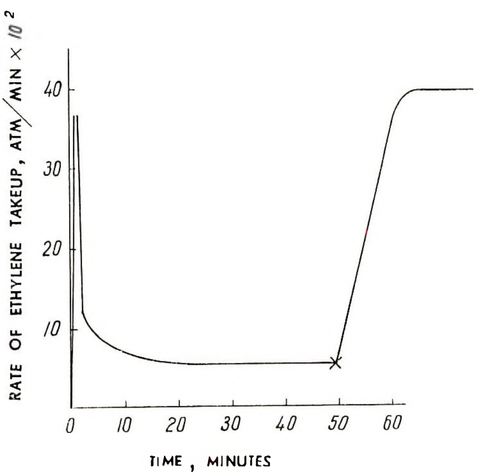


Fig. 1. Change in the rate of ethylene takeup in time in the course of polymerization on a chromic oxide catalyst in the absence of solvent at 80°C., 10–13 atm. pressure.

Polymerization of ethylene in a solvent was carried out at 25°C. and 17–20 atm. The results are presented in Figure 2.

Whenever the catalyst was introduced into the reaction zone at 25°C. a considerable induction period ensued (45–75 min.), and the rate of the reaction was very low (Fig. 2, curve *1*). If the catalyst was introduced into the reaction zone at 140°C. and rapid cooling was commenced some minutes later, at the same time letting out the ethylene, the reaction rate was 20 times as high as in the previous test, and there was no induction period (Fig. 2, curves *3* and *4*). A similar result was obtained when polymerization was carried out preliminarily for 2 hr. without solvent (at 80°C.) and then the ethylene was let out, the system evacuated and flushed with purified nitrogen, the solvent introduced, the mixture heated in a nitrogen atmosphere without stirring to 140°C., and cooling to 25°C. started 5 min. later (Fig. 2, curve *2*). Preliminary 5-min. treatment of the catalyst with the solvent at 140°C. in the absence of ethylene not only failed to activate it, but even lowered its activity (the reaction had not started after 90 min.).

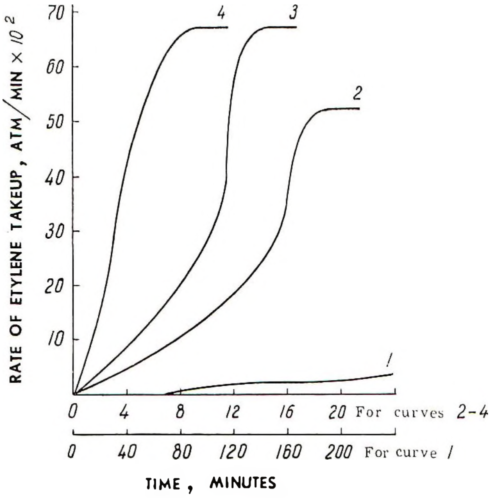


Fig. 2. Change in the rate of ethylene takeup in time in the course of polymerization on a chromic oxide catalyst in a solvent at at 25°C., 17–20 atm. pressure: (*1*) catalyst added to reaction mixture containing ethylene and solvent at 25°C.; (*2*) catalyst first kept in contact with ethylene at 80°C. and 13 atm. for 2 hr.; (*3*) catalyst first kept in contact with solvent and ethylene at 140°C. and 8 atm. for 10 min.; (*4*) catalyst first kept in contact with solvent and ethylene at 140°C. and 40 atm. for 1 min.

The results obtained indicate that an active surface forms on the chromic oxide catalyst only as a result of its interaction with ethylene. They also confirm that the appearance of a narrow signal in the EPR spectrum of the chromic oxide catalyst when it is reduced with the solvent, as described in the literature[6–15] and attributed to Cr^{+5} atoms, is not related to the activity of the catalyst, as some workers have assumed.[12–15] Besides, it is known from the literature[6,11] that the most intense narrow line is observed when the

CrO_3 is applied to aluminum oxide, though the latter is a much less effective carrier than alumosilicate.

The formation of Cr^{+5} on the surface of chromic oxide catalysts is not very probable in any case. The chromium oxides of the valencies intermediate between +6 and +3 are unstable and have defied attempts to separate them. On detailed study the supposed intermediate oxide has always turned out to be a chemical compound of CrO_3 and Cr_2O_3.[16]

A narrow signal is also observed in the EPR spectrum of the chromium chromates.[17] Its width is larger than that of the chromic oxide catalysts after reduction with the solvent, but the carrier may have a considerable effect on the width and shape of the signal.[11,15]

Thus, the reduction product of Cr^{+6} under the conditions studied could apparently have been nothing but Cr^{+3}.

TABLE I

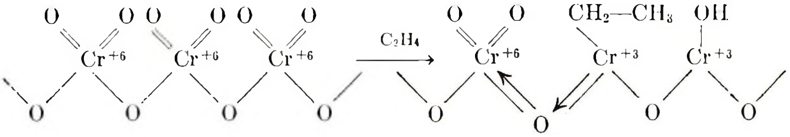
Polymerization of Ethylene on a Chromic Oxide Catalyst in a Solvent at 140°C., 40 atm. Pressure

Catalyst	Cr^{+6} content, %	$Al(i\text{-}C_4H_9)_3$ added, mole/mole Cr	Duration, min.	Yield of polymer, g./g. of catalyst/hr.
Initial	3.3	0	10	655
Reduced with alcohol	0	0	180	0
Reduced with alcohol	0	2	10	100

Table I shows the results of tests which demonstrated that a catalyst which contains no Cr^{+6} owing to reduction by alcohol, is inactive. Hence, the presence of hexavalent chromium atoms is necessary for activity of the catalyst. However, as the catalyst becomes active only after it is partly reduced, there are grounds to assume that the active component contains Cr^{+6} and Cr^{+3} atoms simultaneously.

The same suggestion was put forth in somewhat different form by Cooper.[18]

In a paper published at an earlier date[19] a direct dependence had been established between the oxidative capacity of the chromium oxide catalyst and its activity, and it had been demonstrated that the role of the carrier depends on its effect on the oxidative capacity of the chromic anhydride. These data, together with the fact that the active surface forms only as a result of interaction between the catalyst and the olefin molecule, make it possible to picture the initiation reaction as follows. At the initial stage a π-complex of ethylene is formed with the Cr^{+6} atom. Then several reactions ensue simultaneously as a result of the interaction between the CrO_3 and the ethylene: oxidation of the ethylene, reduction of part of the Cr^{+6} to Cr^{+3}, opening of the double bond of the ethylene molecule, and saturation of one of the resultant free valencies with a hydrogen atom, alkylation of trivalent chromium to form a Cr^{+3}—C bond.


(1)

Further growth of the chain is by addition of monomer molecules at the Cr^{+3}—C bond thus formed.

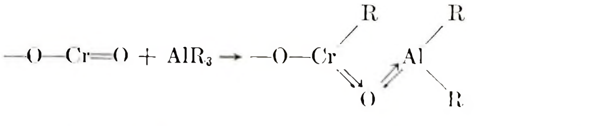
The Me—C bond in organic compounds of transitional metals (Me) is unstable unless the substituents are electron-withdrawing groups. These compounds conduct olefin polymerization only in the presence of Lewis acids.

In chromium oxide catalysts, the role of the Lewis acid is played by the Cr^{+6} atom in the active complex. Drawing electrons away from the Cr^{+6} atom, it raises its positive valency, which assumes a value intermediate between +3 and +6. The decrease in electron density on the Cr^{+3} atom augments the stability of the Cr^{+3}—C bond and simultaneously makes the Cr^{+3} atom capable of coordinating with the olefin molecule. Coordination occurs as a result of the π-electrons of the double bond being drawn over to the *d* shell of the Cr^{+3} atom, and weakens the Cr^{+3}—C bond of the growing polymer chain. The coordinated olefin molecule is inserted at the weakened Cr^{+3}—C bond, after which the stability of the bond increases again until the Cr^{+3} atom coordinates with the next monomer molecule. The entire process is possible only because of the high lability of the *d*-electrons in the chromium atoms.

Thus, the reason for the appearance of a narrow signal in the EPR spectra of chromium oxide catalysts is evidently the redistribution of the electron density between the Cr^{+6} and Cr^{+3} atoms in the chromium chromates formed when these catalysts are reduced by the solvent or the monomer.

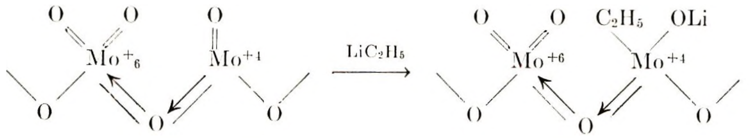
Increase of the electron density on the Cr^{+6} atom lowers its oxidative capacity. Therefore, after formation of the active surface is complete, the catalyst becomes stable towards the reducing action of the monomer and the solvent.

The possibility of formation of an active Cr^{+3}—C bond is also borne out by the experimental data given in Table I, which showed that a catalyst sample which as a result of complete reduction of Cr^{+6} to Cr^{+3} has lost its ability to conduct ethylene polymerization, regains its activity in the presence of triisobutylaluminum. In this case the role of the Lewis acid lowering the electron density on the Cr^{+3} atom is apparently played by the alkyl aluminum compound.


(2)

The oxidative capacity of MoO_3 is much lower than that of CrO_3. We found that the degree of reduction of these oxides on alumsilicate by benzene in the course of one hour is 37% for MoO_3 at 250°C. and 60% for CrO_3

at 140°C. Therefore, in the absence of promoters molybdic oxide catalysts are not very active. The cocatalytic effect of the promoter obviously consists in alkylation of Mo^{+4}. The formation of an active complex in the presence of LiH and ethylene may be pictured as shown in eq. (3).



(3)

Apparently, the mechanism of chain growth on oxide catalysts is similar to that on Ziegler-Natta catalysts.

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Résumé

La polymérisation de l'éthylène sur un catalyseur à base d'oxyde de chrome dans un solvant et en absence de celui-ci a été étudiée. On a trouvé que la surface active du catalyseur est formée exclusivement comme résultat de son interaction avec l'éthylène. Cette interaction est accompagnée de la formation de produits qui empoisonne la surface du catalyseur lorsqu'ils sont absorbés en absence de solvant. Un catalyseur qui ne contient pas d'atomes de chrome hexavalent par suite de la réduction par un alcool est inactif. Par ailleurs, un catalyseur qui contient uniquement des atomes de chrome hexavalent devient actif uniquement lorsqu'il a été partiellement réduit. Les produits le plus probables de cette réduction sont les atomes de chrome trivalent. Les résultats obtenus ont confirmé l'hypothèse que les complexes actifs contiennent à la fois des atomes de chrome hexa et trivalent. Un mécanisme possible de la réaction est discutée. Par suite de la réaction oxydante de CrO_3 sur les molécules d'éthylène une partie des Cr^{+6} est réduite en Cr^{+3} et le chrome trivalent devient alcoylés. La molécule monomérique est additionnée aux liens Cr^{+3}—C formés. L'acide de Lewis fort, CrO_3, diminue la densité électronique d'un atome trivalent. Ceci augmente la force de la liaison chrome^{+3}-carbone et la possibilité de l'atome de Cr^{+3} à coordonner une molecule de monomère. La molécule monomèrique entre dans la chaîne au moment où la force du lien Cr^{+3}—C est relachée par suite de la coordinance de la molécule avec un atome de Cr^{+3}.

Zusammenfassung

Die Polymerisation von Äthylen an einem Chromoxydkatalysator in Gegenwart und Abwesenheit eines Lösungsmittels wurde untersucht. Es wurde gefunden, dass die aktive Katalysatoroberfläche ausschliesslich als Ergebnis der Wechselwirkung mit Äthyllen gebildet wird. Diese Wechselwirkung wird von der Bildung von Produkten begleitet, welche bei ihrer Sorption an die Katalysatoroberfläche in Abwesenheit eines Lösungsmittels diese vergiften. Ein Katalysator ohne Gehalt an Cr^{+6}—Atomen als Ergebnis einer Reduktion durch Alkohol ist inaktiv. Andrerseits wird ein Katalysator, der nur Cr^{+6}—Atome enthält, erst nach partieller Reduktion aktiv. Das wahrscheinlichtste Produkt dieser Reduktion sind dreiwertige Chromatome. Die erhaltenen Ergebnisse lassen die Annahme begründet erscheinen, dass der aktive Komplex Cr^{+6}—und Cr^{+3}—Atome enthält. Ein möglicher Reaktionsmechanismus wird diskutiert. Wegen der oxydierenden Wirkung von CrO_3 auf die Äthylenmoleküle wird ein Teil des Cr^{+6} zu Cr^{+3} reduziert und das dreiwertige Chrom wird alkyliert. Das Monomermolekül wird an die so gebildete Cr^{+3}—C—Bindung addiert. Eine starke Lewis-Säure, CrO_3, erniedrigt die Elektronendichte am Cr^{+3}—Atom. Dadurch wird die Festigkeit der Cr^{+3}—C—Bindung und die Fähigkeit des Cr^{+3}—Atoms zur Koordination mit dem Monomermolekül erhöht. Das Monomermolekül tritt in die Kette in dem Augenblick ein, in welchem die Festigkeit der Cr^{+3}—C—Bindung durch die Koordination dieses Moleküls mit dem Cr^{+3}—Atom geschwächt wird.

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How $TiCl_3$ Catalysts Control the Texture of As-Polymerized Polypropylene

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Synopsis

Within a family of catalyst systems wherein $TiCl_3$ was made by mixing $TiCl_4$ and aluminum alkyl solutions, the primary particles of $TiCl_3$ were usually thin, flat polygons with average diameters ranging from 300 to 1000 A. Even in unused catalyst these primary catalyst particles were bound together into large (~30 μ) secondary particles. A small amount of polyolefin which formed from the aluminum alkyl reducing agent aided in cementing the particles. When propylene monomer was introduced to a slurry of secondary catalyst particles in a liquid hydrocarbon, polymer formed at the surfaces of the ultimate solid particles. The resulting polymer flakes, i.e., particles of as-polymerized polypropylene, were several times larger than the secondary catalyst particles from which they grew but they retained the same shape. The primary catalyst particles, not visibly altered by the catalytic reaction which they propagated, were distributed uniformly throughout the flake polymer. Each polymer flake consisted of many thousands of cohering roundish flakelets about a $^1/_2$ μ in diameter. How the flakelets are agglomerated and the extent to which they are coalesced accounts for the flakes' texture. The basic morular structure of the flakes, which was manifested further by their papillary surfaces, was not altered by purification procedures which removed catalyst from the nascent polymer. Although all the flakes had the same basic small-scale structure there were significant coarse textural dissimilarities among them. Some catalysts gave rise to flakes with an open porous texture: other catalysts gave rise to flakes which were dense and compact. In the former, the flakelets were less tightly appressed, and fissures and slits were larger and more numerous than in the latter. The genetic basis for the differences in flake texture resides in the parent catalyst. Secondary catalyst particles whose constituent primary particles are held together in a dense mass produce dense flakes. Conversely, loose aggregates of primary particles produce flakes with loosely aggregated flakelets. Briefly, dissimilarities in catalyst structure carry over to the texture of the flake progeny. Such textural differences contribute importantly to properties of the flake polymer.

INTRODUCTION

In Ziegler-Natta catalyst complexes, heterogeneity of the catalytic system is an essential factor for the polymerization of aliphatic olefins to isotactic polymers. Just how the solid component of the catalyst ensures the formation of stereoregular crystallizable molecules has not been fully explained. It is generally accepted, however, that the crystallographic configuration of the surface of the solid plays a role in the mechanism of the reaction.[1-3] Hargitay et al.[4] observed visually, by light microscopy, that polymer growth occurred only at the edges of the catalyst crystals when ethylene was admitted to $TiCl_3$ catalyst. By electron microscopy, where the higher resolution revealed finer details, Rodriguez and Gabant[5] also observed that the active centers of polymerization were located along growth spirals of the catalyst crystals. These observations were taken to mean that the reaction is linked to properties of certain crystal faces of the catalyst. Surface configuration is not the only regulator of catalyst behavior, however. Catalyst particle size, shape, and agglomeration also contribute importantly to the overall course of the polymerization and to the morphology of the resulting polymeric material. It is with these aspects of the problem that this paper is concerned. Although the aforementioned properties of $TiCl_3$ catalyst and of "flake" polymer, i.e., particles of as-polymerized polypropylene, are amenable to investigation by microscopy, relatively little along these lines has been published. However, Stauffer Chemical Company's Technical Bulletin[6] states that "the physical form of the polymer particle closely resembles that of the $TiCl_3$ particle, except that it is larger in size." Paleev et al.[7] pointed out that in their catalyst systems the rate of ethylene absorption and the yield of polymer were directly related to the degree of dispersion of the solid titanium organometallic complex, as measured by microscopy. Berger and Grieveson[8] followed, by light microscopy, the course of polymerization of ethylene by a Ziegler-Natta catalyst. They observed that the polymer seemed to precipitate around the catalyst clusters. They noted further that the 1-μ particles visible in their pictures may not be whole crystals of $TiCl_3$ but loose aggregates of microcrystalline material which are easily disrupted by the growing polymer.

EXPERIMENTAL

Catalyst and Polymer Samples

The experimental $TiCl_3$ was made by mixing two solutions, viz., $TiCl_4$ and an aluminum alkyl. The catalyst systems consisted of particles of the $TiCl_3$ [δ crystallographic modification[9]] suspended in heptane under positive nitrogen pressure. Flake polymer before purification was likewise suspended in heptane. The purified polymer was a dry white powder.

Methods and Procedures

Because the catalyst was sensitive to air and moisture, special techniques of specimen preparation were necessary, especially for electron microscopy. Safeguards included the use of only thoroughly dry utensils and liquids for diluting, transferring, and embedding the samples. The main features of some of the less routine handling procedures are outlined below.

Specimens of catalyst for electron microscopy were made by placing a droplet of diluted catalyst slurry on a carbon-filmed screen. The operation was carried out in a glove bag secured to the column of the microscope. From the bag, through which a stream of nitrogen flowed, the specimens were inserted in the microscope.

To shadow specimens, heptane-diluted catalyst slurry to which 0.2% ethylaluminum sesquichloride had been added to further scavenge any air, was heat-sealed in a glass ampule. The ampule was then properly positioned in a vacuum evaporator. When a high vacuum was obtained in the bell jar, the tip of the ampule was broken off by means of a solenoid actuated arm. The slurry was, thereby, sprayed onto carbon-filmed specimen screens which had been taped to a glass slide. The liquid component of the catalyst slurry vaporized quickly and the high vacuum was restored. The dried catalyst specimens were then shadowed with uranium, at a 30° angle. Nitrogen was admitted to the bell jar. The glass slide with its attached specimen screens was placed, while still under the bell jar, into a small nitrogen-flushed and screw-capped jar. The latter was then transferred to the glove bag and the specimen screens were placed in the microscope. This procedure may also be used to replicate catalyst specimens with carbon while they are in the vacuum evaporator.

Flake surfaces were replicated by a three-stage technique involving first gelatin, then nitrocellulose and finally carbon. The dry flakes of purified polymer were used directly. To replicate the surface of unpurified flakes, small amounts of slurry were first evaporated to dryness in a stream of dry nitrogen.

To cut thin sections of polymer flakes for transmission electron microscopy, the flake was embedded in epoxy resin. The dry purified flake presented no special problems. To embed the unpurified flake, the heptane vehicle was first replaced with propylene oxide, which was then drawn off before the resin was added.

RESULTS AND DISCUSSIONS

Secondary Catalyst Particles

The catalyst slurries contained, as shown by light microscopy, many large, optically dense catalyst particles (Fig. 1). These so-called secondary catalyst particles were more or less round. Most of them had diameters which ranged from 20 to 40 μ. Consequently, they were too thick

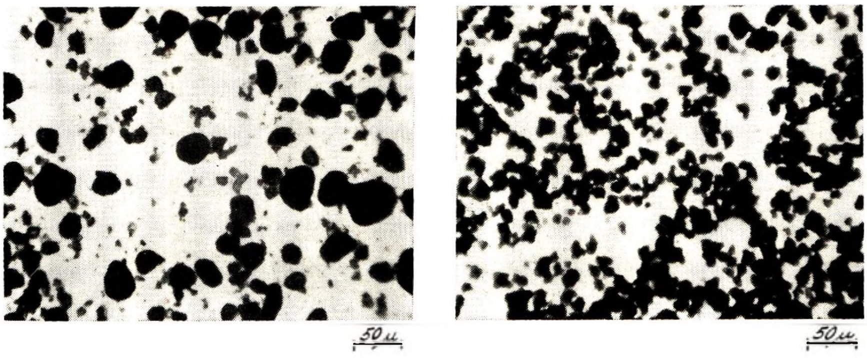

Fig. 1. Secondary catalyst particles in two different slurries.

for direct examination by electron microscopy. The slurries also contained some small secondary catalyst particles. The latter accounted for only a small fraction of the weight of the solid component but, fortunately, they were thin enough to be examined by transmission electron microscopy.

