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Metal-Containing Initiator Systems. V. Radical and Cationic Polymerizations with Initiator Systems of Reduced Nickel and Chlorosilanes

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Synopsis

The polymerizations of methyl methacrylate, styrene, and isobutyl vinyl ether with the binary systems of reduced nickel and chlorosilanes [$(CH_3)_nSiCl_{4-n}$, $n = 0$–3] have been investigated. It was found that these systems could act as both radical and cationic initiators, depending on the nature of vinyl monomers used. The kinetic investigations indicated that methyl methacrylate polymerized via a radical mechanism, and the initiating activity of chlorosilanes decreased in the following order: $SiCl_4 > CH_3SiCl_3 > (CH_3)_2SiCl_2 > (CH_3)_3SiCl \simeq 0$. Cationic initiations were observed in the polymerizations of styrene and isobutyl vinyl ether. In the latter case, the activity of chlorosilanes was in the following order: $(CH_3)_3SiCl > (CH_3)_2SiCl_2 > CH_3SiCl_3 \simeq SiCl_4$. From the results obtained, a possible mechanism of selective initiation with these systems is proposed and discussed.

INTRODUCTION

Recently it was reported that the systems of reduced nickel and various organic halides having rather weak chemical bonds such as C—X, O—X, N—X, or Si—X, where X is a halogen, initiate vinyl polymerization.[1,2] From the results of copolymerization of styrene with methyl methacrylate, polymerization with these systems was thought to proceed via a free-radical mechanism.[3] Further evidence for this has been obtained from the kinetic studies on the polymerizations of styrene[4] and methyl methacrylate.[3]

In a previous communication,[2] we have pointed out that the systems of reduced nickel and some alkyl chlorosilanes induce the cationic polymerization of isobutyl vinyl ether as well as the radical polymerization of methyl methacrylate. The present paper describes the detailed experimental results on both radical and cationic polymerizations and proposes a possible selective initiation mechanism for the polymerizations with these initiator systems.

EXPERIMENTAL

Materials

Methylchlorosilanes, $(CH_3)_nSiCl_{4-n}$ (n = 0–3), were obtained commercially and purified by distillation with care from the contamination with moisture before use. Methyl methacrylate, styrene, and isobutyl vinyl ether were purified by ordinary methods and distilled in a stream of nitrogen before use. The other solvents and precipitants were used after ordinary purification, followed by distillation.

Reduced nickel (Nikki Chemical Co.) which consists of 50% Ni on kieselghur, was used after activation by hydrogen according to the method described in the previous paper.[3]

Polymerization Procedure

The polymerizations and copolymerizations were carried out in a sealed tube without diffused light under shaking in a thermostat maintained at a given temperature. The methods were the same as described in detail in the previous paper.[3]

Analysis of Polymers

The composition and reduced viscosity of the copolymers of methyl methacrylate with styrene were determined by elementary analysis on carbon and by use of an Ubbelohde viscometer in benzene at 30°C, respectively.

The intrinsic viscosity $[\eta]$ of poly(methyl methacrylates) was determined in their dilute benzene solutions at 30°C, and the number-average molecular weight ($\bar{M}_n$) was calculated from the following equation:[5]

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_n^{0.76}$$

The number-average molecular weight of polystyrenes obtained was determined by vapor-pressure osmometry.

The tacticities of poly(methyl methacrylate)[6] and poly(isobutyl vinyl ether)[7] were estimated by their infrared spectra and by solubilities in methyl ethyl ketone.

RESULTS

Polymerization of Methyl Methacrylate

The results of the polymerization of methyl methacrylate with the system of reduced nickel and chlorosilanes in benzene at 60°C are shown in Table I. No polymer was obtained when the reduced nickel alone was used.

In the absence of the reduced nickel, all chlorosilanes used showed no activity for the initiation of polymerization, but in the presence of the reduced nickel, tetrachlorosilane and methyltrichlorosilane initiated the polymerization of methyl methacrylate to give a high molecular weight

TABLE I
Polymerization of Methyl Methacrylate with the System of Chlorosilanes and Reduced Nickel in Benzene at 60°C[a]

Chlorosilane	Polymer yield, %[b]	$\bar{M}_n$
$SiCl_4$	5.9 (0.2)	10.7×10^5
CH_3SiCl_3	3.8 (—)	7.4×10^5
$(CH_3)_2SiCl_2$	0 (trace)	—
$(CH_3)_3SiCl$	Trace (trace)	—

[a] Time, 4 hr; [M] = 4.7 mole/l.; [chlorosilane] = 0.1 mole/l.; [Ni] = 0.4 g-atom/l.; in benzene.

[b] Values in parentheses show the yield obtained in the absence of reduced nickel.

polymer. With the system of dimethyldichlorosilane or methyl trichlorosilane and reduced nickel, however, no polymerization has occurred.