Primary Catalyst Particles

Electron microscopy revealed that the secondary particles consisted of aggregates of thin, flat, polygonal primary particles (Fig. 2), although there were some deviations from this typical crystal habit. The size of the polygonal particles, which are the dark spots shown in the micrograph, ranged from 100 to 1000 A. These somewhat coin-shaped crystals of $TiCl_3$ were enmeshed in a thin, structureless film of polyolefin. The polyolefin, which evidently formed from the aluminum alkyl used in making the catalysts, was already present in unused catalyst systems. It was identified as such—after recovery from butanol, which dissolved the $TiCl_3$—by both x-ray diffraction and by infrared absorption. Moreover, in the dried-down state, in which the polymer was examined, it was crystalline.

Because the primary particles were surrounded by polyolefin film their heights could not be measured accurately by shadow casting. However, the metal chloride particles were at least semitransparent to the electron beam, so that they cannot be many Angstroms thick. Except for instances where one particle either rested or grew on another, the uniform semiopacity of the crystals from one side to the other indicates that they are essentially flat.

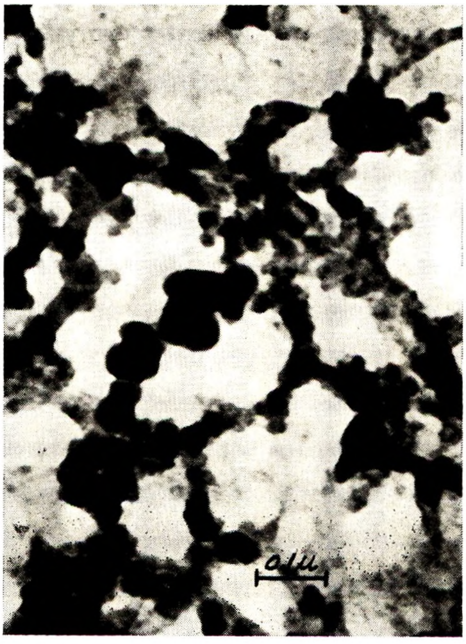

Fig. 2. Primary catalyst particles catenated by a thin film of polyolefin.

Fig. 3. Metal-shadowed primary catalyst particles.

The primary particles of the metal chloride gave a diffraction pattern which, not unexpectedly, persisted in the electron beam. When the catalyst was deliberately exposed to air, the diffraction pattern changed, evidently as Al and Ti compounds were hydrolyzed or oxidized. At the same time, the particles underwent a visible change, viz., they acquired a sort of frothy granularity. The absence of this air-generated artifact in electron microscopical specimens served as a check on the adequacy of the specimen-preparing techniques.

Even by repeatedly centrifuging unused catalyst in hot Decalin containing hydrogen, not all the polyolefin which was bonded to the unused catalyst particles could be removed. Consequently, "free" metal surfaces could not be examined by such generally rewarding techniques as shadow casting and replication. Figure 3 shows a shadowed specimen of unused catalyst. The surfaces show an interesting pattern of parallel striations, but the significance of the pattern is highly conjectural.

Catalyst in Unpurified Flake Polymer

When, under appropriate conditions, monomer (propylene) was introduced to a slurry of secondary catalyst particles in diluent, polymer formed around the solid particles in the system. The resulting flakes of polymer were several times larger than the secondary catalyst particles but they maintained the same shape. After the unpurified flake polymer was dissolved in hot Decalin, primary catalyst particles were recovered by centrifuging. They appeared to be identical with the primary particles in the

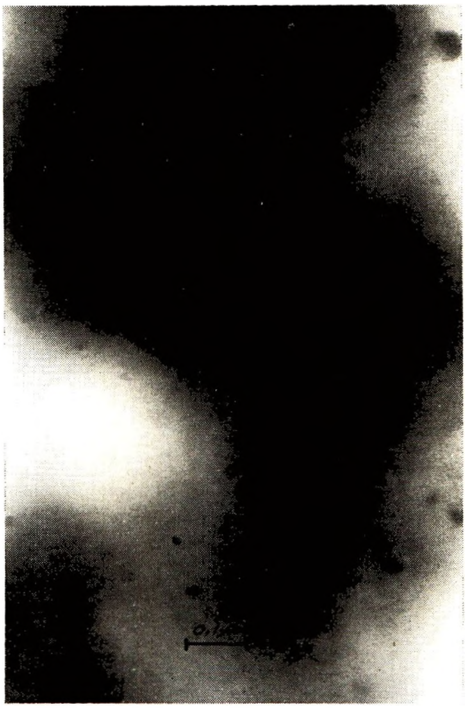

Fig. 4. Primary catalyst particles in ultrathin section of unpurified flake polymer.

original unused catalyst. Moreover, they were present in sufficient number to indicate that their number as well as their nature does not change during polymerization.

If, as just explained, visibly unchanged primary catalyst particles can be recovered from solutions of unpurified polymer, the surviving catalyst should be visible in thin sections of the flake. Figure 4 shows, at 144,000 × magnification, primary catalyst particles surrounded by polymer. The particles occur singly. They are polygonal, but they look that way only when lying in the plane of the section. The uniformly distributed catalyst residue is removed during purification of the flake.

Texture of Purified Flake Polymer

An electron microscopical examination of sections of polypropylene flake, both unpurified and purified, indicated that the flakes are microporous. Each flake consists of flakelets about $^1/_2$ μ in diameter (Fig. 5). The latter are variously appressed and coalesced into a coherent whole. A flake contains many interstices whose size and shape depend on how the individual flakelets of polymer adhere. Frequently, these holes are small, i.e., tenths of a micron, and nearly equidimensional.

Sometimes the flakelets are arranged in a concentric pattern of alternating layers resembling the assemblage of scale leaves in an onion bulb. The alternating layers differ in porosity, i.e., a layer with many open spaces alternates with a layer containing fewer open spaces and, correspondingly, more polymer. Typical flakelets were present right out to the flake surface. There was no morphologically differentiated skin. The flakes' pa-

Fig. 5. Section of purified flake, showing constituent flakelets.

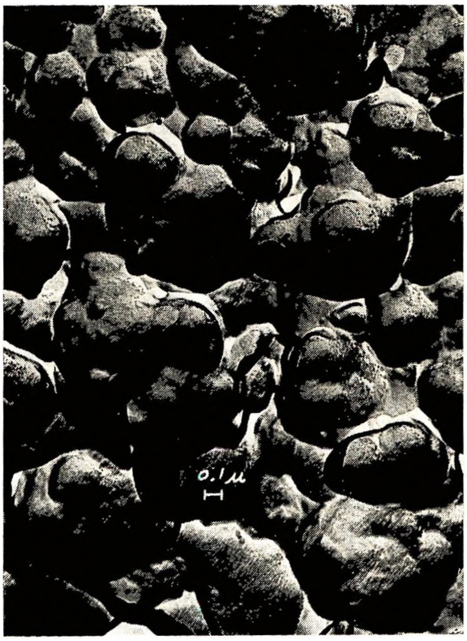

Fig. 6. Papillary surface of flake polymer.

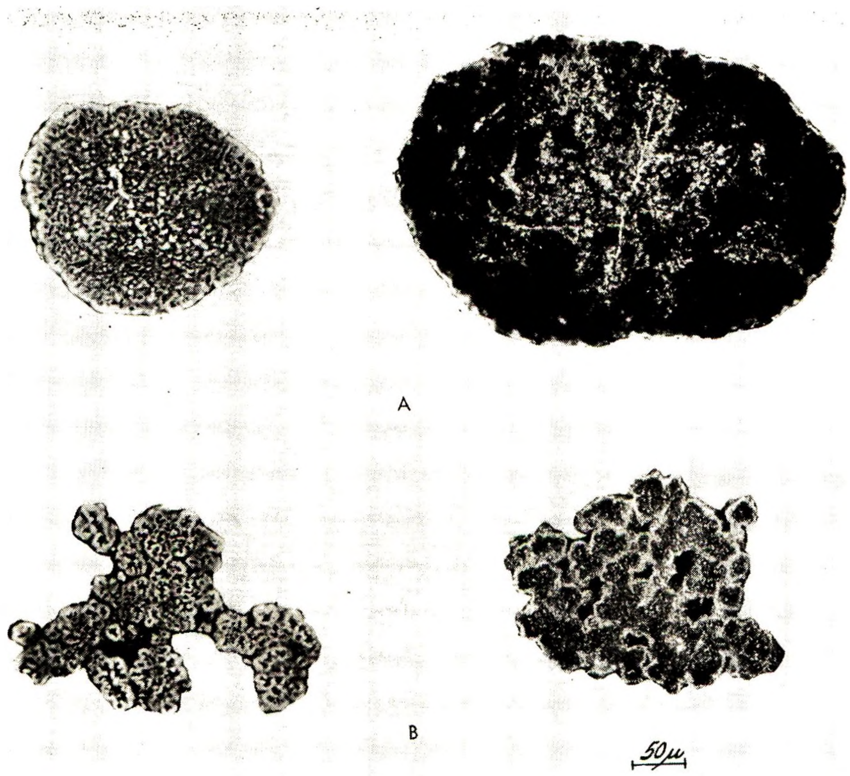

Fig. 7. Sections through flake polymer showing differences in texture: (*A*) dense flake; (*B*) porous flake. Photographed by transmitted light and by dark field illumination.

pillary surfaces are just a further manifestation of the flakes' basic morular structure (Fig. 6).

Light microscopy revealed coarser textural dissimilarities. Sections through a highly porous flake, illustrated by Figure 7*B*, show innumerable, uniformly distributed small holes on the order of a few microns. There is also a smaller number of large holes whose size ranges from 10 to 20 μ. A less porous flake is shown in Figure 7*A*. It is denser, especially away from the center, because there are fewer holes. Textural differences such as these contribute importantly to the physical properties of flake polymer.

Structure of Secondary Catalyst Particles

As pointed out in a preceding section, the large secondary catalyst particles consist of agglomerates of the smaller primary ones. The texture of the secondary particles depends on how tightly those primary particles are held together and in what manner they are arranged with respect to each other. The texture of the flakes depends, in turn, on the texture of the secondary catalyst particles which gave rise to the polymer. Figure 8*A* shows sections through dense secondary catalyst particles. The catalyst

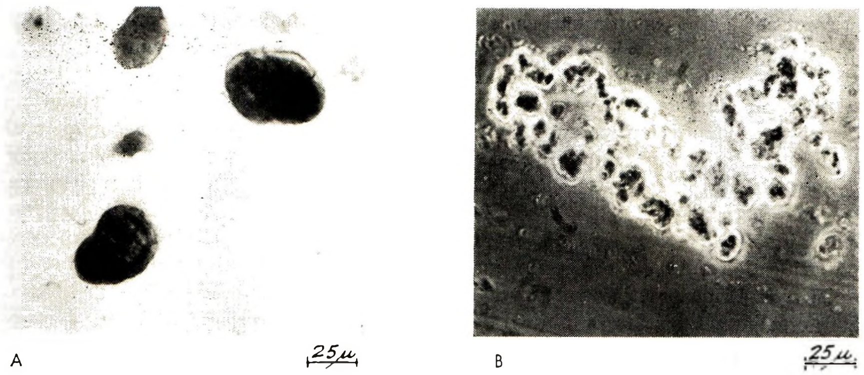

Fig. 8. Sections through two different secondary catalyst particles showing differences in texture: (*A*) dense catalyst; (*B*) porous catalyst.

structure is so dense that it was not possible to cut a section thin enough to reveal much internal detail. Flake originating from such catalyst particles is also dense, as illustrated by Figure 7*A*. Figure 8*B* shows a section through a secondary catalyst particle of the type from which the polymer flakes shown in Figure 7B formed. Both the catalyst and the polymer are highly porous. In short, dissimilarities in catalyst texture carry over to the flake progeny.

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Résumé

Au sein d'une famille de systèmes catalytiques où le chlorure de titane était obtenu par mélange du $TiCl_4$ et de solutions d'alcoylaluminium les particules primaires du $TiCl_3$ étaient habituellement des polygones plats fins avec des diamètres moyens variant de 300 à 1000 Å. Même dans le catalyseur non-utilisé, ces particules primaires de catalyseur étaient liées entre elles en particules secondaires plus grandes de l'ordre de 30 microns. Une petite quantité de polyoléfine qui était formée au départ d'alcoylaluminium comme agent réducteur facilitait l'adhésion de ces particules entre elles. Lorsque le propylène est introduit à cette boue de particules secondaires des catalyseurs au sein d'un hydrocarbure liquide, le polymère est formé à la surface de ces particules solides. Le polymère en résultant sous forme de flocons, c'est-à-dire des particules de polypropylène polymérisé, était plusieurs fois plus grandes que les particules de catalyseur secondaires par lesquelles elles se sont formées mais dont elles retiennent la forme. Les particules primaires de catalyseur qui ne sont pas visiblement altérées par la réaction catalytique au cours de la propagation sont distribuées uniformément à travers le polymère en flocons. Chaque grain de polymère consiste en plusieurs milliers de granulés d'environ $^1/_2$ mu de diamètre. Pour connaître la texture du grain, il faut savoir le mode d'agglomération des granulés et leur degré de cohésion. L'unité structurale des grains telle qu'elle se manifeste par la structure granuleuse de la surface n'est pas altérée par le processus de purification qui enlève le catalyseur du polymère en fabrication. Quoique tous les grains aient la même microstructure de base, il existe certaines dissemblances de texture. Avec certains catalyseurs, on obtient des grains poreux à texture ouverte, avec d'autres catalyseurs on obtient des grains denses et compacts. Dans le premier cas les granulés sont moins comprimés et le nombre de fissures et de fentes est plus important que dans le second cas. L'origine de ces différences provient du catalyseur. Des particules secondaires de catalyseur, qui constituent les particules primaires des grains, sont tenues ensemble dans la masse très dense des grains compacts. Par contre, des aggrégats peu denses de particules primaires rendent les granulés peu aggloméré. En résumé, ce sont les différences de structure du catalyseur qui sont responsables des différences rencontrées dans la texture du grain. De telles différences de texture ont une influence très grande sur les grains du polymère.

Zusammenfassung

Innerhalb einer Familie von Katalysatorsystemen, bei welchen $TiCl_3$ durch Mischen von $TiCl_4$ und Aluminiumalkyllösungen erzeugt wurde, bildeten die $TiCl_3$-Primärpartikel gewöhnlich dünne, flache Vielecke mit einem mittleren Durchmesser im Bereich von 300 bis 1000 Å. Auch in ungebrauchten Katalysatoren waren diese Katalysatorprimärpartikeln zu grossen ($\sim 30\ \mu$) Sekundärpartikeln vereinigt. Eine kleine, aus der reduzierenden Aluminiumalkylverbindung gebildete Polyolefinmenge war als Zement für die Partikel wirksam. Bei Einführung von Propylen in eine Aufschwemmung der Katalysatorsekundärpartikel in einem flüssigen Kohlenwasserstoff bildete sich Polymeres an der Oberfläche der festen Grundteilchen. Die entstandenen Polymer-"flocken," d.h. die Teilchen von aufpolymerisiertem Polypropylen, waren einige male grösser als die Katalysatorsekundärteilchen, aus welchen sie gewachsen waren, behielten aber die gleiche Gestalt bei. Die Primärpartikel des Katalysators wurden durch ihre katalytische Wirksamkeit nicht sichtbar verändert und waren durch die Polymerflocken gleichmässig verteilt. Jede Polymerflocke bestand aus vielen tausend kohärenten abgerundeten Flöckchen mit etwa $^1/_2\ \mu$ Durchmesser. Die Art der Agglomerierung und das Ausmass der Coalescenz der Flöckchen bestimmt die Textur der Flocken. Die Morula-Grundstruktur der Flocken, welche sich auch in ihrer warzenförmigen Overfläche äusserte, wurde durch die Reinigungsverfahren zur Entfernung des Katalysators aus dem nascenten Polymeren nicht geändert. Obwohl alle Flocken die gleiche Grundfeinstruktur besassen, bestanden wesentliche Unterschiede in der Grobtextur. Einige Katalysatoren lieferten Flocken mit einer offenen Porentextur, andere Katalysatoren dichte und kompakte Flocken. In ersteren waren die Flöckchen weniger dicht zusammengepresst und Risse und Spalten waren grösser und zahlreicher als in letzteren. Die genetische Grundlage für die Unterschiede in der Flockentextur liegt im erzeugenden Katalysator. Sekundäre Katalysatorteilchen aus primären, in einer dichten Masse zusammengehaltenen Partikeln erzeugen dichte Flocken. Umgekehrt führen lose Aggregate von Primärteilchen zu Flocken mit lose aggregierten Flöckchen. Kurz gesagt übertragen sich Verschiedenheiten in der Katalysatorstruktur auf die Texture der Flockennachkommenschaft. Solche Texturunterschiede liefern einen wichtigen Beitrag zu den Eigenschaften des Flockenpolymeren.

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Application of Molecular Weight and Particle Growth Measurements in Continuously Uniform Latices to Kinetic Studies of Styrene Emulsion Polymerization*

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Synopsis

It is possible to generate, in specially formulated styrene emulsion polymerizations, latices in which the monomer-polymer particles are uniform through all stages of growth. These latices are kinetically similar to their polydispersed counterparts and can therefore be used as model systems in generalized kinetic studies of emulsion polymerization. The most important feature of these systems is the fact that the particles are uniform throughout the reaction with regard to all intrinsic properties and rate processes, and the particles can be characterized by this complete, continuous uniformity. Certain remarkably simple, but precise, relationships exist between the overall, measurable kinetic parameters and the individual particle kinetic parameters, thereby resulting in a heretofore unrealized analytic accessibility. Molecular weight kinetic analyses are an order of magnitude more accurate than in non-uniform systems. Application of these continuously uniform systems in actual kinetic studies indicates an inconsistency in the current concepts of emulsion polymerization, i.e., the generation of polymer at a constant molecular weight is predicted while an increase of several fold is observed. Before the situation can be clarified, further studies with continuously uniform systems are needed to evaluate molecular weight development, molecular weight distribution, and molecular structure and also to re-evaluate the rate and diffusion processes which control these structural features.

INTRODUCTION

Recent literature reviews[1-4] indicate that the qualitative and some of the quantitative aspects of the emulsion polymerization reaction are well understood. This assertion is especially true for systems of the classical type, as exemplified by styrene emulsion polymerization with potassium persulfate as initiator in a dilute aqueous solution of fatty acid soap. The quantitative aspects, which are the chief concern of this paper, are cur-

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rently being described in terms of either of two steady-state theories: the Smith-Ewart theory[5-7] or the Medvedev theory.[8,9]

The constant recurrence and apparent major significance of the particle size variable in the rationale of emulsion polymerization reaction kinetics prompted us to continue and to extend the heretofore limited practice of using latex systems of uniform particle size for these studies. Vanderhoff and his associates[10,11] utilized competitive growth studies, starting each experiment with uniform particle size seed latices which were always larger than about 1200 A. in diameter. Roe and Brass[12] and Zimmt[13] also employed uniform particle size latices in such kinetic studies, but they took no specific advantage of this fact in their analyses.

Our studies first involved an investigation of particle size uniformity and particle growth over all ranges of conversion in systems which were known to generate uniform particle size latices as products.[14] Electron microscope studies of the initial latex product resulted in the rather startling and significiant discovery that the initial particles were remarkably uniform in size—generally on the order of 300–400 A. in diameter. The formation of all particles must have occurred, therefore, within a very short interval of time. Further electron microscope studies at progressively higher degrees of conversion and particle growth seemed to indicate that particle growth proceeded via the usual mechanism except for the fact that the particles were all uniform in size and grew at the same rate. It therefore seemed that these particular latex systems could be utilized to extend the use of uniform latices into the period of "ideal" emulsion polymerization,[4] which is generally over by the time the particles reach 1200–1300 A. in diameter.[4,15] As will be seen, this contention was completely borne out in a kinetic similarity study of monodispersed and classical polydispersed latices.

In the ensuing discussion, particular emphasis is placed on the analytical accessibility which these continuously uniform particle size systems exhibit in kinetic analyses—a property not exhibited by their polydispersed counterparts. Styrene emulsion polymerization in a classical type formulation is of particular interest here, but the notion that continuously uniform latices offer a particularly powerful analytical tool in generalized emulsion polymerization kinetic studies can be extended to other types of systems as well. The value of our approach is illustrated in a case study of the currently popular theories of emulsion polymerization to reveal a heretofore unrecognized anomaly in these theories.

EXPERIMENTAL

In general, the approaches to producing continuously uniform latices in emulsion polymerization processes involve the use of special soaps or the manipulation of the manner in which soap is formed or added to the reaction vessel. For the most part, generation of these uniform latices remains an industrial art. Specific formulations have not been published to any great extent,[12-14,16,17] although these are generally well known.

Polymerization

The general techniques of emulsion polymerization are well known and are extensively described in the literature. Polymerization experiments were conducted in a bottle polymerizer which was maintained at 60 ± 1°C. In this study, the uniform latices were generated by slow soap additions.[14] The standard formulation is as follows: 180 g. water, 100 g. styrene monomer, 0.5 g. potassium persulfate, x g. preformed potassium laurate soap. The soap was used in the following amounts: run C, 0.0035 mole; run B, 0.007 mole; run A, 0.014 mole per charged bottle. The initial charge consisted of 155 g. water and 25% of the total soap charge. The initiator was dissolved in 10 g. of water and was charged to the sealed bottle just prior to placing the bottles in the bath. The remaining 75% of the soap charge was dissolved in 15 g. of water and added in 1-ml. increments every 12 min. after the reactions began. Data for one run were secured from several supposedly identical reaction bottles. Since relatively large samples were required early in a run to obtain a sufficient amount of polymer for analysis, it was necessary to utilize the contents of an entire bottle for one sample. To enhance data reproducibility between bottles within a run, stock solutions of initiator, soap, and styrene were prepared for all bottles within a run.

Conversion

Since the latices were continuously uniform the extent of reaction could be determined in two ways: (*1*) by taking the ratio of the cubes of the intermediate to final particle diameters and (*2*) by gravimetric means. Both methods gave the same results within the limits of experimental error.

Electron Microscopy

The method of Maron et al.[18] served as a basis for the measurement of latex particles by electron microscopy. A JEM-6A electron microscope was used in these studies, magnifications generally ranging from 10,000 to 30,000×. Particle size uniformity is reported as the ratio of weight-average to number-average particle diameter.

To prevent drifting of the specimen under observation, the Collodion film was reinforced with a thin film of metal deposited by vacuum evaporation. When it was necessary to shadow the specimen, as with the small particle size latices, support was accomplished as a secondary effect. When

TABLE I

Diameter, A.	Standard deviation	Lot number	Number of measurements
880	80	LS-040-A	1164
1880	76	LS-055-A	1065
2640	60	LS-057-A	577
3650	79	LS-061-A	438

shadowing was not necessary, a thin film of chromium was deposited on the naked Collodion film before the latex samples were deposited in the usual manner.

Sufficient accuracy of particle size measurement was obtained by calibrating each micrograph with an internal standard mixed with the sample before deposition. The Dow uniform polystyrene latices listed in Table I were used for these purposes.

Intrinsic Viscosity and Molecular Weight

Intrinsic viscosities were calculated by the one-point method of Maron[19] from relative viscosities of dilute toluene solutions measured at 30°C. in Cannon dilution viscometers. In the exponential relationship $[\eta] = KM^a$, the constants of Goldberg et al.[20] were used: $K = 3.7 \times 10^{-4}$ and $a = 0.62$.

Monomer–Polymer Ratio

The equilibrium monomer–polymer ratio at room temperature was determined by steam-distilling monomer from a saturated latex from which the emulsified monomer had been removed by centrifugation.

PARTICLE SIZE UNIFORMITY

Particle size data for unswollen latex particles from several typical runs are shown in Table II. One can readily see from the uniformity ratios and standard deviations that particle size uniformity was developed very early in any given run and was maintained for the duration of that run. Since it is safe to presume that for any stage of the reaction the monomer–polymer ratio was the same for all particles, the swollen particles as they existed in the actual reaction medium must have also been uniform in size. Thus, the latex particles were continuously uniform in size throughout the growth process.

Figures 1–4 show electron micrographs of particle size samples taken during a typical run. The data in Table II were taken from such micro-

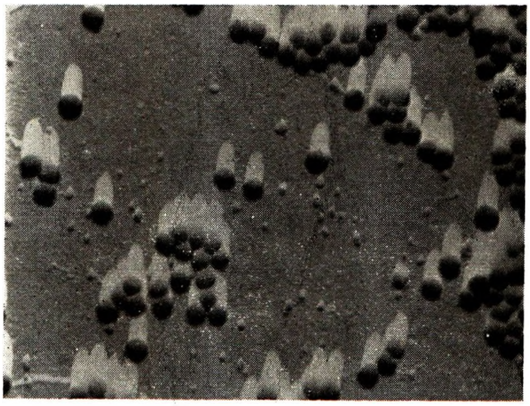

Fig. 1. Sample B-1. Particle diameters: sample = 325 A. as determined by shadow width measurement, standard = 880 A. 29,800×.

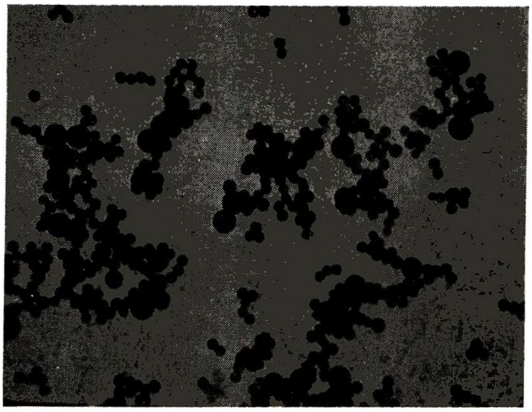

Fig. 2. Sample B-3. Particle diameters: sample = 935 A., standard = 1880 A. 19,000×.

Fig. 3. Sample B-5. Particle diameters: sample = 1335 A., standard = 1880 A. 19,500×.

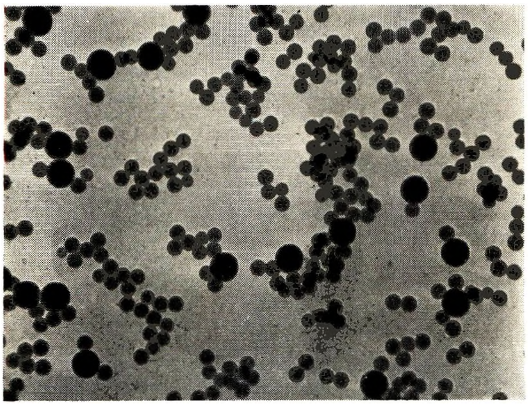

Fig. 4. Sample B-final. Particle diameters: sample = 1490 A., standard = 2640 A. 19,600×.

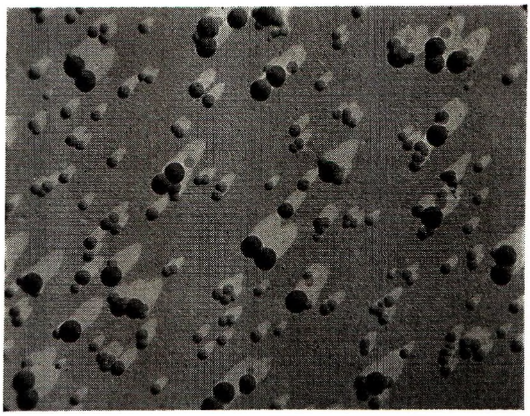

Fig. 5. Sample from run based on a soap content of 0.008 mole lithium stearate and 0.0002 mole lithium oleate, all of which was charged initially. Particle diameters: sample average = 440 A., minimum = 240 A., standard = 880 A. Sample time = 6 min. 29,350×.

graphs. Of the two sizes of particles seen in each micrograph, one is the standard while the other is the sample. Figure 5 is particularly interesting, in that it represents a sample taken, in this case, only 6 min. after the reaction was initiated. The smallest particle observed was 240 A., and

TABLE II
Particle Size Uniformity

Run	Soap concn. per charge, mole	Sample no.	Time, min.	Particle diameter, A.	Standard deviation	Uniformity ratio	No. particles counted
A	0.014	1	15	370	3	1.031	7
		2	45	835	80	1.024	15
		3	75	925	57	1.009	19
		4	105	1090	62	1.011	14
		5	135	1250	2	1.010	19
		6	180	1245	66	1.010	17
		Final	—	1290	64	1.008	21
B	0.007	1	15	325	3	1.040	11
		2	35	900	18	1.005	7
		3	45	935	57	1.017	16
		4	90	1135	82	1.001	13
		5	150	1335	48	1.004	19
		6	210	1435	36	1.003	16
		Final	—	1490	45	1.002	18
C	0.0035	1	5	520	1	1.009	5
		4	90	1375	9	1.025	10
		5	150	1600	1	1.000	8
		6	240	1915	3.5	1.006	11
		7	330	2090	2.4	1.001	11
		8	420	2360	2.3	1.001	10
		10	600	2585	9	1.004	14
		Final	—	2900	5	1.002	19

none smaller was ever observed in any other sample during the entire series of these studies. In samples taken very early in any run (less than 5 or 6 min.) no particles were observed.

KINETIC BEHAVIOR AND PROPERTIES

To establish the fact that the principle of kinetic similarity was to be maintained in these studies, the kinetic behavior and properties of these monodispersed latices were compared with those of their classical counterparts. Because of the similarities noted below, the uniform systems herein described should be valid model systems for generalized kinetic studies of classical emulsion polymerization types.

Formulations are Essentially the Same

The formulations used in these studies closely match those of typical classical formulations: 180 parts water, 100 parts monomer, 3–5 parts

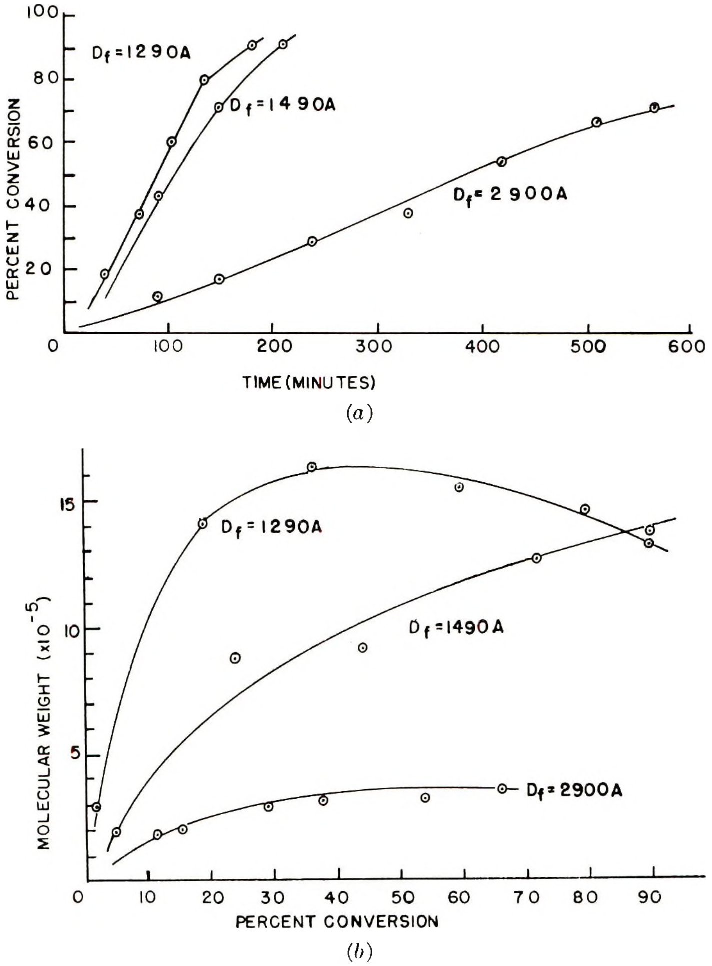

Fig. 6. Kinetic data for monodisperse latices: (*a*) conversion vs. time; (*b*) molecular weight vs. conversion.

TABLE III
Kinetic Data for Uniform System Runs A, B, and C

Run	Soap concn./charge, mole	Sample no.	Time, min.	Particle diameter, A.	Intrinsic viscosity	Molecular weight $\times 10^{-6}$	Conversion, %
A	0.014	1	15	370	0.903	0.291	2.36
		2	45	835	2.405	1.412	19
		3	75	925	2.631	1.632	35.8
		4	105	925	2.560	1.556	60.5
		5	135	1250	2.544	1.546	80.5
		6	180	1245	2.306	1.319	90.2
		Final	—	1290	2.23	1.257	100
B	0.007	1	15	325	0.659	0.175	10.4
		1	35	900	—	—	21.8
		3	45	935	1.80	0.885	24.2
		4	90	1135	1.85	0.925	44.5
		5	150	1335	2.274	1.275	72.2
		6	210	1435	2.375	1.385	90.7
		Final	—	1490	2.200	1.223	100
C	0.0035	2	15	520	0.433	0.089	0.6
		4	90	1375	0.808	0.187	10.65
		5	150	1600	0.688	0.120	16.8
		6	240	1915	0.713	0.243	28.9
		7	330	2090	0.811	0.308	37.7
		8	420	2360	0.967	0.313	54.2
		9	510	2540	0.969	0.956	67.2
		10	600	2585	1.486	—	71.0
		Final	—	2900	—	—	100

fatty-acid soap, and 0.3–0.5 parts potassium persulfate. These were kept as simple as possible to avoid undue complications in these preliminary kinetic studies. The only significant difference arises in the amount of soap used and its method of addition to the reaction vessel.

Colloidal Properties are Similar

The number of particles per milliliter in the uniform systems could range from 6.6×10^{14} for 1000 A. (diameter) particles to 3.0×10^{13} for 1300 A. (diameter) particles.* This range compares favorably with that generally observed in polydispersed systems: 10^{14}–10^{15} particles/ml.[6]

For typical polydispersed latex particles, Maron et al.[21] report latex surface areas per gram of latex ranging from about 120 m.^{2}/g. for 500 A. particles to about 48 m.^{2}/g. for 1300 A. particles. For uniform latex particles this range would run from about 120 m.^{2}/g. for 500 A. particles to 46 m.^{2}/g. for 1300 A. particles. The agreement here is indeed excellent.

Colloidal equivalence is especially important from the viewpoint of the transport processes which take place in this colloidal system, e.g., with

* Such numerical examples are based on a knowledge of the geometry and formulation of the system.

nearly identical surface areas the free-radical efficiency should be the same in both systems.

Rate Curves Are Similar

Figure 6*a* shows rate curves for some typical uniform system runs (Table III) while Figure 7*a* shows comparable data obtained by Smith[7] for typical nonuniform system runs (Table IV). They both exhibit constant rate periods, followed by periods of decreasing rates, due presumably to the decrease in monomer concentration within the particles.

TABLE IV

Kinetic Data for Nonuniform System Runs[a,b]

Temperature, °C.	Sample no.	Time, min.	Conversion, %	Intrinsic viscosity	Molecular weight × 10^{-6}
30.5	1	60	3.25	8.39	5.4
	2	120	6.72	11.9	10.0
	3	180	14.8	15.6	16.5
	4	240	22	16.1	18.0
	5	300	30	17.4	20.5
	6	330	33.4	17.3	20.5
50	1	30	5.75	5.82	2.8
	2	60	15.65	7.6	4.35
	3	90	35.5	8.83	5.9
	4	120	49.0	9.23	6.4
	5	150	67.1	9.72	7.0
	6	180	80.6	9.63	6.9
	7	240	88.5	9.01	6.2
70	1	10	13.6	4.28	1.6
	2	20	32.1	4.8	2.0
	3	30	50.0	5.38	2.45
	4	40	65.5	5.05	2.1
	5	50	83.0	5.29	2.35
	6	60	88.0	5.07	2.1
	7	90	93.5	3.86	1.35
90	1	5	17.4	1.25	0.265
	2	10	44.7	1.36	0.29
	3	15	66.7	1.43	0.35
	4	20	84.0	1.42	0.35
	5	25	91.0	1.39	0.32
	6	30	92.5	1.42	0.35

[a] Data of Smith.[7]

[b] Formulation: 3.0 ml. (0.55 wt.-%) S. F. flakes; 0.3 ml. 1.81% $K_2S_2O_8$ solution; 2.0 ml. distilled styrene.

Development of the Viscosity-Average Molecular Weight is Similar

Figure 6*b* shows the development of viscosity-average molecular weight for the uniform system runs (Table III) shown in Figure 6*a*, while Figure 7*b* shows the same for the nonuniform systems (Table IV) shown in Figure 7*a*.

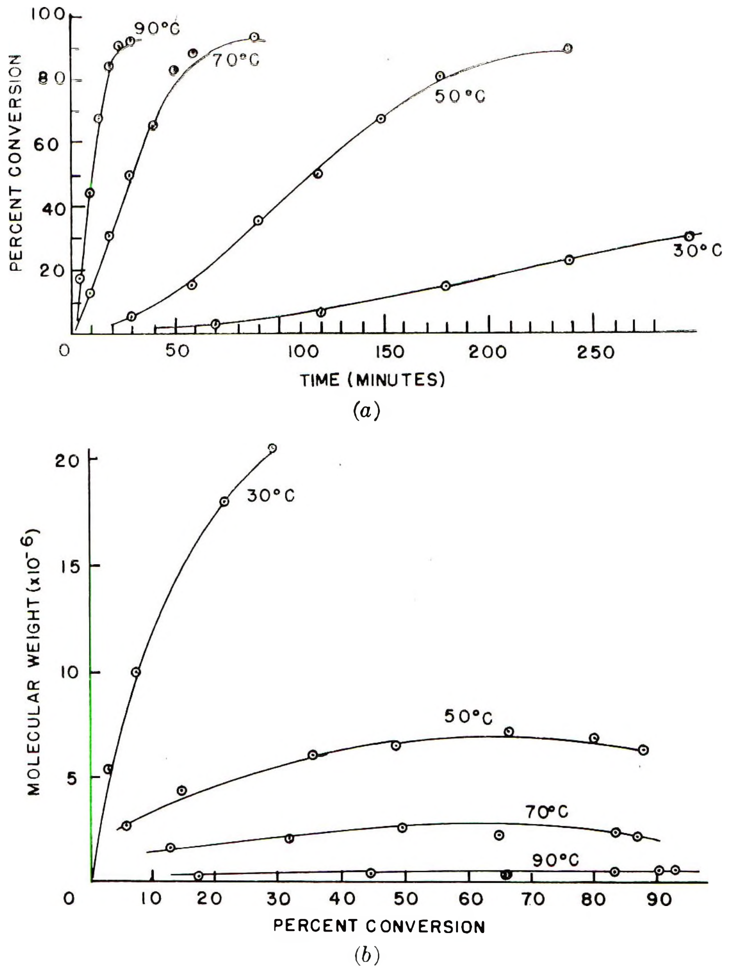

Fig. 7. Kinetic data for polydisperse latices: (*a*) conversion vs. time; (*b*) molecular weight vs. conversion.

These molecular weight development curves are best compared on the basis of the nonuniform particle size data taken at 50°C., since the initiation conditions correspond more to those employed in these studies. Under the conditions of Smith's runs, the rate of generation of free radicals was about 0.45×10^{13}/ml.-sec. at 50°C. while under the conditions described for our runs this rate was about 0.62×10^{13}/ml.-sec. For the runs selected for comparison, the viscosity-average molecular weight increases several fold with the extent of reaction to a maximum and then decreases. This maximum corresponds roughly to the points of departure from constant rate.

Monomer–Polymer Ratios Are About the Same

Several workers have investigated the monomer–polymer ratio of nonuniform particle size systems.[2,4,6,11,22] They found values between 1.2 and

TABLE V
Monomer–Polymer Ratio for Monodispersed Latices

Sample no.	Particle diameter, A.	Solids, %	M/P
1	740	5.8	0.8
2	915	11.2	1.7
3	1090	3.2	1.45
4	1200	14.25	1.55
5	1245	10.8	1.3

2.0. These results have been confirmed for the proposed model system in equilibrium measurements of latex particle swelling. These data are shown in Table V.

ANALYTIC ACCESSIBILITY

The most important aspect of continuously uniform particle size systems is the dynamic equivalence that will exist between the identically sized particles during the reaction. That is, dynamic equivalence will remove the ambiguities imposed by a particle size distribution in the analysis of individual particle reaction parameters. To amplify: the intrinsic properties associated with the individual particles will be identical for each and every particle, and such properties as the molecular weight and monomer–polymer ratio of each particle will be the same as the overall bulk values. Also, the rate of any event associated with an individual particle will be exactly equal to the overall respective rates divided by the number of particles present. The relationships associated with the consequences of dynamic equivalence are summarized in Table VI. Furthermore, since all particles are identical in all respects throughout the reaction process, the particles are completely uniform in a continuous fashion. Hereafter, "uniformity" will mean this complete uniformity.