Figure 1 shows the relationship between the rate of polymerization of methyl methacrylate and the square root of concentration of methyltrichlorosilane at constant concentrations of both the monomer and the reduced nickel. A straight-line relationship between them was observed. This result suggests that radical polymerization was induced with these systems.

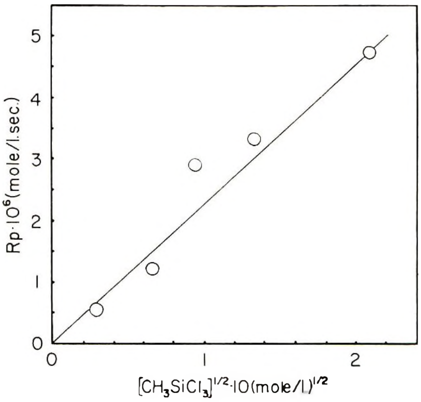

Fig. 1. Relationship between rate of polymerization R_p of methyl methacrylate and concentration of CH_3SiCl_3 at 60°C. [M] = 4.7 mole/l.; [Ni] = 0.4 g-atom./l.; in benzene.

The overall activation energy for polymerization with this initiator system in the temperature range 45–80°C was determined. From the Arrhenius plot for the polymerization rates shown in Figure 2, the overall activation energy was obtained as 14.1 kcal/mole, which is considerably lower than that with azobisisobutyronitrile and somewhat higher than that with the system of reduced nickel and carbon tetrachloride (7.5 kcal/mole).[3]

The infrared spectra of poly(methyl methacrylates) obtained with these systems were almost identical to those with typical radical polymers, indicating that the polymerizations proceeded via radical mechanism.

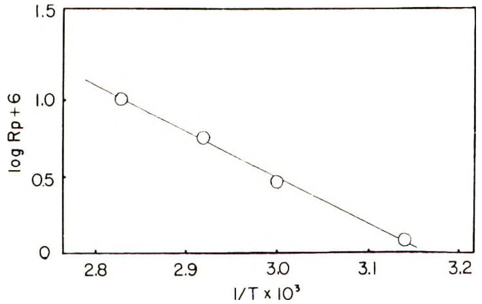

Fig. 2. Arrhenius plot for the rate of polymerization of methyl methacrylate initiated by the system of reduced Ni and CH_3SiCl_3. [M] = 4.7 mole/l.; [CH_3SiCl_3] = 1.7 × 10^{-2} mole/l.; [Ni] = g-atom/l.; in benzene.

Polymerization of Styrene

Table II shows the results of polymerization of styrene at 60°C. Styrene was polymerized quite readily with the systems involving all chlorosilanes, while the very low molecular weight polystyrenes ($\bar{M}_n$ = 790–830) were obtained. In the absence of the reduced nickel, chlorosilanes were ineffective for initiation, as is shown in Table II. This result might be understandable, if the polymerization of styrene proceeded via a cationic mechanism.

TABLE II
Polymerization of Styrene with the System of Chlorosilanes and Reduced Nickel in Benzene at 60°C[a]

Chlorosilane	Polymer yield, %[b]	$\bar{M}_n$
$SiCl_4$	93.0 (1.5)	790
CH_3SiCl_3	88.8 (0.6)	930
$(CH_3)_2SiCl_2$	94.0 (0.2)	930
$(CH_3)_3SiCl$	94.4 (0.2)	830

[a] Time, 4 hr; [M] = 4.1 mole/l.; [chlorosilane] = 0.1 mole/l.; [Ni] = 0.4 g-atom/l.; in benzene.

[b] Values in parentheses show the yield obtained in the absence of reduced nickel.

Copolymerization of Styrene and Methyl Methacrylate

The copolymer composition curves for the copolymerization of methyl methacrylate and styrene are shown in Figure 3. Almost the same results were obtained regardless of the kinds of chlorosilanes used. In the lower concentration range of styrene in the monomer mixture, the composition curve of Figure 3 was in agreement with that obtained with an ordinary radical initiator and also with the system of carbon tetrachloride and reduced nickel which was proved[3] to act as a free-radical initiator. In the higher concentration range of styrene, however, this curve was found to deviate from the ordinary radical curve to a higher side of styrene content in the copolymer. Since the reactivity of styrene toward a cation is higher