The relationships of Table VI hold the key to the marked improvement witnessed in the analytic accessibility of continuously uniform systems

TABLE VI
Relationships of Individual Particle Kinetic Parameters in Continuously Uniform Emulsion Polymerization Reactions[a]

Intrinsic properties	Rate processes	Steady-state relationships
$(M/P)_p = (M/P)$	$R_{pp} = R_p/N$	$\bar{X}_{np} = \dfrac{2R_{pp}}{R_{ip}} = \dfrac{2R_p}{R_i}$
$\bar{X}_{np} = \bar{X}_n$	$R_{tp} = R_t/N$	—
	$R_{ip} = R_i/N$	—

[a] (M/P) = overall monomer–polymer ratio, $(M/P)_p$ = particle monomer–polymer ratio; $\bar{X}_n$ = overall number-average degree of polymerization, $\bar{X}_{np}$ = particle number-average degree of polymerization; R_{yp} = a rate process per particle, R_y = an overall rate process, and $y = p, t,$ or i, corresponding to propagation, termination, or initiation, respectively; N = total number of particles.

compared to polydispersed systems. This newfound accessibility applies to theoretical and experimental analyses alike. In general, we must anticipate that the individual reaction parameters, such as the various rate processes, molecular weight, molecular weight distribution, and monomer–polymer ratio, will depend on particle size. With uniform systems, we will be in a position to measure this dependence in a precise fashion. On a theoretical basis, we will be able to express these parameters as explicit functions of particle size and later superpose the effect of particle size distribution for the general case.

Steady-state theory relates the number-average degree of polymerization to the rate processes according to the following relationship for termination by combination:

$$\bar{X}_n = 2R_p/R_t = 2R_p/R_i \tag{1}$$

As a direct consequence of dynamic equivalence in these uniform systems,

$$\bar{X}_{np} = 2R_{pp}/R_{ip} = 2R_p/R_i \tag{2}$$

Thus, if a steady-state mechanism prevails in emulsion polymerization, eq. (2) provides us with a remarkably simple relationship between particle molecular weight and the overall rate processes. Since R_p can be measured and since R_i can be determined independently, it should be possible to predict numerical values for $\bar{X}_{np}$ at least an order of magnitude more accurately than for polydispersed systems.[6] We illustrate below the theoretical utility of these uniform systems in an evaluation of current steady-state theories.

Before proceeding, however, we must digress briefly to discuss the consequences of having measured the viscosity-average molecular weight $\bar{M}_v$, instead of $\bar{M}_n$. According to Tanford's[23] analysis of the free-radical reaction at steady state,

$$\bar{M}_w/\bar{M}_n = (2 + \alpha)/2 \tag{3}$$

where

$$\alpha = k_p[\mathrm{M}]/\{k_p[\mathrm{M}] + (k_t/R_i)\}^{1/2} \tag{4}$$

and k_p = rate constant of polymerization, k_t = rate constant of termination, and [M] = monomer concentration. Since, to a first approximation, the monomer concentration within the latex particles is constant[2,4,6,11,22] during the "ideal" period of emulsion polymerization, eq. (3) indicates that $\bar{M}_w/\bar{M}_n$ and hence $\bar{M}_v/\bar{M}_n$ should be approximately constant if a steady-state mechanism prevails. Development of $\bar{M}_n$ and $\bar{M}_v$ during the reaction should, therefore, follow similar patterns.

APPLICATION TO CURRENT STEADY-STATE THEORY

The generation of free radicals from potassium persulfate in the aqueous phase occurs at a constant rate and 100% efficiency.[24–27] The overall rates of initiation and the rates of initiation per particle are, therefore, constant and directly obtainable from the decomposition kinetics of potassium persulfate. Since R_i and R_p are constant during the constant rate period, eq. (2) and the rationale associated with it predict that the polymer generated during the constant rate period should be characterized by a constant molecular weight, but the data shown in Figure 7*b* for uniform systems indicate that a substantial increase in molecular weight—on the order of 400–800%—occurs during this period. Unfortunately, at this time, there are not sufficient published data on the development of molecular weight and its distribution in emulsion polymerization reaction systems to form an unequivocal explanation for the behavior just observed. Several observations can be made, however, which are based on our current understanding.

If we first consider the simplest possible case with a constant rate of initiation per particle at 100% free-radical efficiency, no chain branching, and termination exclusively by combination, we see from eq. (2) that the rate of termination per particle must decrease during the constant rate period to account for the observed increase in molecular weight. At a constant rate of initiation per particle this can only mean the existence of an unsteady-state polymerization mechanism.

Secondly, since the trend of increasing molecular weight with conversion is generally substantial, it should take more than a minor variation in any of the foregoing case conditions to account for this trend. The fact that termination occurs by combination in styrene polymerization is a well-established experimental fact. Under the conditions where the free-radical efficiency is not 100%, it has been proposed that the efficiency should increase with increasing conversion, since the surface area is likewise increasing.[12,13] If such were the case, the rate of initiation per particle should increase, and eq. (2) predicts that the molecular weight should decrease. Branching could cause an increase in the $\bar{M}_v$ observed, but it is believed that branching is rare in polystyrene.[24,28–30]

In light of the results cited herein, further studies are required on the development of molecular weight and its distribution as well as the reaction parameters associated with its development before the mechanism of emulsion polymerization can be fully elucidated.

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Résumé

Il est possible de former au cours de polymérisations en émulsion du styrène bien spécifié, des latex dans lesquels les particules de monomères-polymères sont uniformes tout au cours des étapes de croissance. Ces latex sont cinétiquement similaires à leurs contreparties polydispersées et peuvent dès lors être utilisés comme substances modèles pour les études générales cinétiques de la polymérisation en émulsion. Le fait le plus important de ces systèmes consistent en ce que les particules sont uniformes tout au long de la réaction en ce qui concerne toutes les propriétés intrinsèques et les processus de vitesse et ces particules peuvent être caractérisées par cette uniformté complète et continue. Il existe des relations remarquablement simples mais précises entre les paramètres cinétiques mesurables globaux et les paramètres cinétiques des particules individuelles permettant ainsi une accessibilité analytique non réalisée dans les systèmes hétérogènes. Les analyses cinétiques des poids moléculaires sont un ordre de grandeur plus précis que dans les systèmes non uniformes. L'application de ces systèms continuellement uniformes à des études cinétiques actuelles indique l'inconsistance des notions courantes concernant la polymérisation en émulsion. La génération de polymères à des poids moléculaires constants est prévue alors qu'une augmentation d'un facteur multiple est observée. Avant que la situation puisse être clarifiée, de nouvelles études avec des systèmes continuellement uniformes sont indispensables pour mesurer la variation du poids moléculaire, leur distribution de structure moléculaire, et également réévaluer des processus de vitesse et de diffusion qui contrôlent ces phénomènes de structure.

Zusammenfassung

Es ist möglich, bei besonders ausgeführter Styrolemulsionspolymerisation Latices zu erhalten, bei welchen die Monomer–Polymerpartikel während der gesamten Wachstumsstadien einheitlich sind. Diese Latices sind den polydispersen Systemen kinetisch ähnlich und können daher als Modellsysteme bei der Untersuchung der allgemeinen Kinetik der Emulsionspolymerisation verwendet werden. Die wichtigste Eigenschaft dieser Systeme liegt darin, dass die Partikel während der gesamten Reaktion in bezug auf alle spezzifischen Eigenschaften und Geschwindigkeitsprozesse einheitlich sind und durch diese vollständige und kontinuierliche Einheitlichkeit charakterisiert werden können. Zwiscchen den messbaren kinetischen Bruttogrössen und den individuellen kinetischen tikelgrössen bestehen bestimmte, bemerkenswert einfache aber doch exakte Belehungen, die eine bisher nicht erreichte analytische Behandlung erlauben. Die kinnetische Analyse auf Grund des Molekulargewichts ist um eine Grössenordnung genauer als in nicht einheitlichen Systemen. Die Anwendung dieser kontinuierlich einheitlichen Systeme für kinetische Untersuchungen lässt einen Widerspruch in den üblichen Ansätzen für die Emulsionspolymerisation erkennen: diese lassen die Bildung von Polymeren mit konstantem Molekulargewicht erwarten, während eine Zunahme auf das mehrfache beobachtet wird. Vor einer endgültigen Klärung sind weitere Untersuchungen an kontinuierlich einheitlichen Systemen notwendig, um die Molekulargewichtsentwicklung, die Molekulargewichtsverteilung und die Molekülstruktur zu ermitteln und auch die Geschwindigkeits- und Diffusionsprozesse zu bestimmen, die diese Struktureigenschaften kontrollieren.

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Diffusion of Methanol in Polydimethylsiloxane

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Synopsis

The permeation and sorption of methanol in polydimethylsiloxane at 10 and 30°C. has been measured and the results analyzed to determine the concentration dependence of the steady-state diffusion coefficient D which is found to decrease as the total concentration C is increased. An analysis of the isotherms indicates that clustering of the methanol occurs in the polymer, becoming more predominant as the concentration is increased. A polymerization model used to describe the shape of the D versus C curve for water in polydimethylsiloxane has been modified and applied with some success to describe the shape of the isotherm and the D versus C curve for methanol. The linearity of the permeation rate with relative pressure in this and a number of water-polymer systems is briefly commented on.

For a number of water-polymer systems a steady-state analysis indicates that the diffusion coefficient of the water in the polymer decreases with increasing concentration of the water.[1-4] The concentration dependence of the diffusion coefficient in these systems has been largely attributed to the formation of water clusters such that the proportion of unassociated water decreases as the total concentration is increased. In this way the effective overall mobility of the water is decreased. Similar behavior may be expected with other strongly hydrogen-bonded liquids such as methanol, and in the present investigation the sorption and diffusion of this vapor in polydimethylsiloxane has been studied.

EXPERIMENTAL

Polydimethylsiloxane sheets 1.8 mm. thick were supplied by Imperial Chemical Industries and were prepared from a polydimethylsiloxane gum crosslinked by curing with 1% by weight of 2,4-dichlorobenzoyl peroxide. Sorption isotherms were obtained with a conventional calibrated silica spiral[2] and a Bourdon-type glass spiral gage used for the measurement of pressure. A few sorption-kinetic measurements were made with small increments in the vapor pressure by using a Sartorious electronic microbalance and a Honeywell strip chart recorder. Steady-state permeation rates were measured as a function of the ingoing vapor pressure by sorbing the effluent vapor in a dehydrated aluminosilicate suspended from a calibrated silica spiral.[2]

Results

The sorption isotherms at 10 and 30°C. are shown in Figure 1. There was no evidence of hysteresis in the isotherms and values of ΔH and ΔS, the heat and entropy of dilution, respectively, were calculated by using standard thermodynamic formulae. These values are given in Table I and are sufficiently accurate to show their variation with the concentration.

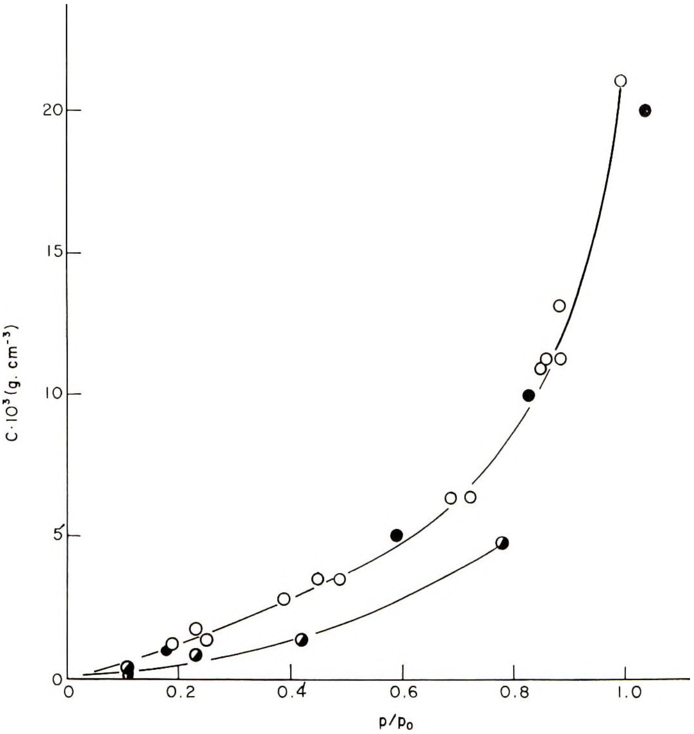

Fig. 1. Sorption isotherms for the methanol–polydimethylsiloxane system: (○) 30°C.; (◑) 10°C.; (●) calculated from eq. (11).

Zimm[5] and Zimm and Lundberg[6] developed a theory based on the statistical mechanics of fluctuations which gives a measure of the extent of nonrandom mixing in a two-component system. The analysis has been applied to several polymer–solvent systems[7] and to water–polymer systems, in par-

TABLE I
Heats and Entropies of Dilution at 293°K.

C, g./cm.³	ΔH, kcal./mole	ΔS, cal./mole-deg.
1×10^{-3}	4.5	20
3×10^{-2}	2.5	10
1×10^{-2}	1.5	5.5

TABLE II
Clustering Function for Methanol

Temp., °K.	a_A	$\Phi_A \times 10^3$	$\Phi_A G_{AA}/V_A$
303	0.9	16.4	2.9
	0.7	7.63	0.91
	0.5	4.71	0.29
	0.3	2.57	0.14
283	0.8	7.18	1.9
	0.5	2.75	0.38
	0.3	1.45	0.15

In the calculation of Φ_A additivity of volumes was assumed for the system.

ticular by Starkweather.[8] The quantity of interest is $\Phi_A G_{AA}/V_A$, where Φ_A, V_A and G_{AA} denote the volume fraction, partial molecular volume, and cluster integral of the penetrant, respectively. It is a measure of the mean number of type A molecules in excess of the mean concentration of type A molecules in the neighborhood of a given type A molecule and as such is a measure of the extent of clustering by penetrant. A tendency for penetrant to cluster is revealed by values of $G_{AA}/V_A > -1$, and the mean size of the cluster is given by $\Phi_A(G_{AA}/V_A) + 1$. Zimm[5] also showed that

$$\Phi_A G_{AA}/V_A = -(1 - \Phi_A)[\partial(a_A/\Phi_A)/\partial a_A]_{PT} - 1 \tag{1}$$

where a_A is the activity of the sorbed vapor and is approximately equal to the equilibrium relative pressure. Values of the clustering function are given in Table II.

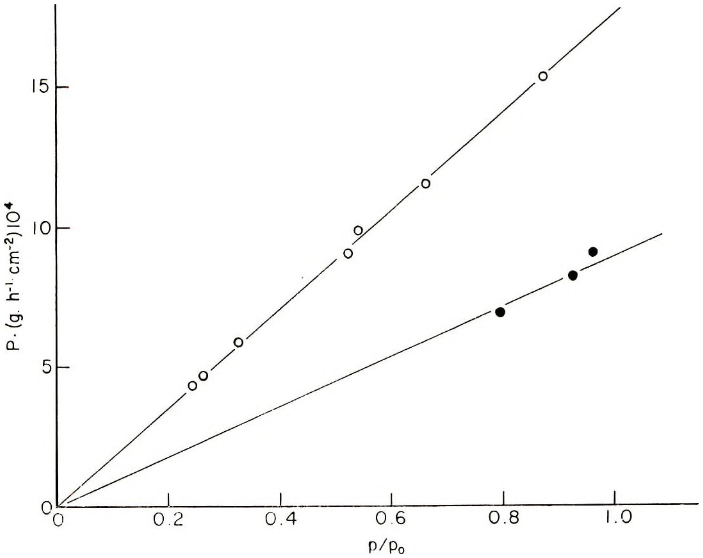

Fig. 2. Permeation rate vs. the relative pressure of methanol at the ingoing face: (○) 30°C.; (●) 10°C.

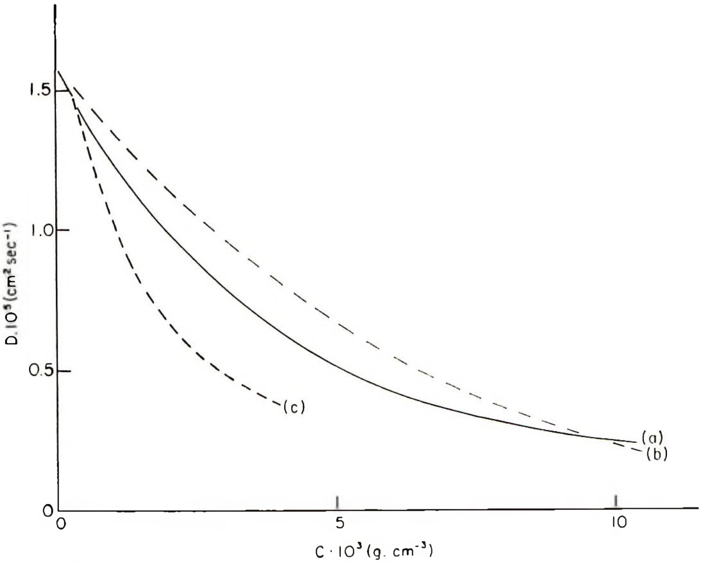

Fig. 3. Concentration dependence of the diffusion coefficient of methanol in polydimethylsiloxane: (*a*) 30°C.; (*b*) calculated from eqs. (6) and (12); (*c*) 10°C.

The permeation rate P was linear with the ingoing relative pressure as shown in Figure 2. With P in units of grams per square centimeter per second and concentration C in grams per cubic centimeter, the diffusion coefficient was obtained by graphical differentiation from $D = l\, dP/dC$ where l is the thickness (in centimeters) of the membrane. The concentration dependence of D is shown in Figure 3. A few values of D obtained from differential sorption rate curves were in agreement with corresponding steady-state coefficients within experimental error. The activation energy for diffusion E_D increased from ~2 to ~6.5 kcal./mole over the range of concentration 10^{-3} to 4×10^{-3} g./cm.^{2}. As with the water–polymethylsiloxane system,[4] the permeability coefficient $\bar{P}$ ($= Pl/p_1$, where p_1 is the pressure at the ingoing face) decreased with temperature from 8.2 to 5.6×10^{-9} in the range 10–30°C.

The permeation data at 10°C. were well represented by the relation

$$C/Pl = mc + n \tag{2}$$

where m and n are constants. The corresponding data at 30°C. obeyed eq. (2) only over the lower half of the concentration range. The corresponding D versus C relation is

$$D = n/(mc + n)^2 \tag{3}$$

which, when introduced into Frisch's equation for the time lag L as a function of concentration,[9] gives

$$L = \frac{nl^2}{m} \frac{(mc + n)}{c} \left\{ \frac{mc + 2n}{2mc} - n \frac{(mc + n)}{m^2c^2} \log \frac{(mc + n)}{n} \right\} \tag{4}$$

The values of L for a membrane 1.8 mm. thick are given in Table III.

TABLE III

Concentration Dependence of the Time Lag at 30°C. for $m = 6.7(17.6) \times 10^{6}$, $n = 6.3(5.3) \times 10^{1}$[a]

C, g./cm.^{3}	L, min.
0	4.2
10^{-3}	4.5
10^{-2}	6.5

[a] The values in parentheses are those at 10°C.

With the present apparatus, a variation in L of this magnitude would be difficult to detect. A few measurements of L at different ingoing pressures were made but showed no significant trend with concentration within the experimental error and had an average value approximately equal to that at zero concentration.

Discussion

The positive heat of dilution and the decrease in both $\Delta\bar{H}$ and $\Delta\bar{S}$ with concentration as the concentration is increased are compatible with association or clustering of the methanol in the polymer. The results of the Zimm analysis in Table II also indicate that clustering occurs over most of the relative pressure range and becomes increasingly significant as the concentration is increased.

To describe the concentration dependence of the diffusion coefficient it is assumed to a first approximation only that associated water does not contribute significantly to the flux. For the lower polymeric forms of water this will be a decided oversimplification. It follows that

$$P = -D_1 \partial C_1/\partial x = -D\,\partial C/\partial x \tag{5}$$

where D_1 and C_1 refer to monomeric water. The experimental diffusion coefficient is then given by

$$D = D_1\,dC_1/dC \tag{6}$$

For the water–polydimethylsiloxane system, Barrie and Platt[4] evaluated dC_1/dC from a model in which the water molecule was regarded as a tetrafunctional monomer of the type A_4 undergoing random polymerization by hydrogen-bond formation in a relatively inert medium.[10] A more realistic model for the water molecule is that of an A_2B_2-type monomer polymerizing with AB bond formation only. Methanol, on the other hand, can be regarded as an AB_2-type monomer which polymerizes with AB bond formation only. Flory[11] gives for the polymerization of an AB_{f-1} monomer the following expression for the weight fraction of x-mer w_x,

$$w_x = \frac{[1 - \alpha(f-1)]\alpha^{x-1}(1-\alpha)^{fx-2x+1}(fx - x)!}{(x-1)!(fx - 2x + 1)!} \tag{7}$$

For methanol, $f = 3$ and

$$C_1/C = (1-\alpha)^2(1-2\alpha) \tag{8}$$

where α is one half of the fraction of hydroxyl groups reacted. For the equilibrium constant K for the breakage of a hydrogen bond one has,

$$K = C(1 - 2\alpha)(1 - \alpha)/\alpha \tag{9}$$

from which

$$\alpha = \frac{1}{4}\left(3 + \frac{K}{C}\right) - \left\{\left[\frac{1}{4}\left(3 + \frac{K}{C}\right)\right]^2 - 0.5\right\}^{1/2} \tag{10}$$

the positive root of the quadratic being discarded as it leads to $\alpha \geq 0.5$. Following Gordon et al.,[10] Barrie and Platt identified the gel point of the polymerization with the saturation point of the water–polydimethylsiloxane system, which enabled them to evaluate K from eq. (9) by making use of the critical value of α for the system.[4] However, unless one allows for unequal reactivities of the functional groups, monomers of the type AB_{f-1} do not gel until the reaction is complete ($\alpha = {}^1/_2$), and for this reason an independent evaluation of K as for the water–polydimethylsiloxane system is not possible. In what follows K is treated more as an adjustable parameter. The polymerization models are also approximate, in that no allowance is made for intramolecular bonding leading to ring formation.