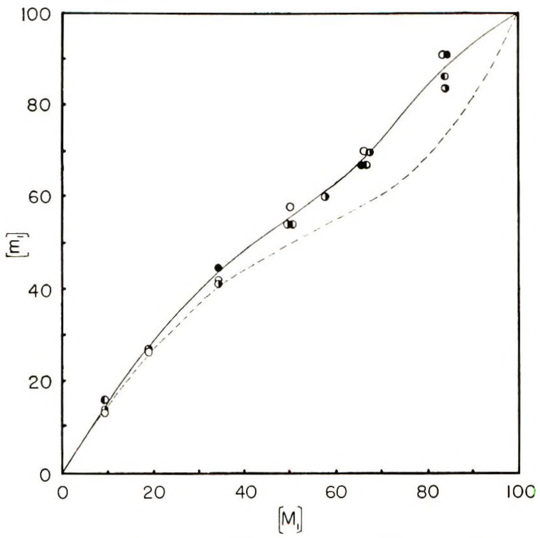

Fig. 3. Monomer–copolymer composition curves in the copolymerization of styrene (M_1) and methyl methacrylate (M_2) at 60°C. with various initiator systems: (○) $SiCl_4$–Ni; (◑) CH_3SiCl_3–Ni; (◐) $(CH_3)_2SiCl_2$–Ni; (●) $(CH_3)_3SiCl$–Ni; (- -) CCl_4–Ni. $[M_1 + M_2]$ = 50 vol-% in benzene; [chlorosilane] = 0.1 mole/l.; [Ni] = 0.4 g-atom/l.; in benzene; time, 4 hr.

than methyl methacrylate, it is impossible to neglect the participation of cationic propagation in the copolymerization with these systems.

The relationship between the polymer yield and the monomer composition is shown in Figure 4. The rate of polymerization of styrene abruptly decreased when a small amount of methyl methacrylate was present. Figure 5 also shows the relationship between the solution viscosity of the resulting copolymer and the feed monomer composition.

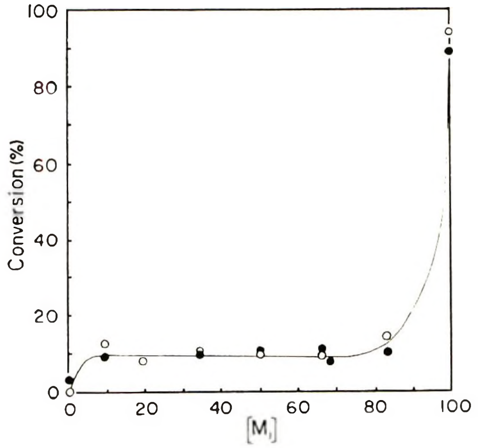

Fig. 4. Relationship between conversion and monomer composition in the copolymerization of styrene (M_1) and methyl methacrylate (M_2) at 60°C with various initiator systems: (○) $(CH_3)_2SiCl_2$–Ni; (●) CH_3SiCl_3–Ni. Conditions as for Fig. 3.

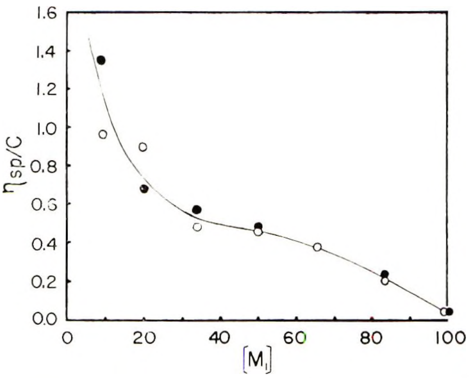

Fig. 5. Relationship between specific viscosity of the polymers obtained and monomer composition in the copolymerization of styrene (M_1) and methyl methacrylate (M_2) at 60°C: with various initiator systems: (○) $(CH_3)_2SiCl_2$–Ni; (●) CH_3SiCl_3–Ni. Conditions as for Fig. 3. Viscosity was determined in benzene at 30°C (c = 0.5 g/dl).

Polymerization of Isobutyl Vinyl Ether

Isobutyl vinyl ether was polymerized very rapidly with the systems of chlorosilanes and reduced nickel as is shown in Table III. In the absence of reduced nickel, the chlorosilanes used were ineffective for the initiation as in the cases mentioned above. No polymer was obtained with reduced nickel alone.

TABLE III
Polymerization of Isobutyl Vinyl Ether with the System of Chlorosilanes and Reduced Nickel in Benzene at Room Temperature[a]

Chlorosilane	Polymer yield, %[b]	η_{sp}/c[c]
$SiCl_4$	38.9	0.75
CH_3SiCl_3	34.5	0.84
$(CH_3)_2SiCl_2$	68.2	1.27
$(CH_3)_3SiCl$	76.7	—

[a] Time, 30 min; [M] = 3.8 mole/l.; [chlorosilane] = 0.1 mole/l.; [Ni] = 0.4 g-atom/l.; in benzene.

[b] No polymer was obtained with chlorosilanes or Ni alone.

[c] c = 0.5 g/dl in benzene at 30°C.