If it is assumed that the concentration of monomeric methanol in the polymer is always sufficiently small for a Henry's-law equilibrium to be established with the vapor phase, then the isotherm equation for the polymerization model is

$$p = (C/\sigma)(1 - \alpha)^2(1 - 2\alpha) \tag{11}$$

where σ is the Henry's law solubility constant for the monomeric methanol. With $\sigma = 3 \times 10^{-4}$, corresponding approximately to the initial slope of the isotherm at 30°C., and with $K = 2.5 \times 10^{-2}$, reasonable agreement is obtained with the experimental data as shown in Figure 1.

From eq. (8) one obtains

$$dC_1/dC = \frac{K}{2C}\,\frac{\alpha[(1 - \alpha)^2 + (1 - 2\alpha)(1 - \alpha)]}{\alpha - \frac{1}{4}\left(3 + \frac{K}{C}\right)} + (1 - \alpha)^2(1 - 2\alpha) \tag{12}$$

As $C \rightarrow 0$, $dC_1/dC \rightarrow 1$, and at zero concentration D_1 can be identified with $D_{C=0}$. Further as the concentration of monomer is relatively small, D_1 may be regarded as constant and equal to $D_{C=0}$ over the whole of the concentration range. With an extrapolated value of $D_{C=0} = 1.6 \times 10^{-5}$ at 30°C. and the same value of K as used to fit the isotherm data, the D versus C curve was constructed from eqs. (12) and (6) as shown in Figure 3. In view of the limitations of the model, the agreement is not unsatisfactory and tends to confirm the clustering hypothesis The increase in the energy of activation for diffusion E_D with concentration is also consistent with this hypothesis. As the temperature is increased clustering will become less so that the temperature coefficient of dC_1/dC will have the same sign as that of D_1 in eq. (6). Since $dC_1/dC \rightarrow 1$ as $C \rightarrow 0$ at all temperatures and since it decreases with increasing concentration, it follows E_D will increase with C.

The linearity of the permeation rate with ingoing pressure as in Figure 2 is observed with a surprisingly large number of water–polymer systems, particularly when D decreases with concentration. Several authors[12–14] have in fact suggested that the diffusion flux be proportional to the activity gradient. This is equivalent to formulating the flux as proportional to the product $a\,\partial\mu/\partial x$ rather than $c\,\partial\mu/\partial x$, where a and μ are the activity and chemical potential, respectively, of the penetrant in the polymer. As the relative pressure of the vapor in equilibrium with the penetrant–polymer mixture is a measure of its activity, this formulation of the flux would lead to a linear dependence of P on p. On the other hand, from Fick's equation

$$P = -D\,dc/dx = -(D\,dc/dp)(dp/dx) \tag{13}$$

and any linear relation would suggest a somewhat fortuitous cancellation of the concentration dependences of D and dc/dp. This cancellation is not so improbable in terms of the simple model adopted for clustering, thus eq. (6) becomes

$$D = D_1\sigma(dp/dc) \tag{14}$$

and the term $(D\,dc/dp)$ in eq. (13) is constant. It also follows that if the monomer concentration gradient in the steady state is constant, then the steady-state total concentration distribution will be identical to that obtained from the equilibrium isotherm by assuming a linear drop in vapor pressure across the membrane, as appears to be the case with the water–natural rubber system.[15]

For a number of water–polymer systems it has been observed that although the steady-state diffusion coefficient decreased with concentration, the time lag L was independent of C, indicating that D was constant.[3] These differences are still largely unresolved, but it is clear from the data of Table III that whereas D decreases by a factor of ~8 over the concentration range, L increases by a factor of ~1.5 only. The concentration dependence of L is therefore considerably less than that of D and correspondingly the more difficult to detect or measure accurately.

This work is part of an investigation of water and similar vapors in polymer films. The investigation was aided by a grant from the Research Fund of the University of London.

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Résumé

La perméation et là sorption du méthanol dans le polydiméthylsiloxane à 10 et 30°C ont été mésurées et les résultats analysés en vue de déterminer la dépendance de la concentration du coefficient de diffusion stationnaire qui décroît lorsque la concentration totale croît. Une analyse des isothermes indique que l'agrégation du méthanol se passe au sein du polymère et devient plus importante à mesure que la concentration croît. Un modèle de polymérisation utilisé pour décrier l'allure de la courbe de D en fonction de C pour l'eau dans le polydiméthylsiloxane a été modifié et appliqué avec succès pour décrire l'allure de l'isotherme et l'allure de la courbe de D en fonction de C pour le méthanol. La linéairté pour la vitesse de perméation avec la pression relative dans ce système et dans un nombre de systèmes eau–polymère est brièvement commentée.

Zusammenfassung

Die Permeation und Sorption von Methanol in Polydimethylsiloxan bei 10 und 30°C wurde gemessen und aus den Ergebnissen die Konzentrationsabhängigkeit des Diffusionskoeffizienten *D* für den stationären Zustand bestimmt. Er nimmt mit steigender Gesamtkonzentration ab. Eine Analyse der Isothermen zeigt, dass mit steigender Konzentration *C* eine Clusterbildung des Methanols im Polymeren immer stärker hervortritt. Ein zur Beschreibung der Gestalt der Kurve für *D* gegen *C* für Wasser in Polydimethylsiloxan verwendetes Polymerisationsmodell wurde modifiziert und mit einigem Erfolg zur Beschreibung der Gestalt der Isotherme und der *D*–*C*-Kurve für Methanol angewendet. Eine kurze Bemerkung zur Linearität der Permeationsgeschwindigkeit mit dem relativen Druck bei diesem und einer Anzahl von Wasser–Polymersystemen wird gemacht.

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Solution Polymerization of Acrylonitrile Catalyzed by Sodium Triethylthioisopropoxyaluminate: A Polyacrylonitrile with High Structural Regularity

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Synopsis

A new catalyst for the polymerization of acrylonitrile has been found by reacting sodium aluminum tetraethyl with a stoichiometric amount of oxygen, alcohols, or mercaptans, etc. The catalyst prepared by reacting $NaAlEt_4$ with RSH remains active at temperatures as low as −78°C., polymerizing acrylonitrile into high molecular weight polymers with high conversions. At −78°C., the propagating chain remains active over a period of days, and the chain length increases with time or conversion. At high conversions the molecular weight of the polymer is directly proportional to the concentration of the monomer, the catalyst concentration being kept constant. The efficiency of the catalyst expressed as the ratio of the number of the polymer molecules produced to the number of the sulfur atoms used is in excess of 80%. The weight-average molecular weight of the polymer measured by light scattering is roughly equal to the number-average molecular weight determined by sulfur analysis assuming only onesulfur atom in each polymer molecule. Although the data given here are only qualitative in nature, it is nevertheless evident that this system bears great resemblances to anionic polymerizations resulting in "living polymers." The polymer obtained with the $NaAlEt_3S(i\text{-}Pr)$ catalyst at −78°C. differs from free-radical polyacrylonitrile in exhibiting substantially lower solubility, higher melting point, and higher rate of crystallization than that for the free-radical polymer. The polymer is also free from structural mpurities; it does not cause fluorescence in dilute solutions and has no absorption peak at 265 mμ; both these effects are produced by impurities in free-radical polyacrylonitrile. It is concluded that the polymer reported here is more regular in structure than free-radical polyacrylonitrile.

INTRODUCTION

Acrylonitrile can be polymerized by organometallic compounds such as BuLi,[1-4] Grignard reagents,[5] NaOEt,[1,6] KOR,[7] $NaNH_2$,[1,8] $CaZnEt_4$,[9] triethylphosphine,[10,11] biphenylsodium,[12] diphenylmethylsodium,[13,14] ketyls,[15] $NaCH(COOEt)_2$,[16] $ZnBu_2$ complexed with chromium acetylacetonate,[17] sodium acetylide,[18] cyclopentadienylsodium,[19] etc. A number of initiators have been reviewed by Thomas.[20] The reaction initiated by these catalysts usually proceeds so fast that it becomes uncontrollable even at room temperature. Furthermore, the reaction mixtures are often yellow, and the polymer thus obtained may be white or yellow. A still further disadvantage is that it has been difficult, if not impossible, to obtain polymers with high molecular weights. The main difficulty involved in the polymerization of acrylonitrile with these catalysts lies in the fact that both the functional groups, the ethylenic double bond and the nitrile group in the monomer, are susceptible to the attack of the catalyst. In the presence of a base or ionic catalyst, side reactions take place, producing structural impurities in the sample which affect the properties of the polymer and interfere with infrared analyses and density measurements.

The objectives of this investigation are severalfold: (*a*) to develop new catalysts which initiate the polymerization of acrylonitrile at convenient rates, (*b*) to prepare a polyacrylonitrile free from structural irregularities (tacticity notwithstanding) and free from undesirable color, and (*c*) to study the effect of polymerization conditions on the properties of the polymer.

The nature and kinetics of polymerization will be reported in a later communication.

EXPERIMENTAL

Materials

Monomer. Monsanto polymerization grade acrylonitrile was redistilled azeotropically with added benzene to remove moisture. Distillation was carried out under nitrogen using hydroquinone to prevent thermal polymerization. Only middle fractions were collected and stored at 0°C. under nitrogen in the dark.

Toluene. Mallinckrodt reagent grade toluene was purified by washing several times with concentrated sulfuric acid until no further discoloration was noticed. The acid was then poured off and the toluene was washed with dilute $NaHCO_3$ solution and with water, then dried with $MgSO_4$ and distilled over $MgSO_4$.[21]

Dimethylformamide. DMF was rigorously purified according to the procedure of Thomas and Rochow.[21a] The distilled DMF was used without further treatment or dried by passing through molecular sieves prior to use, as indicated. The molecular sieves were activated by heating in a furnace at about 350°C. overnight.

Preparation of the Catalyst

The basic material of our catalyst is sodium aluminum tetraethyl which can be conveniently prepared by one of the following methods.

Method of Ziegler.[22] When $AlEt_3$ is allowed to react with a stoichiometric quantity of NaOEt, $NaAlEt_3OEt$ is first formed [reaction (1)], which reacts further with the excess $AlEt_3$ present [reaction (2)].

$$AlEt_3 + NaOEt \rightarrow NaAlEt_3OEt \tag{1}$$

$$NaAlEt_3OEt + AlEt_3 \rightarrow 3NaAlEt_4 + AlEt_2OEt \tag{2}$$

Aromatic hydrocarbons are convenient solvents.

Direct Union of Metallic Sodium and $AlEt_3$.[23] Since $NaAlEt_4$ is solu-

$$3Na + 4AlEt_3 \rightarrow 3NaAlEt_4 + Al \tag{3}$$

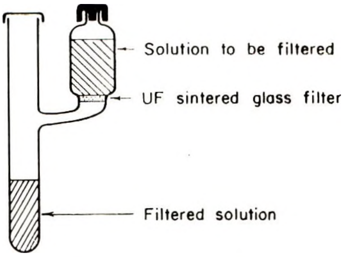

Fig. 1. Apparatus for filtration and storage of catalyst solutions.

ble in benzene and toluene at about 80°C. but insoluble at room temperature, it can be purified conveniently by recrystallization. Since reaction (3) is simpler and gives the product that can be isolated readily from the reaction mixture, it was used as our routine method of catalyst preparation.

In a typical example, 0.668 g. (29.0 mmole) of sodium (metals or fine dispersions) were suspended in about 2 cc. of purified, degassed toluene in a closed vessel filled with nitrogen. To the stirred dispersion, 17 cc. of a 25% solution of $AlEt_3$ in toluene containing 2.93 g. or 25.6 mmole of $AlEt_3$ was added intermittently. The mixture was heated to about 100°C. for 1 hr. with constant agitation. The solution containing $NaAlEt_4$ was removed from the unreacted sodium and the aluminum, and filtered under nitrogen at 90°C. in an apparatus as shown in Figure 1. The product was purified by recrystallization several times from toluene. The aluminum content was determined gravimetrically as 8-hydroxyquinolate. The melting point of the sodium aluminum tetraethyl after careful crystallization was found to be 125.2°C., in excellent agreement with the value reported by Baker and Sisler.[24]

The active catalysts are prepared by reacting $NaAlEt_4$ in toluene with a stoichiometric amount of oxygen, alcohols or mercaptans, etc., according to eqs. (4)–(6).

$$NaAlEt_4 + O_2 \rightarrow [NaAlEt_3O\text{-}OEt] \xrightarrow{NaAlEt_4} 2NaAlEt_3OEt \qquad (4)$$

(Caution: $NaAlEt_4$ reacts with pure O_2 *violently*, but with diluted O_2 smoothly.)

$$NaAlEt_4 + ROH \rightarrow NaAlEt_3OR + C_2H_6 \qquad (5)$$

$$NaAlEt_4 + RSH \rightarrow NaAlEt_3SR + C_2H_6 \qquad (6)$$

The atomic ratio of Al determined as 8-hydroxyquinolate to that of S determined by radioactive assay was 1:1. (For polymerization a slight excess of $NaAlEt_4$ was present.) The reaction product was dissolved in DMF and used as the polymerization catalyst.

Polymerization

Polymerizations were carried out in DMF under nitrogen in reaction flasks equipped with rubber serum caps. The flasks were flamed and degassed with a high vacuum pump and flushed with nitrogen several times. Then 100 cc. of the solvent containing 0.07 mmoles of the catalyst was added directly into the flask. After the temperature of the flask had come to the temperature of the bath, 5 cc. (75 mmole) of acrylonitrile (diluted with 5 cc. DMF) was injected through a syringe needle into the reaction mixture. The temperature range was made as wide as possible. In general, elevated temperatures are not desirable because the reactions are too fast and side reactions hard to prevent. The lower range of the temperature is limited by the activity of the catalyst.

Dissolution and Crystallization Temperatures

The measurement of the dissolution and crystallization temperatures of polyacrylonitrile has been reported previously[25,26] and is not repeated here.

RESULTS AND DISCUSSION

Polymerization with Purified $NaAlEt_4$

Polymerization of acrylonitrile with the carefully purified $NaAlEt_4$ is usually slow, especially at low temperatures. At room temperature, polymers of molecular weights ranging from 20,000 to 65,000 were obtained. Both $AlEt_3$ and $AlEt_2OEt$ are inactive toward the polymerization of acrylonitrile.

Effect of Oxygen

$NaAlEt_4$, after being contaminated with air, becomes extremely active. It is well known that a great variety of metal alkyls react with oxygen to form alcoholates (the net reaction proceeds as if oxygen atoms were inserted between the aluminum atom and the ethyl group). Table I shows the effect of oxygen on the polymerization. For example, at 0°C. the conversion was only 7.5% in 20 hr. when $NaAlEt_4$ alone was used as the catalyst as compared to 96% in 3 hr. when $NaAlEt_4$ with added oxygen was used under otherwise identical conditions. The melting point depression of the catalyst, shown in the same table, serves as a direct measure of the amount of oxygen absorbed.

TABLE I
Effect of Oxygen on the Melting Point and Activity of $NaAlEt_4$ in the Polymerization of Acrylonitrile[a]

Ratio: oxygen atom / $NaAlEt_4$	Melting point, °C.	Conversion, %
0	125.2	7.5 (20 hr.)
0.23	100–107	75 (20 hr.)
0.47	75–77	96 (3 hr.)

[a] Polymerization conditions: temperature 0°C., monomer 75 mmoles, catalyst 0.3 mmole based on aluminum, DMF 100 cc.

It was suspected that $NaAlEt_4$, like BEt_3, might form free radicals with oxygen and initiate polymerization, but the oxygen-modified catalyst fails to polymerize vinyl acetate, styrene, vinyl chloride, etc. Therefore, it is concluded that the reaction is not free-radical in nature.

Effect of Alcohols and Mercaptans

When the effect of oxygen was established, it became clear to modify the catalysts with alcohols and mercaptans. All the modified catalysts are indeed very active, capable of polymerizing acrylonitrile into polymers of molecular weight in the range of 100,000–800,000 at −30 and −80°C., depending upon the conditions of polymerization. The activity of the catalyst prepared by reacting $NaAlEt_4$ with ROH is very similar to that of the catalyst prepared by reacting $NaAlEt_4$ with the molecular oxygen. This is expected because the reaction products are essentially the same in both cases, namely $NaAlEt_3OEt$. Results together with the conditions of polymerization are given in Table II.

TABLE II
Polymerization of Acrylonitrile in DMF at Various Temperatures

Catalyst	Polymerization temperature, °C.	Conversion, %	$\bar{M}_v \times 10^{-3}$	Dissolution temperature, °C.
"Purified" $NaAlEt_4$				
	25	52	65	55–60
	50	45	63	38–40
	75	82	19	ca. 37
$1:{}^1/_2$ $NaAlEt_4:O_2$	0	89	115	79–90
1:1 $NaAlEt_4$:ROH	−10	80	175	90–125
	0	88	205	90–110
1:1 $NaAlEt_4$:i-C_3H_7SH	−78	90	215	130–165
	−30	76	210	75–110
	0	53	69	25–65
	25	25	12	<25
	50	20	14	<25
	75	25	21	<25

$NaAlEt_3S$(*i*-Pr) Catalyst

Of particular interest is the mercaptan-modified $NaAlEt_4$ catalyst because of its high activity, no impurities produced in the reaction mixture, the improved "whiteness" of the polymer, and the wide range of the temperature over which the polymerization can be carried out. With this catalyst, the temperature of polymerization can be extended to −78°C. At this low temperature, the side reactions such as cyanoethylation and polymerization through the nitrile group are altogether surpressed. As a result, the reaction mixture is completely colorless and the recovered polymer is "whiter" than any other polyacrylonitrile we have so far been able to prepare.

The catalyst can be stored in DMF at −78°C. for a long period of time without losing its activity.

An interesting experiment was conducted in the following manner. A small amount of acrylonitrile was introduced into a DMF solution containing a large excess of the catalyst at, for example, a molar ratio of $[M]/[Cat] = 60$, all the monomers were used up, but the propagating chain remained active and grew further into a high molecular weight polymer upon the addition of more monomers several days later. Thus the growing polymer is "living" at −78°C. However, it decays into an inactive polymer with a half-life of approximately 11 min. at −30°C.

Further experimental evidences in support of the idea that the polymer is "living" are given below. First of all, the molecular weight of the sample isolated from the reaction medium at various time increases with time and hence conversion. This is the usual phenomenon observed in vinyl polymerization which proceeds by insertion mechanisms. Table III represents some results obtained on polymerization of acrylonitrile with the mercaptan-modified catalyst. It is seen in this table that the weight-average molecular weights obtained by light-scattering measurements are very close to the number-average molecular weights determined by sulfur analyses, assuming that there is only one sulfur atom in each polymer molecule. While this latter assumption may be questionable, the possibility that the agreement between the weight-average molecular weight obtained by light scattering and the average number-average molecular weights obtained by sulfur analyses is purely coincidental is highly unlikely. If we can show that the light-scattering molecular weights and the osmotic pressure molecular weights are equal, then we can feel certain that each polymer contains only one sulfur atom, the latter being incorporated in the polymer during initiation, and that the polymer prepared by this system has a very narrow molecular weight distribution.

TABLE III

Polymerization of Acrylonitrile with the $NaAlEt_3S(i\text{-}Pr)$ in DMF at −78°C.[a]

Wt. acrylonitrile, g.	Wt. DMF, g.	Conversion, %	$\bar{M}_w \times 10^{-3}$	S, % (obs.)	$\bar{M}_s \times 10^{-3}$ [b]
5	60	100	98	0.017	188
5	60	100	138	0.020	160
5	60	100	151	0.017	188
16	230	100	389	0.0069[c]	463

[a] The amount of catalyst used varied from 0.05 to 0.1 mmole based on sulfur.

[b] $\bar{M}_s$ denotes the molecular weight calculated on the assumption that there is only one sulfur atom in each polymer molecule. The fact that $\bar{M}_s$ is higher than $\bar{M}_w$ is probably due to experimental uncertainties.

[c] The sulfur content was determined by radioactive assay.

TABLE IV
Polymerization of Acrylonitrile with the $NaAlEt_3S(i\text{-}Pr)$ in DMF at −60°C. at Varying Monomer-to-Catalyst Ratios[a]

Catalyst concn., mmole/100 g. DMF	Wt. acrylonitrile, g.	Wt. DMF, g.	Conversion, %	$[\eta]$[b]	Efficiency[c]
0.126	0.4	63.5	90	0.164	0.945
0.126	0.6	63.5	92	0.240	0.855
0.126	0.8	59.5	98	0.410	0.595
0.126	1.2	63.0	91	0.400	0.865
0.126	1.6	58.0	97	0.570	0.780

[a] The DMF used in this experiment was purified by the procedure of Thomas and Rochow[21] and distilled under high vacuum directly into the reaction flask. The catalyst was prepared prior to use.

[b] Measured in DMF at 25°C.

[c] The efficiency is calculated from the number of the polymer molecules produced to that of sulfur atoms used. The number-average molecular weight is assumed arbitrarily to be 10% lower than that of the weight-average molecular weight. The value of $\bar{M}_w/\bar{M}_n = 1.1$ is likely a realistic ratio. If the ratio $\bar{M}_w/\bar{M}_n$ is higher than 1.1, the efficiency calculated here will be higher than 90%.

The efficiency of the catalyst as shown in Table IV is very high, being in the range of 80–100%. Transfer and deactivation processes can probably be ruled out and the rate of initiation can be assumed to be fast as compared to the rate of propagation. In these respects the system bears great resemblances to ionic polymerizations resulting in "living" polymers.

To test the idea further, polymerizations with the $NaAlEt_3S(i\text{-}Pr)$ catalyst were carried out in DMF at −78°C., varying the monomer concentration and keeping the catalyst concentration constant. As shown in Table IV, the reaction went nearly to completion, and the molecular weights of the polymer increased proportionally with the concentration of

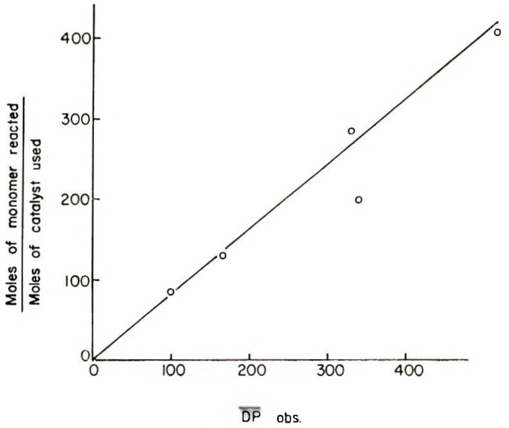

Fig. 2. Polymerization of acrylonitrile with the $NaAlEt_3S(i\text{-}Pr)$ catalyst at −78°C.

the monomer (Fig. 2). This can again be interpreted by the simple mechanism that the catalyst reacts with the monomer and starts to grow until all the monomers are used up. As a result the length of the growing chain is only limited by the amount of the monomer available for the polymerization and the molecular weight is directly proportional to the concentration of the monomer.

Effect of Polymerization Temperature on the Dissolution and Crystallization Temperatures of Polyacrylonitrile

Polyacrylonitriles prepared here are characterized by the dissolution and crystallization temperatures measured in a borderline solvent, e.g., propylene carbonate at elevated temperatures.[25,26] The dissolution temperatures measured on carefully crystallized samples afford a sensitive test of the chain regularity in the sample. As shown in Table II, polyacrylonitriles prepared (in DMF at 0°C.) with the oxygen- and alcohol-modified catalysts had a dissolution temperature of 90–110°C., while those prepared with the $NaAlEt_3S(i\text{-}Pr)$ catalyst in DMF at −78°C. had a dissolution temperature as high as 165°C., the dissolution temperature of the sample prepared with the same catalyst at −30°C. being in the intermediate range. Polyacrylonitrile prepared with a persulfate–sulfite initiator in an emulsion system had a dissolution temperature of 125°C. Results on dissolution temperatures of polyacrylonitriles prepared under widely different conditions are given elsewhere.[26]

Properties of High-Melting Polyacrylonitrile

Properties of a typical polymer prepared with the $NaAlEt_3S(i\text{-}Pr)$ catalyst in DMF at −78°C. (also referred to as high-melting polyacrylonitrile) are listed in Table V. The properties of a standard free-radical

TABLE V
Properties of High-Melting Polyacrylonitrile

	High-melting PAN	Free-radical PAN
Dissolution temperature, °C.[a]	165	125
Highest crystallization temperature, °C.[a]	130	95–100
Melting point, °C.	>390[b]	319[c]
Linear growth rate of single crystals measured in propylene carbonate at 100°C., μ/hr.	1.4	0.03
Fluorescence in DMF	Not detected	Detected
Absorption at 265 mμ	Not detected	Detected
Density at 25°C., g./cc.	1.172	1.174–1.178

[a] Measured in propylene carbonate.[25,26]

[b] Extrapolated from data on concentrated dimethyl sulfoxide solutions by Flory's melting-point-depression equation.

[c] Data of Krigbaum and Tokita.[27]

polymer are also given for the purpose of comparison. The high-melting polyacrylonitrile is characterized by its high dissolution and crystallization temperatures, its low solubility in organic solvents, and its ability to crystallize. The linear growth rate of the crystal measured in propylene carbonate at 100°C. by electron microscopy is about 50 times higher than that of free-radical polyacrylonitrile. The polymer does not cause fluorescence in dilute solutions, nor does it contain impurities which exhibit absorption at 265 mμ in the ultraviolet spectrum as in the case of free-radical polymer.[28] It is apparent that the high-melting polyacrylonitrile is more regular in structure than free-radical polyacrylonitrile.

CONCLUSIONS

From the above discussion, it is concluded that a polyacrylonitrile which is more regular in structure has been synthesized by the solution polymerization of acrylonitrile with the $NaAlEt_3S(i\text{-}Pr)$ catalyst carried out at very low temperatures. The difference in physical properties between the high-melting polyacrylonitrile and free-radical polymer is attributed directly to the chain regularity in the sample. The question whether the difference is due to the degree of stereoregularity or other structural regularities requires further clarification.

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Résumé

Un nouveau catalyseur pour la polymérisation de l'acrylonitrile a été trouvé en faisant réagir le sodium aluminium tétraéthyle avec une quantité stoechiométrique d'oxygène, d'alcools, ou de mercaptans, etc. Le catalyseur préparé par réaction de $NaAlEt_4$ avec RSH reste à une température aussi basse que −78°C et provoque la polymérisation de l'acrylontrile en des polymères des poids moléculaire élevé avec des taux de conversions élevés également. A −78°C, al chaîne de propagation reste active sur une période de plusieurs jours et la longueur de chaîne s'accroît avec la durée ou la conversion. A conversions élevées, le poids moléculaire est directement proportionnel à la concentration en monomère, la concentration en catalyseur étant gardée constante. L'efficacité du catalyseur étant exprimée comme étant le rapport du nombre de molécules de polymères produites par nombre d'atomes de soufre utilisés est trop élevé l'augmentation étant de 80%. Le poids moléculaire moyen en poids du polymère mesurés par diffusion lumineuse est approximativement égal au poids moléculaire moyen en nombre déterminé au départ de l'analyse du soufre en admettant un atome de soufre par molécule polymerique. Bien que les résultats donnés ici sont uniquement de nature qualitative, néanmoins il est évident que ces systèmes présentent une grande ressemblance avec les polymérisations anioniques au cours desquelles se forme des polymères vivants. Les polymères obtenus avec le catalyseur $NaAlEt_3S(i\text{-}Pr)$ à −78°C diffère du polyacrylonitrile obtenu par radicaux libres en ce sens qu'ils manifestent une solubilité nettement plus faible, un point de fusion plus élevé, une vitesse de cristallisation plus élevée et un coefficient secondaire viriel plus bas que celui pour le polymère obtenu radicalairement. Le polymère est également libre de toute impureét structurale, il ne cause pas de fluorescence en solution élevée et ne présente pas d' absorption à 265 mμ, deux effets qui sont produits par des impuretés dans le polyacrylonitrile obtenu au moyen de radicaux libres. On en conclu que le polymère rapporté ici est plus régulier de structure que le polyacrylonitrilee radicalaire

Zusammenfassung

Ein neuer Katalysator für die Polymerisation von Acrylnitril wurde durch die Reaktion von Aluminiumtetraäthylnatrium mit einer stöchiometrischen Menge von Sauerstoff, Alkoholen oder Merkaptanen etc dargestellt. Der durch Reaktion von $NaAlEt_4$ mit RSH gebildete Katalysator bleibt bis hinunter zu Temperaturen von −78°C aktiv und polymerisiert Acrylnitril mit hohem Umsatz zu hochmolekularen Polymeren. Bei −78°C bleibt die wachsende Kette über einen Zeitraum von Tagen aktiv und die Kettenlänge nimmt mit der Polymerisationsdauer oder dem Umsatz zu. Bei hohem Umsatz ist das Molekulargewicht des Polymeren bei konstant gehaltener Katalysatorkonzentration der Monomerkonzentration direkt proportional. Die Katalysatorausbeute, als Verhältnis der Zahl der gebildeten Polymerimoleküle zur Zahl der angewendeten Schwefelatome ausgedrückt, liegt oberhalb 80%. Das durch Lichstreuung bestimmte Gewichtsmittelmolekulargewicht des Polymeren entspricht etwa dem durch Schwefel-

analyse bestimmten Zahlenmittelwert, wenn pro Polymermolekül ein Schwefelatom angenommen wird. Obgleich die hier mitgeteilten Daten nur qualitativer Natur sind, kann doch gesagt werden, dass das vorliegende System grosse Ähnlichkeit mit der anionischen, zu "lebenden Polymeren" führenden Polymerisation besitzt. Das mit dem NaAlEt$_3$S(i-Pr)-Katalysator bei −78°C erhaltene Polymere unterscheidet sich von radikalisch gebildetem Polyacrylnitril durch eine wesentlich geringere Löslichkeit, einen höheren Schmelzpunkt, eine höhere Kristallisationsgeschwindigkeit und einen niedrigeren zweiten Virialkoeffizienten. Das Polymere is auch frei von strukturellen Verunreinigungen; es verursacht keine Fluorszenz in verdünnter Lösung und besitzt kein Absorptionsmaximum bei 265 mμ, was beides durch Verunreinigungen in radikalisch erzeugtem Polyacrylnitril hervorgerufen wird. Das hier beschriebene Polymere besitzt offenbar eine regelmässigere Struktur als radikalisch gebildetes Polyacrylnitril.

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Copolymerization of Styrene and Methyl Methacrylate with Lithium as Initiator

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Synopsis

Copolymers of styrene and methyl methacrylate prepared with lithium dispersion as initiator do not contain random sequences of both monomers. Fractionation of the copolymers with acetonitrile and the NMR spectra of the insoluble fractions show that these are block copolymers which consist of a polystyrene portion and a poly(methyl methacrylate) portion. When the copolymerization is stopped at low conversion the copolymer has a high styrene content, which sometimes exceeds the value expected for radical copolymerization. This fact would indicate that styrene is preferentially polymerized at the early stages of chain propagation. When the copolymerization is carried to high conversion some crosslinked polymer is formed which contains more styrene than the soluble part of the same experiment. When a piece of metallic lithium is used as initiator, it is found that the crosslinked polymer is formed on the surface of the metal. The addition of lithium phenoxide or β-naphthoxide to the system eliminates the formation of crosslinked polymer. A possible mechanism is proposed.

INTRODUCTION

In the polymerization of an equimolar mixture of styrene and methyl methacrylate, anionic initiators give copolymers which consist of about 1% of styrene while radical initiators give copolymers which contain about 50% of styrene.[1] In 1958 these monomers were copolymerized by using lithium dispersion as the initiator.[2] It was found that more styrene was incorporated into the copolymers than would be expected for a usual anionic polymerization. As a possible explanation, a radical-anion mechanism for this polymerization was proposed, for which styrene and methyl methacrylate were randomly copolymerized at the radical end while at the anionic ends methyl methacrylate was propagated.

It was pointed out by Mulvaney et al.[3] that these results could also be interpreted by another mechanism. Since the polymerization was heterogeneous with respect to the initiator, styrene molecules could be initiated on a statistical basis and be polymerized during the ensuing anionic propagation. George and Tobolsky,[4] however, pointed out that the number of styrene units per chain was too large to be totally explained by the mechanism suggested by Mulvaney et al.[3] They also asserted that the possi-

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bility of purely anionic propagation could not be ruled out and such a mechanism would require a more subtle explanation to explain the experimental results.

In the preceding paper,[5] Overberger and Yamamoto reported that there was no random sequence of styrene and methyl methacrylate units in these copolymers and therefore there was no radical propagation in this copolymerization. This conclusion was based on the comparison of the NMR spectra of the copolymers prepared with lithium dispersion with the spectra of model polymer mixtures. We now wish to report further studies on the mechanism of the lithium-initiated copolymerization of styrene and methyl methacrylate.

RESULTS AND DISCUSSION

To begin with, the results reported by Tobolsky et al.[2,4] were reinvestigated by copolymerizing an equimolar mixture of styrene and methyl methacrylate with the use of lithium dispersion in tetrahydrofuran as described.[2] Moreover, the amount of initiator was varied to obtain a wider range of conversions. The relation between copolymer composition and conversion is shown in Figure 1. Tobolsky examined this relation in the range of 15–50% conversion, and in this range our results agreed with his. However, some interesting phenomena were observed at lower and higher conversions. When the polymerization was stopped at a conversion of 0.37%, the copolymer had a high styrene content of 47.3%. The high styrene content at low conversions was also observed by Tobolsky[2] for bulk copolymerizations, but it was attributed to the low ionizing power of the medium, and thus, to the low contribution of anionic propagation. How-

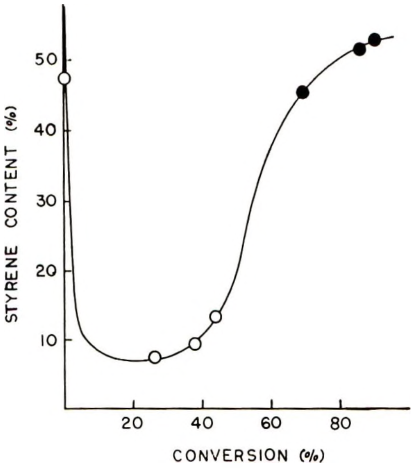

Fig. 1. Relation between copolymer composition and conversion in the copolymerizations of an equimolar mixture of styrene and methyl methacrylate with lithium dispersion in tetrahydrofuran at 20°C. The filled circles (●) indicate the formation of some insoluble polymers.

ever, this explanation does not account for the fact that the same phenomenon was observed even when tetrahydrofuran was used as solvent. The high styrene content at low conversions seems to suggest that a preferential initiation or propagation takes place with styrene at the beginning of polymerization. When the polymerization was carried to high conversions, the composition of the copolymers naturally approached that of the monomer feed. In addition, some part of the polymer became insoluble and precipitated out as small gel particles.

The homopolymerizations of styrene and methyl methacrylate were also carried out with the use of the same system. Styrene polymerized very rapidly and almost quantitatively. Although Tobolsky[2] reported that methyl methacrylate does not polymerize by lithium dispersion in tetrahydrofuran at 20°C., we found that it did polymerize under similar conditions. The initial reaction was rather rapid, but the conversion did not exceed 50% even after 24 hr., even though the solution remained yellow. It appears that some sort of termination reaction is competing with propagation.

From the NMR study,[5] it was revealed that there was no random styrene–methyl methacrylate sequence in the copolymer prepared with lithium dispersion. Therefore, the polymer must be either a mixture of homopolystyrene and homopolymethyl methacrylate or a copolymer consisting of two homopolymer blocks which may be contaminated with the homopolymers. To clarify this point the copolymers were fractionated with acetonitrile. As mentioned above, the copolymers at higher conversions contained some tetrahydrofuran-insoluble materials and these were removed prior to fractionation with acetonitrile. The results are shown in Table I.

The acetonitrile-soluble fractions had relatively high styrene content› while random copolymers having approximately the same compositions and viscosities were totally insoluble in acetonitrile. Therefore, the styrene units in the soluble fraction must be incorporated into the copolymer as a polystyrene block. The NMR spectrum of an acetonitrile-insoluble fraction showed a sharp peak at 6.38 τ which was assigned by Bovey[6] to the methoxyl protons in a sequence of methyl methacrylate units. The spec-

TABLE I
Fractionation of Copolymers by Acetonitrile

Samples			Soluble part		Insoluble part	
Conversion, %	Styrene content, %	$[\eta]^a$	Fraction, %	Styrene content, %	Fraction, %	Styrene content, %
14.0	56.7	0.140	55.8	40.0	44.2	78.1
12.8	57.1	0.136	66.0	43.7	34.0	74.8
91.0	36.7	0.464	68.4	9.5	31.6	90.2

[a] Chloroform solution, 25°C.

trum of a random copolymer of the same composition did not have this peak. Since the homopolymer of methyl methacrylate is soluble in acetonitrile, the methyl methacrylate units in the acetonitrile-insoluble fraction must exist as the poly(methyl methacrylate) part of a block copolymer. The acetonitrile-insoluble fraction was further treated with cyclohexane. Essentially no polymer was extracted from the fraction by cyclohexane. This indicated that there was no polystyrene in this fraction. From these facts it may be concluded that the copolymer is a block copolymer which consists of polystyrene and poly(methyl methacrylate) parts. It is not contaminated with the homopolomer of styrene but it may contain some pure poly(methyl methacrylate).

Since the poly(methyl methacrylate) anion cannot add styrene molecules,[7] it seems that the initiation mainly takes place on styrene molecules; and the propagating polystyryl anions are then taken over by methyl methacrylate molecules thus forming the block copolymer. To prove this hypothesis the polymerizations were terminated at very low conversions. The reaction mixture was allowed to absorb a very small amount of water by exposing it to humid air before the degassing process. The water would terminate the growing chain at an early stage of propagation before the addition of many methyl methacrylate molecules. Hopefully, the copolymer would be of low molecular weight and rich in styrene.

The results confirmed our hypothesis. A copolymer prepared from a 70:30 mixture of styrene and methyl methacrylate with 0.7% conversion had an intrinsic viscosity of about 0.07 and contained 83.1% of styrene. Another experiment using a 90:10 styrene–methyl methacrylate mixture gave a copolymer containing 88.8% of styrene. Its intrinsic viscosity was about 0.09 and the conversion was 1.6%. The calculated styrene content of copolymers prepared with a radical initiator from 70:30 and 90:10 styrene–methyl methacrylate mixtures are 64.9 and 84.4%, respectively, (on the basis of $r_1 = 0.52$ and $r_2 = 0.46$,[8] styrene as monomer 1). The copolymers obtained above contain more styrene than expected by a simple radical mechanism. On the other hand, the radical-anion mechanism predicts that the copolymer compositions should be between the values expected for radical and anionic copolymerizations.

As stated above, some insoluble polymer was formed and precipitated out from the tetrahydrofuran medium as gellike particles when the polymerization was carried to high conversion. The solubility behavior of this material in chloroform, benzene, tetrachloroethane, chlorobenzene, and tetrahydronaphthalene at their boiling points was examined. It did not dissolve in any of these solvents and, therefore, it may be concluded that the insoluble polymer is crosslinked.

Some copolymerizations were carried out with the use of a few pieces of metallic lithium as initiator instead of lithium dispersion. The rate of polymerization was much slower in these experiments than when the dispersion was used. This can be attributed to the small surface area of the initiator. In 2 hr. the surface of the lithium became yellow, and at the

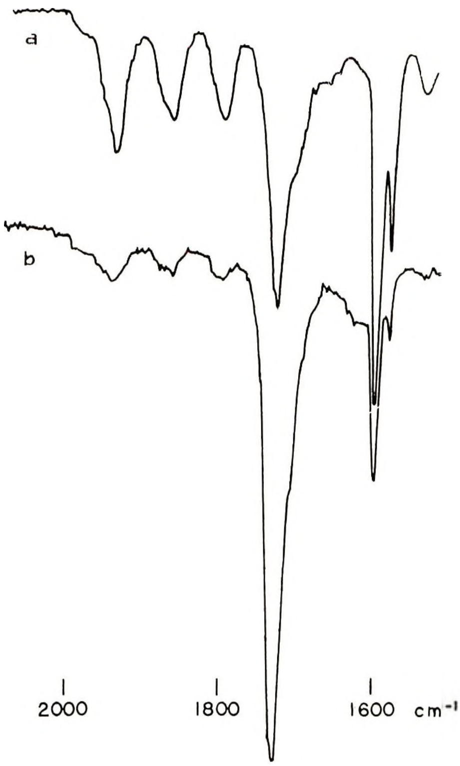

Fig. 2. Infrared spectra of (*a*) crosslinked product and (*b*) soluble product of same experiment.

same time some crosslinked polymer was formed on the surface. The formation of the crosslinked polymer seemed to start at much lower conversion when pieces of metal were used in contrast to the experiments where lithium dispersion was used. The crosslinked polymer kept growing only on the surface of the metal and developed to a thickness of about 3 mm. after 48 hr. The solution phase became more and more viscous and yellow with time, but it remained clear and essentially no crosslinked polymer was observed in it. These observations indicated that the crosslinking reaction takes place in the surface of the lithium. Furthermore, it would be reasonable to assume that the same crosslinked polymer formation is taking place on the surface of the lithium particles when the dispersion is used as initiator. The heterogeneity of the initiator would cause this crosslinked polymer.

In the homopolymerization of styrene or methyl methacrylate under the same conditions no crosslinked polymers were observed, even at high conversions. Therefore, the crosslinking must be either a reaction between the styryl anion and poly(methyl methacrylate) or vice versa. Since the growing species are polymer dianions formed by one-electron transfer and coupling, the attack of these chain ends on other polymer chains would

TABLE II
Crosslinked Polymer Formation[a]

Conversion, %	Soluble part Fraction, %	Soluble part Styrene content, %	Crosslinked part Fraction, %	Crosslinked part Styrene content, %
13.8	99.7	64.6	0.3	—
16.5	99.8	67.6	0.2	—
21.8	98.7	69.2	1.3	75.4[b]
22.4	99.1	74.6	0.9	—
34.4	93.3	77.3	6.7	91.5
37.5	92.5	77.4	7.4	93.7
79.5	71.3	77.4	28.7	90.2
80.4	70.4	76.5	29.6	95.6
81.4	67.9	77.4	32.1	94.8
83.7	65.8	77.2	34.2	90.4

[a] Polymerization conditions: styrene, 35 mmole; methyl methacrylate, 15 mmole; tetrahydrofuran, 44.4 ml.; lithium dispersion (Li 36%), 100 mg.; 30°C.

[b] Not reliable, analysis done with a small quantity of material.

cause gel formation. The nucleophilic attack of the styryl anion on the ester group of polymethyl methacrylate seems to be the most probable explanation.

The infrared spectra of the soluble and crosslinked fractions from the same experiment were examined. The sample was prepared from a 70:30 mixture of styrene and methyl methacrylate and fractionated with chloroform. The spectra between 2000 and 1500 cm.$^{-1}$ are shown in Figure 2. The absorptions of the phenyl group at 1603 cm.$^{-1}$ and between 1800 and 1950 cm.$^{-1}$ are much stronger in the spectrum of the crosslinked fraction than in that of the soluble fraction. On the other hand, the ester-carbonyl absorption at 1730 cm.$^{-1}$ is much stronger in the soluble fraction than in the crosslinked fraction. Obviously, the crosslinked part contains more styrene than the soluble part from the same experiment. Some more copolymerizations with various conversions were carried out and the copolymers were fractionated with chloroform. The styrene content of each fraction was calculated from its carbon content. The results are listed in Table II. Since the crosslinking reactions take place on the lithium surface, the abundance of styrene in the crosslinked polymer would suggest that the polymerization on the metallic surface incorporates more styrene than that in solution.

When the initiation step of this polymerization is written as

$$\mathrm{Li} + \mathrm{M} \rightarrow \mathrm{Li}^{+}\mathrm{M}^{-}\cdot$$

$$2\mathrm{Li}^{+}\mathrm{M}^{-}\cdot \rightarrow \mathrm{Li}^{+}{}^{-}\mathrm{MM}^{-}\mathrm{Li}^{+}$$

it might give the impression that a lithium cation goes into solution as soon as an electron is transferred from the metal to a monomer molecule. Thus, it might be expected that the polymerization proceeds in solution like the normal homogeneous anionic polymerization initiated by butyllithium or sodium naphthalene. This copolymerization system is not so simple. Even if an electron is transferred from a lithium particle to a monomer molecule, a lithium cation need not go into solution immediately. Instead, the particle could stay in a positively charged state. A lithium particle 15 μ in diameter contains about 8×10^{13} lithium atoms and an equal number of valence electrons. It could support, to some extent, a positive potential without releasing lithium cations. The anionic ends of the growing polymer chains would adhere to the surface of the positively charged metal and the polymerization would proceed on the surface.

The styrene molecule is planar and has eight π-electrons which form a relatively dense electron cloud. Although the molecule of methyl methacrylate is more polar than styrene, it does not have as dense an electron cloud as styrene. Therefore, it is reasonable to assume that styrene molecules are more easily adsorbed on the surface of the positively charged particle, and the relative styrene concentration at that locus would become higher than that in solution. At the very beginning of the polymerization, the propagation would take place only on the surface where the styrene concentration is high, thus giving a copolymer of high styrene content at very low conversions. The high styrene content of the crosslinked polymer could also be explained by this mechanism because the crosslinking is essentially a reaction occurring on the metal surface. The anionic chain ends on the surface of the positively charged metal do not have counterions, in a true sense. They are more like free ions, which are much more reactive than ion-pairs. Thus, they would be able to attack the ester groups of poly(methyl methacrylate) chains easily to form crosslinked polymers. The heterogeneous character of alkali metal-initiated polymerizations has also been observed by several other workers. Medvedev[9] and Bolland[10] reported that the sodium-initiated polymerization of butadiene proceeded on the metal surface. Okamura[11] studied the polymerization of styrene with metallic sodium in toluene at 30°C. and found that amorphous polymer was formed in the homogeneous solution phase while crystalline stereoregular polymer was formed on the surface of the metal.

The initiation reaction would continue with time, and the lithium particle would become more and more positively charged until it could no longer maintain its high positive potential. It would be at this stage that a lithium cation goes into solution with a polymeric anion end. In solution the mode of reaction would become simple anionic and the propagating chain end would be taken over by methyl methacrylate. After this stage the polymerizations on the surface as well as in solution would proceed together by different mechanism. Thus the copolymer composition becomes richer in methyl methacrylate with increasing conversion until a certain value of conversion is reached, as can be seen in Figure 1.

The peculiarity of the lithium-initiated copolymerization of styrene and methyl methacrylate can be attributed to the adsorption of styrene molecules on the surface of the positively charged lithium metal and to the free ion character of the growing chain ends on the surface. Hence, it was expected that this peculiarity would disappear if the adsorption of styrene and the polymerization on the metallic surface were prevented. Lithium phenoxide and lithium β-naphthoxide, which are structurally similar to styrene, would compete with styrene molecules for the surface of the metal. They would also neutralize any positive charge on the metal particles. The lithium ions would serve as counterions of the anionic chain ends. The strong tendency of anionic chain ends to form ion-pairs with cations in tetrahydrofuran is well known. As a result, these ends could go into solution as ion-pairs apart from the surface of the metal. The propagation reaction would then become the same as that of the homogeneous system. Therefore, crosslinked polymer formation would not occur even with metallic lithium as initiator.

Copolymerizations in the presence of these salts and some control experiments were carried out, and the copolymers obtained were fractionated to yield a soluble part and a crosslinked part. The results are listed in Table III. When no salts were added and a piece of lithium metal was used as initiator, the formation of the crosslinked polymer began at low conversions. This fact should be noted in comparison to the results obtained from the copolymerizations with lithium dispersion. The copolymers prepared with a piece of lithium contained an appreciable amount of crosslinked material at about 20% conversion, while those prepared with lithium dispersion contained only about 1% of crosslinked fraction at similar conversions. Since the crosslinking is essentially a surface reaction, one of the factors which influence the formation of crosslinked polymer would be the

TABLE III
Copolymerization in the Presence of Lithium Phenoxide and Lithium β-naphthoxide[a]

Additive and amt. mmole	Conversion, %	Soluble part, %	Crosslinked part, %
None	19.7	84.7	15.3
None	21.5	91.8	8.2
None	25.8	75.9	24.1
None	42.2	64.3	35.7
None	49.3	66.5	33.5
None	50.0	66.0	34.0
None	81.6	86.2	13.8
None	84.8	82.0	18.0
PhOLi, 68	50.2	99.2	0.8
PhOLi, 50	57.3	99.7	0.3
PhOLi, 20	76.4	99.4	0.6
NapOLI, 50	29.1	100	0.8
NapOLi, 10	49.3	99.2	0

[a] Polymerization conditions: styrene, 7 mmole; methyl methacrylate, 3 mmole; tetrahydrofuran, 20 ml.; lithium metal, 0.1 g.; room temperature.

conversion per unit surface area. About 0.1 g. of a piece of lithium metal has hundreds of times less surface area than 36 mg. of lithium dispersion. When this much of lithium dispersion was used, a conversion of 50% was obtained in less than a minute, while several hours of reaction time was necessary to get the same conversion with a piece of lithium metal. Even if the overall conversion were low in the case of a piece of lithium metal, the local concentration of anionic ends on the surface would be high enough and the reaction time sufficiently long to allow the crosslinking reaction to proceed. When lithium phenoxide or lithium β-naphthoxide was added to the reaction mixture, the amount of crosslinked polymer formed was remarkably decreased. This fact further enforces the hypothesis that the peculiarity of the lithium-initiated copolymerization of styrene and methyl methacrylate can be attributed to the reaction on the surface of the metal.

Tobolsky[2,12] examined the effects of the solvent composition and the polymerization temperature on the copolymer compositions. When the solvent was changed from tetrahydrofuran to heptane the styrene content of the copolymer increased. This fact was attributed to the low ionizing power of the medium, which decreased the rate of anionic growth without affecting the rate of radical growth. It was also observed that the styrene content was decreased by lowering the reaction temperature. This was attributed to the slower rate of radical propagation at lower temperatures. Since we have shown that there is no radical propagation, these dependencies of the copolymer compositions on the solvent and on the temperature could be explained by considering the propagations on the surface of the initiator and in solution. The propagation on the surface of the initiator would preferentially form polystyrene while that in solution would involve mainly methyl methacrylate molecules. The ratio of surface to solution propagations would be decided by the tendency of lithium cations to go into solution.

When a part of the tetrahydrofuran is replaced by a nonpolar solvent, fewer tetrahydrofuran molecules are available for the solvation of lithium cations, and a stronger driving force would be necessary to make lithium cations go into solution. Therefore, in a medium of less ionizing power the positive charge of the initiator particle would remain at a high level, and fewer lithium cations would go into solution. Since the relative concentrations of chain ends in solution and on the initiator surface depend on the ionizing power of the medium, changing the solvent should change the mode of polymerization. If the ionizing power of the medium is low, this will favor the surface reaction over that occurring in solution. This could explain why the introduction of heptane into the medium increased the styrene content of the copolymer.

During the process in which a lithium cation is transferred from a positively charged lithium particle into the tetrahydrofuran medium there are three energy factors to be considered: lattice energy, electrostatic energy, and the heat of solvation. The evaluation of the change in the electrostatic energy is very difficult, and the heat of solvation of lithium cations in tetrahydrofuran has not yet been reported. However, the whole process would probably be exothermic because the lattice energy of lithium is small and the changes in the other two forms are assumed to be exothermic on theoretical grounds. If this process is exothermic, the decrease in temperature would favor the transfer of lithium cations into solution. Thus the polymerization in solution would be favored, and the styrene content of the copolymer would be decreased.

So far the anionic copolymerization of styrene and methyl methacrylate has been discussed based on the copolymer compositions. However, the concept of the initial copolymer composition has only a semiquantitative meaning for this system. If an initiation reaction takes place on a styrene molecule, the composition of this polymer chain will be 100% styrene as long as it reacts with styrene molecules. Once it happens to react with a methyl methacrylate molecule, then only methyl methacrylate will be added to the chain on further propagation and the styrene content of the polymer chain will keep decreasing. What should be discussed in this system is the average number of styrene units per chain. The fraction of initiation on styrene r and that of the styryl anion propagation on styrene p may be expressed by eqs. (1) and (2).

$$r = k_{i1}[M_1]/(k_{i1}[M_1] + k_{i2}[M_2]) \tag{1}$$

$$p = k_{11}[\mathrm{M}_1]/(k_{11}[\mathrm{M}_1] + k_{12}[\mathrm{M}_2]) \tag{2}$$

If most of the polymer chains are long enough to have a methyl methacrylate unit at the growing end, the average number of styrene units per kinetic chain would be expressed as

$$\begin{aligned} n_1 &= r + rp + rp^2 + rp^3 + \ldots \\ &= r(1 + p + p^2 + p^3 + \ldots) \\ &= r/(1 - p) \end{aligned} \tag{3}$$

which upon substitution for r and p gives

$$p_1 = \frac{1 + (k_{11}[\mathrm{M}_1]/k_{12}[\mathrm{M}_2])}{1 + (k_{i2}[\mathrm{M}_2]/k_{i1}[\mathrm{M}_1])} \tag{4}$$

Rearrangement of this equation leads to an expression

$$k_{11}/k_{12} = (n_1 - 1)[\mathrm{M}_2]/[\mathrm{M}_1] + n_1([\mathrm{M}_2]/[\mathrm{M}_1])^2\, k_{i2}/k_{i1} \tag{5}$$

Since n can be determined from the composition and the number-average molecular weight and $[\mathrm{M}_2]/[\mathrm{M}_1]$ is known from the experimental conditions, the values of k_{11}/k_{12} and k_{i2}/k_{i1} can be obtained by the intersection method.

EXPERIMENTAL

Copolymerizations with Lithium Dispersion

Styrene (Matheson) was washed with 10% potassium hydroxide and with water, three times each. At the third washing with water the aqueous phase was neutral. The inhibitor-free styrene was treated overnight with Drierite, distilled under argon, and stored over calcium hydride. Methyl methacrylate (Matheson) was purified in the same way except that it was stored without calcium hydride. Tetrahydrofuran (Matheson) was distilled under argon and stored over calcium hydride. Lithium dispersion (Lithium Corporation of America) was composed of 36% lithium, 62% petroleum wax, and 2% oleic acid. The metal particles were less than 30 μ in diameter, chiefly in the 10–15 μ range.

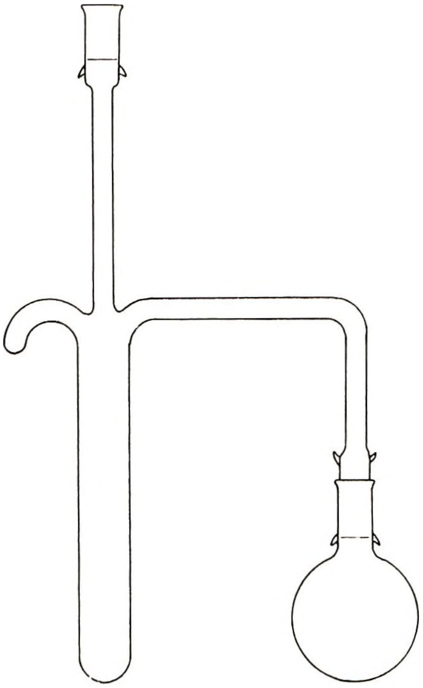

Fig. 3. Polymerization tube.

For the copolymerization of styrene and methyl methacrylate the polymerization tube shown in Figure 3 was used. The total amount of monomers used was 50 mmole and the volume of the solution was made 50 ml. by adjusting the amount of tetrahydrofuran. A 100-ml. flask containing this solution and a small amount of calcium hydride was attached to the long arm of the tube; the lithium dispersion was placed in the short arm. The tetrahydrofuran solution was degassed by two freeze–thaw cycles and the vacuum was broken with argon which was dried by passing through a xylene solution of benzophenone ketyl and a trap at Dry Ice–acetone temperature. The solution was kept overnight at 0°C. for drying. The tetrahydrofuran solution was degassed by two freeze–thaw cycles at a pressure of about 10^{-2} mm. Hg and one at about 10^{-4} mm. Hg. The solution was distilled into the polymerization tube from the flask and the long arm was sealed off. After repeating another freeze–thaw cycle at about 10^{-4} mm. Hg the neck of the tube was sealed off.

The polymerization tube was placed in a constant temperature bath at 30°C. A small amount of the solvent was distilled into the short arm to dissolve the wax in the dispersion, leaving a suspension of finely divided lithium. Upon mixing the monomer solution with the initiator, polymerization began immediately, as evidenced by the evolution of heat and the formation of a yellow color. During polymerization, the tube was vigorously shaken. The copolymer was precipitated with methanol and dried at 60°C. *in vacuo*.

Copolymerizations with Pieces of Metallic Lithium

Lithium wire, about 4 mm. in diameter, was cut into pieces about 2 cm. in length and treated with methanol to obtain a fresh surface. The pieces were washed five times with dry tetrahydrofuran in an argon atmosphere. In a typical experiment, 0.6 g. of freshly cleaned lithium wire was added to 50 ml. of tetrahydrofuran solution containing 70 mmole of styrene and 30 mmole of methyl methacrylate. The reaction was carried out at 30°C. with stirring. The solution was degassed by three freeze–thaw cycles, and the flask was sealed under pressure of 0.1 mm. Hg. The mixture was stirred in a constant temperature bath at 30°C. After 48 hr. the polymer was precipitated with methanol. The conversion was 90.8%.

Copolymerizations in the Presence of Lithium Phenoxide and Lithium-β-Napthoxide

Phenol was distilled at atmospheric pressure. β-Naphthol was recrystallized three times from carbon tetrachloride. Lithium wire was treated with methanol to remove the oxidized surface and washed with tetrahydrofuran as described above. In an experiment, 1.88 g. of phenol was dissolved in 20 ml. of tetrahydrofuran in a 50-ml. round-bottomed flask equipped with a stirrer, and 154 mg. of lithium was added. The reaction proceeded with gas evolution, and the lithium was observed to decrease in size. When the dimensions of the wire no longer changed, the reaction mixture was heated at reflux for 3 hr. After cooling, 7 mmole of styrene, 3 mmole of methyl methacrylate, and about 0.1 g. of lithium wire were added. The flask was degassed by three freeze–thaw cycles and sealed under a pressure of 0.1 mm. Hg. The flask was attached to a shaker, and the polymerization proceeded at room temperature with shaking. After 48 hr. the polymer was precipitated, and 76.4% of conversion was obtained. Preparations of lithium β-naphthoxide and polymerizations in the presence of this salt were carried out in exactly the same way as with phenoxide. Several experiments were carried out without added lithium salts for purposes of comparison. The amounts of monomers, solvent, and initiator were the same as those in the experiments with the salts.

Fractionation of Copolymers with Acetonitrile

In a 250-ml. centrifuge bottle 300 mg. of a sample was mixed with 80 ml. of acetonitrile, and the suspension was gently refluxed for 2 hr., after which the insoluble part was separated by centrifugation. The solution containing the soluble part was separated by decantation, concentrated to about 3 ml., and then added to methanol to precipitate the polymer. The insoluble part was removed from the bottle by dissolving it in chloroform. The chloroform solution of the acetonitrile-insoluble part was concentrated, and the polymer was precipitated in the same way.

Fractionation of a Copolymer with Cyclohexane

To 25 mg. of an acetonitrile insoluble fraction containing 74.8% of styrene, 5 ml. of cyclohexane was added, and the mixture was refluxed for 1 hr. After cooling, it was filtered and the filtrate was added to methanol. No polymer precipitated.

Fractionation of Copolymers with Chloroform

In a 250-ml. Erlenmeyer flask were placed 300 mg. of polymer and 150 ml. of chloroform. The mixture was gently boiled until the volume decreased to 100 ml. The chloroform solution containing some insoluble material was then filtered with a 50-ml. sintered glass filter of medium porosity without applying any vacuum. The crosslinked polymer was washed with chloroform several times and then dried on the filter. After weighing, the crosslinked polymer was boiled in benzene and swelled to a gel. The gellike polymer was triturated with methanol. The filtrate was concentrated to about 3 ml. and the soluble polymer was precipitated with methanol.

This paper comprises a portion of a dissertation submitted by Naoki Yamamoto in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

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Résumé

Les copolymères de styrène et de méthacrylate de mèthyle préparés en présence d'une dispersion de lithium comme initiateur ne présentent pas de séquences statistiques de monomères. Le fractionnement des copolymères avec l'acétonitrile et les spectres NMR des fractions insolubles ont montré qu'il s'agit de copolymères séquencés qui consisten tde parties de polystyrène et de parties de polyméthacylate de méthyle. Lorsque la polymérisation est arrêtée à des faibles degrés de conversion, le copolymère a une teneur en styrène élevée qui parfois dépasse la valeur attendue d'après les donnés de copolymérisation radicalaire. Ce fait indiquerait que le styrène est préférentillement polymérisé dans les premières étapes de la propagation des chaînes. Lorsque la copolymérisation est effectuée à des degrés de conversion élevés, un certain pontage se passe et le polymère contient plus de styrène que la partie soluble obtenue au cours de la même expérience. Utilisant une pièce de lithium métallique, il a été montré que le polymère ponté est formé à la surface du métal. L'addition de phénate de lithium ou de β-naphthalate de lithium à ces systèmes élimine la formation de polymère ponté. Un mécanisme possible a été présenté.

Zusammenfassung

Mit einer Lithiumdispsersion als Starter hergestellte Styrol-Methylmethacrylatcopolymere enthalten keine statistischen Sequenzen beider Monomerer. Fraktionierung der Copolymeren mit Acetonitril und die NMR-Spektren der unlöslichen Fraktion zeigen, dass es sich um Blockcopolymere, bestehend aus einem Polystyrolteil und einem Polymethylmethacrylatteil, handelt. Wird die Copolymerisation bei niedrigem Umsatz gestoppt, so besitzt das Copolymere einen hohen Styrolgehalt, der manchmal den bei radikalischer Copolymerisation zu erwartenden Wert übersteigt. Das bedeutet, dass Styrol im Frühstadium des Kettenwachstums bevorzugt polymiersiert wird. Bei hohem Copolymerisationsumsatz wird etwas vernetztes Polymeres gebildet, welches mehr Styrol enthält als de lösliche Anteil des gleichen Versuches. Durch Verwendung eines Stückes metallischen Lithiums wurde gezeigt, dass das vernetzte Polymere an der Oberfläche des Metalls gebildet wird. Der Zusatz von Lithiumphenoxyd oder -β-naphthoxyd zum System verhindert die Bildung des vernetzten Polymeren. Ein möglicher Mechanismus wurde vorgeschlagen.

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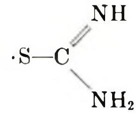
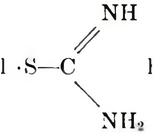
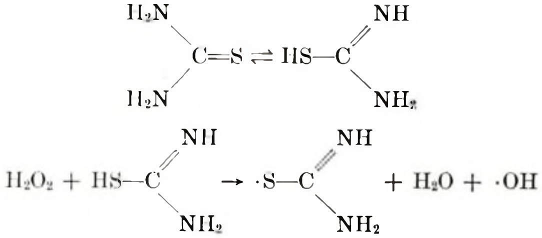
NOTES

On the Identification of the Radical  $\cdot S{-}C(=NH)NH_2$

Thiourea in combination with hydrogen peroxide or ferric salts is well known as an initiator for vinyl polymerization. The generation of the radical  $\cdot S{-}C(=NH)NH_2$ has been predicted by Sugimura[1] and co-workers in their study of the polymerization of acrylonitrile in aqueous phase using thiourea and hydrogen peroxide as initiator. The mechanism of the radical generation suggested by them is



$$(H_2N)_2C{=}S \rightleftharpoons HS{-}C(=NH)NH_2$$

$$H_2O_2 + HS{-}C(=NH)NH_2 \rightarrow \cdot S{-}C(=NH)NH_2 + H_2O + \cdot OH$$

A similar mechanism could possibly be suggested for systems with ferric salts or other oxidizing agents in conjunction with thiourea.

In the present work the identification of the predicted radical has been achieved. Poly(methyl methacrylate) and polystyrene obtained by polymerizing the respective monomers using thiourea and ferric salts as initiator in aqueous,[4] non-aqueous and

TABLE I

Effect of Alkali on the DP and Endgroups of Ferric Salt–Thiourea Initiated Polymers

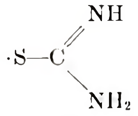
Sample	Nature of polymer	$\bar{P}_n \times 10^3$	Dye partition test using Disulfine Blue VN 150 reagent
			O.D. at 630 mμ of 0.05% polymer solution
A	Poly(methyl methacrylate)	0.5	0.70
A[a]	"	1.2	0.007
B	"	1.1	0.31
B[a]	"	1.8	0.01
C	Polystyrene	1.3	0.29
C[a]	"	2.29	0.004

[a] Samples treated with alkali as mentioned in the text.

mixed-solvent systems[5] were used to identify the radical trapped in the polymer chain as endgroups. The dye partition test using the dye Disulfine Blue VN 150 (known to detect micromolar amounts of long-chain quarternary ammonium compounds[2] and amines[3]) gave very strong response with all the polymers which in all probability indicates the presence of NH_2 groups in the polymers.

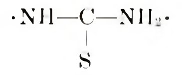
A few representative samples of the polymers giving strong response for amino endgroups were then treated in the following way: to a solution of the polymer (about 0.5 g.) in acetone (sufficient to keep the system homogeneous, about 90–100 ml.) was added dilute alkali to achieve final alkalinity of about $0.15M$. The solution was then warmed to 45–50°C. and kept at that temperature for 40–60 min. Acetone was then removed by distillation and the polymer precipitated by methanol (recovery about 90%). Alkali was thoroughly washed and finally the polymer solution in acetone was acidified with few drops of concentrated HCl and precipitated by methanol. The polymer was purified by precipitation with methanol from solution of poly(methyl methacrylate) in acetonitrile and solution of polystyrene in *N,N*-dimethylformamide. The polymers so treated failed to respond to the dye partition test mentioned earlier. Moreover, the molecular weights of the polymers were found to increase and were almost double their original values. Some typical results are summarized in Table I.

These observations point out that the amino group was present in the polymer adjacent to an alkali labile center. The amino-bearing radical from thiourea could be either



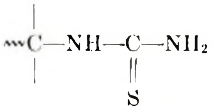
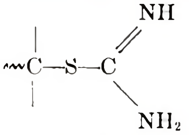
$\cdot S\text{—}C(=NH)NH_2$

or

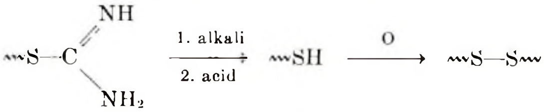


$\cdot NH\text{—}C(S)\text{—}NH_2\cdot$

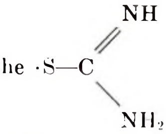
(I) (II)

Initiation through (II) would produce polymers of the type  $\sim\!\sim C\text{—}NH\text{—}C(=S)\text{—}NH_2$ which might respond to the dye partition test initially and also after alkali treatment as it would have produced $\text{—}NH_2$ group, as the result of hydrolysis. Initiation through (I) would produce polymers  $\sim\!\sim C\text{—}S\text{—}C(=NH)NH_2$, the end portion resembling *S*-alkyl isothioureas. In this latter case, while the original polymer would respond to the amino group test, the alkali-treated polymer should not, as *S*-alkyl isothioureas are well known to be unstable in alkali, generating mercaptans.[6]

Moreover, the increase in molecular weight after alkali treatment might be partly due to the formation of disulfide from the macromolecular mercaptans resulting from alkali treatment of the original polymer (macromolecular *S*-alkyl isothiourea).



$$\sim\!\sim S\text{—}C(=NH)NH_2 \xrightarrow[\text{2. acid}]{\text{1. alkali}} \sim\!\sim SH \xrightarrow{O} \sim\!\sim S\text{—}S\sim\!\sim$$

These results demonstrate that the  $\cdot S\text{—}C(=NH)NH_2$ radical is generated in the ferric salt–thiourea reaction and analogous results were obtained in the hydrogen peroxide–thiourea system. Further work in this line is in progress in this laboratory.

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Crosslinking in Lithium-Initiated Anionic Copolymerization of Methyl Methacrylate–Styrene

Tobolsky and his co-workers[1–3] have reported that lithium metal-initiated copolymerization of methyl methacrylate–styrene monomer mixtures involves both free-radical and anionic propagation in each growing chain. Experiments similar to those reported by these authors have confirmed their experimental observations for polymerizations conducted in tetrahydrofuran, see Table I. Polymerization of equal weights of both monomers at total monomer concentrations varying from 1.81 to 5.32 moles/liter in tetrahydrofuran initiated by lithium dispersions resulted in conversions of 18–55%. Over this range of initial monomer concentrations and conversions, polymer intrinsic viscosities were found to increase by only 41%. The essentially constant molecular weight of polymer is ascribed to facile termination of poly(methyl methacrylate) anions on monomer. Other studies[4,5] have indicated the unreactivity of ether-solvated polymethacrylate anions toward termination on poly(methyl methacrylate). From elemental analysis and solubility characteristics, styrene concentrations of 10–20% in polymers were estimated. Solutions in benzene or methyl ethyl ketone of polymers from runs 1 and 2 were turbid but no gel was removed by filtration.

In the absence of a solvent, polymerization of the monomer mixture on lithium mirrors (deposited on the reactor walls by solution in liquid ammonia followed by evaporation and evacuation) proceeded more slowly and resulted at high conversion (40–50%) in high percentages of crosslinked polymers insoluble in toluene, chloroform, or boiling *o*-dichlorobenzene. Undiluted monomers (17.37 g. of styrene and 29.95 g. of methyl methacrylate) were polymerized with lithium dispersion to 26% conversion, see Table I, run 4. Attempts at solution in methyl ethyl ketone produced a highly dilatant gel. Extraction of this polymer for seven days with methyl ethyl ketone dissolved 43.5% of soluble polymer. The intrinsic viscosity of the soluble fraction was 1.55. O'Driscoll[1] has reported a value of $[\eta] = 1.59$ for soluble styrene–methyl methacrylate polymer polymerized in bulk by metallic lithium to $< 12\%$ conversion.

TABLE I
Free-Radical Anionic Copolymerization of Styrene–Methyl Methacrylate at 25°[a] in Tetrahydrofuran[b]

Run	Total monomer conc., mole/l.[c]	Polymer yield, %	$[\eta]$	Styrene by analysis, %
1	1.81	48	0.30	10
2	3.62	55	0.33	16
3	5.32	18	0.43	19
4[d]	9.00	25.9	1.55[e]	

[a] 0.20–0.30 g. of lithium dispersion in petrolatum used in each run. Lithium in a small cup was placed in reactor.

[b] Tetrahydrofuran was refluxed over sodium and stored over sodium in the presence of sodium benzophenone ketyl.

[c] Monomers were freed of inhibitors, dried over CaH_2 and immediately before use distilled under vacuum into calibrated bulbs and from these into the reaction vessels collecting at −70°C. The solvent was then flash distilled from the ketyl into the reactor. Stirring was then started as the contents warmed to room temperature. Reactions were carried out for 60–80 min. Reactions were terminated by addition of methanol and polymers precipitated into methanol.

[d] No solvent used.

[e] Intrinsic viscosity of soluble fraction. All intrinsic viscosities determined at 25° in toluene.

TABLE II

Reactions of Li° and Polystyryl Lithium Dianions with Poly(methyl Methacrylate) at Room Temperature

Run	PMMA wt.,[a] g.	Styrene wt., g.	Solvent, (vol./ml.)	Li° wt., g.	$[\eta]_0$[b]	Polymer wt.,[c] g.	$[\eta]_f$[d]
A	2.00	—	Benzene (70)	0.60	1.45	2.15	1.52
B	2.00	68.0[e]	—	0.20	1.45	5.19	2.20
C	2.00	68.8[f]	—	0.20	1.45	4.57	—
D	1.63	18.2	Dimethoxy ethane (100)	0.30	1.45	19.54	crosslinked

[a] PMMA = poly(methyl methacrylate) purified as indicated in text.

[b] $[\eta]_0$ = intrinsic viscosity before reaction, 25° in toluene.

[c] Wt. of product polymer recovered after precipitation and vacuum drying.

[d] $[\eta]_f$ = intrinsic viscosity of product, 25° in toluene.

[e] Reacted for 5 days in dark at ambient temperature.

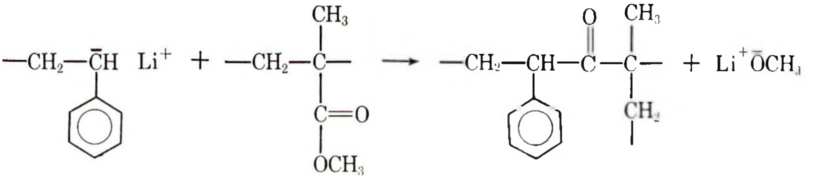
[f] Reacted for 2 days in dark at ambient temperature.

In view of the facts that more styrene was incorporated in the copolymer in the absence of ionizing solvents, such as tetrahydrofuran, and that polymerization in the absence of the ion solvating ether led to polymer crosslinking, a sequence of qualitative experiments was carried out to determine whether crosslinks were due to: (*a*) lithium reacting with the ester functions of the poly(methyl methacrylate); (*b*) nucleophilic displacement of methoxide from poly(methyl methacrylate) ester groups by styryl dianions as has been reported by Schreiber.[6] In Table II, the pertinent stoichiometry of these experiments is presented.

The fact that metallic lithium did not react with ester linkages on poly(methyl methacrylate) to produce crosslinks was unequivocally demonstrated by run A, Table II. Anionic poly(methyl methacrylate) with $[\eta] = 1.45$ was purified by repeated precipitation from benzene into methanol followed by twice freeze-drying from benzene. After freeze-drying, the fluffy polymer was pumped at high vacuum in the reaction vessel for 16 hr. Lithium dispersion in dried benzene was sealed in a vial with a break seal inserted in the reaction vessel before evacuation. Purified benzene was vacuum distilled from sodium into the reaction vessel and after sealing off the vessel under vacuum, the polymer dissolved by stirring. After complete solution of poly(methyl methacrylate), the lithium dispersion was introduced and the mixture of metal and polymer stirred for 24 hr. at 25°. The reaction vessel was opened and the polymer solution filtered free of suspended lithium, precipitated into methanol, and repeatedly washed to remove salts. The slight increase in intrinsic viscosity of recovered polymer ($[\eta] = 1.52$) demonstrated that at the temperature of reaction insufficient reaction of poly(methyl methacrylate) with lithium took place to account for extensive gel formation.

In runs B and C, purified poly(methyl methacrylate) was reacted with styrene (purified by partial prepolymerization over sodium) and lithium dispersion. In each product the polystyrene content (3.19 g., 2.57 g.) was larger than the poly(methyl methacrylate) charged. Repeated extraction with cyclohexane at 40° removed 40% polystyrene of polymer B (checked by infrared spectroscopy) and 32% of polystyrene from C. The residual polymers contained 36% and 39% styrene, respectively. Extraction of the cyclohexane-insoluble fractions with acetonitrile at 50° dissolved half of the residue of B as a turbid solution. Similar treatment of the residue from C dissolved 72%. Infrared spectra of both acetonitrile-soluble and -insoluble fractions (after removal of polystyrene) confirmed that these fractions contained both methyl methacrylate and styrene. Surprisingly, despite the extensive grafting of styryl anions on poly(methyl methacrylate), no insoluble crosslinked product was found.

From experiment D, it was concluded that ether-solvated lithium polystyryl dianions reacted rapidly and completely with poly(methyl methacrylate). In this experiment the lithium dispersion was introduced through a serum stopper into the solution of poly(methyl methacrylate) in styrene and dimethoxyethane. Reaction was instantaneous and quite vigorous, and the temperature rise necessitated cooling the reaction vessel. Conversion of styrene was quantitative in less than one hour. The crosslinked polymer separated as a swollen phase as polymerization progressed. It was interesting to observe that the color of polystyryl lithium did not appear during the rapid reaction. At the end of reaction, the swollen polymeric gel was a pale straw color. Solvated lithium polystyryl dianions reacting with methyl methacrylate ester groups[6]


(1)

apparently did so at a sufficiently rapid rate that the concentration of styryl anions was too low for the characteristic anion color to be observed. The failure to form crosslinked polymer (runs B and C) in the absence of a polar solvent was unexpected. Anionic polymerization of styrene most certainly proceeded through dianions. Despite a high concentration of styrene, neither styrene polymerization or anionic displacement of methoxide from methacrylate ester groups proceeded at a rapid rate. Worsfold and Bywater[7] have reported that the propagation rate for addition of styrene (M) to styryl lithium (M_n^-) in benzene has a rate constant

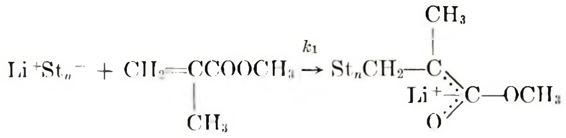
$$M_n^- + M \xrightarrow{k_p} M_{n+1} \tag{2}$$

$k_p = 9.29 \times 10^{-1}$ liter$^{1/2}$/mole$^{1/2}$-min. at 30° and is proportional to $[M_n^-]^{1/2}$. These kinetics should hold for our system of poly(methyl methacrylate) in styrene monomer. The very slow rate of styrene reaction (1–2% conversion/day) may be the result of a very low rate of initiation by metallic lithium or to diffusion-controlled propagation. The observation that few, if any, styryl dianion chains terminated both active ends by nucleophilic displacement on methyl methacrylate may be due to either (*a*) low reactivity of associated styryl lithium ion pair dimers toward ester groups, or (*b*) a slow rate of diffusion of anionic chain ends from initiating sites on the surface of metallic lithium. The formation of large aggregates of undissociated ion pairs as anions are generated on the surface might seriously reduce the rate of diffusion of the active ends into the solution where reaction with dissolved poly(methyl methacrylate) could take place. Another consequence could be a polymerization rate controlled by diffusion of styrene into the ionic sheath on the surface of lithium particles. Both factors (*a*) and (*b*) could contribute to the inefficient grafting of polystyryl anions on preformed poly(methyl methacrylate).

Overberger and Yamamoto[8] have presented evidence for a two-phase polymerization in the methyl methacrylate–styrene system. Their results indicate preferential initiation and anionic propagation of styrene on the lithium surface and predominant methyl methacrylate propagation in tetrahydrofuran. These authors exclude any free-radical propagation on the basis of the occurence of the two monomers in polymer as blocks rather than any random copolymer. Their proposed mechanism for surface phase polymerization of styrene is in accord with (*b*). An ion-solvating medium such as tetrahydrofuran should favor separation of polystyryl lithium ends from the lithium surface. The absence of such solvation, as pertains in our experiments in styrene, should result in greatly reduced diffusion of styryl anions into the liquid phase where reaction with poly(methyl methacrylate) would take place. In addition, our results, particularly the isolation of substantial percentages of polystyrene in experiments B and C, suggest that there may be a much lower nucleophilicity of unsolvated lithium polystyryl toward poly(methyl methacrylate) than for the tetrahydrofuran solvate of experiment D.

In the presence of comonomer methyl methacrylate a polystyryl lithium end which diffuses from the surface into solution can react by several routes: (*a*) initiation of anionic polymerization of methyl methacrylate, (*b*) termination on the ester group of methyl methacrylate, (*c*) termination on poly(methyl methacrylate). As for the relative significances of (*a*), (*b*), and (*c*), the following can be rationalized.

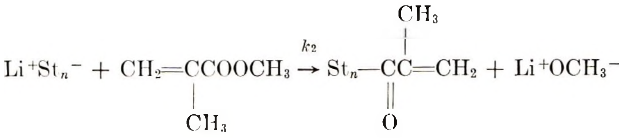
Initiation of methyl methacrylate by sodium triphenyl methide in hydrocarbon solvents has been found to be about 20% efficient at 30° and 40–50% at 0°.[5] Additionally, a large fraction of lithium poly(methyl methacrylate) chains of low DP in hydrocarbon media have been found to not grow to high polymer.[9] It would seem reasonable that reaction of lithium polystyryl ($Li^+St_n^-$) with methyl methacrylate should proceed by reactions:



(3)

(I)

and



$$\mathrm{Li^+St_n^- + CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}COOCH_3 \xrightarrow{k_2} St_n{-}\underset{\displaystyle O}{\underset{\|}{C}}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2 + Li^+OCH_3^-} \qquad (4)$$

(II)

these processes corresponding to (*a*) and (*b*). It is also likely that at 30° $k_2/k_1 > 1.0$.

Reaction by route (c) has already been formulated in equation (1). The absence of measurable polystyrene in the polymer examined by Overberger and Yamamoto we ascribe, not to an absence of termination of styryl anions by (4), which would correspond to 100% conversion of surface polystyrl anions to methacrylate anions in solution polymerization, but instead to involvement of the unsaturated ketone in subsequent polymerization. Trekoval and Lím[10] have demonstrated both monomer termination and crosslinking during anionic polymerization of methyl methacrylate at 0–30°.

It may be that a high local concentration of poly(methyl methacrylate) blocks on initially formed polystyrene still near the lithium surface intercepts the styryl anions as they diffuse away from the surface more efficiently than observed for dissolved poly(methyl methacrylate) in the absence of an ionizing solvent. Any reaction with polymer must be competitive with reactions of styryl anions with methyl methacrylate, however, and in view of the lack of reactivity of lithium with the ester functions of poly(methyl methacrylate) it appears that anionic processes involving some reactive species such as (II) with polystyryl ion pairs at or near the metal surface may be involved as well in crosslinking in a nonpolar medium.

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ERRATUM

Polymerization of Aromatic Nuclei. VIII. Molecular Weight Control in Benzene Polymerization

(article in *J. Polymer Sci. A-1*, **4**, 5–28, 1966)

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On page 6 in Table I, the λ_{max} value for *p*-terphenyl in solution should be 280.

AUTHOR INDEX, VOLUME 4

SUBJECT INDEX, VOLUME 4