Since it is known that this monomer does not undergo radical polymerization, the results of Table III suggest that the polymerization proceeds via a cationic mechanism. The resulting polymers were found to have high molecular weights and to have atactic structure, from both their infrared spectra and their solubilities in methyl ethyl ketone.[7]

DISCUSSION

In the polymerization of methyl methacrylate with these systems (Table I), the order of initiating activity of chlorosilanes used was found to be as follows: $SiCl_4 > CH_3SiCl_3 > (CH_3)_2SiCl_2 \simeq (CH_3)_3SiCl \simeq 0$. This order agrees with that of chloromethanes in the systems of reduced nickel and chloromethanes as stated in the previous paper,[3] i.e., it is the same as the decreasing order in bond-dissociation energy of the carbon–chlorine bonds in the chloromethanes. This result was supported by the recent observation that the chain transfer reactivities of the methylchlorosilanes toward the polystyryl or poly(methyl methacrylate) radical were in the same order.[8] Accordingly, it is considered that the system of chlorosilanes and reduced nickel gives an initiating radical through one-electron transfer reaction, as pointed out in the system of chloromethanes and reduced nickel:[3]

$$\equiv\text{Si—Cl} + \text{Ni} \rightarrow \equiv\text{Si}\cdot + \text{Ni}^+ + \text{Cl}^- \qquad (1)$$

in which the resulting silyl radical induces the radical polymerization of methyl methacrylate, very likely as proved in the addition reaction of organosilyl hydrides to a carbon-carbon double bond.[9]

The evidence for the radical propagation was obtained from the following results: (*1*) the observed square root dependence of the concentration of methyltrichlorosilane on the rate of polymerization (Fig. 1); (*2*) the production of poly(methyl methacrylate) having the same tacticity as the ordinary radical polymer, and (*3*) the ordinary radical copolymer composition curve which was obtained in the copolymerization with styrene at the lower range of the styrene concentrations in the monomer mixture (Fig. 3).

When these systems were used as initiator for the styrene polymerization, however, the polymerization occurred readily to give a quite low molecular weight polymer, as shown in Table II. This result might suggest that the polymerization of styrene with these systems proceeded through a cationic mechanism. Such consideration might also make it possible to explain the results observed in the copolymerization with methyl methacrylate (Figs. 3–5), i.e., in the increased range of the styrene concentrations in the monomer mixture, fast cationic initiation and propagation predominate, but in the low styrene concentration range the contribution of radical species becomes important.

The ability of the cationic initiation with these systems is possible to confirm from the polymerization of isobutyl vinyl ether which polymerizes only by a cationic mechanism. From Table III, the cationic activity of these systems was observed to decrease as follows: $(CH_3)_3SiCl > (CH_3)_2SiCl_2 > CH_3SiCl_3 = SiCl_4$. This order is in reverse as compared with that in the methyl methacrylate polymerization, but it may agree with the increasing order of the polarization of the silicon–chlorine bonds in chlorosilanes used.

However, the existence of siliconium ion, i.e., S_N1 reaction of the silicon atom is not found in the nucleophilic substitution reaction of chlorosilanes.[10] Hence the production of the initiating cation in this case must be considered by the S_N2 type of reaction mechanism. A possible nucleophile is the monomer used and its reactivity toward cationic initiation has been known to facilitate as the electron density of its vinyl group increases.

The other possible nucleophile is a trace amount of water which is impossible to remove completely from the system, for example, the trace water produced during the activation treatment of reduced nickel with hydrogen. It was found that the chlorosilanes did not induce the cationic polymerization in the absence of reduced nickel under the present condition. Confirmation of whether which nucleophiles are the actual species for the initiation may be obtainable from endgroup analysis on silicon atom in the resulting polymer.

From the above considerations, we propose the mechanism shown in eqs. (2)–(4) for the selective initiation with these systems.

$$\equiv\mathrm{Si{-}Cl} + \mathrm{Ni} \rightleftharpoons [\underset{\mathrm{I}}{\equiv\mathrm{Si{:}ClNi}} \leftrightarrow \underset{\mathrm{II}}{\equiv\overset{+}{\mathrm{Si}}\overset{-}{\mathrm{Cl}}\mathrm{{:}Ni}} \leftrightarrow \underset{\mathrm{III}}{\equiv\mathrm{Si}\cdot\overset{-}{\mathrm{Cl}}{:}\overset{+}{\mathrm{Ni}}}] \qquad (2)$$

$$\mathrm{II} + \mathrm{M} \rightarrow \equiv\mathrm{SiM}^+ + (\mathrm{Cl} \rightarrow \mathrm{Ni})^-$$

or

$$\mathrm{II} + \mathrm{H_2O} \rightarrow \equiv\mathrm{SiOH} + \mathrm{H}^+ + (\mathrm{Cl} \rightarrow \mathrm{Ni})^- \qquad (3)$$

$$\mathrm{III} + \mathrm{M} \rightarrow \equiv\mathrm{SiM}\cdot + \mathrm{Ni}^+\mathrm{Cl}^- \qquad (4)$$

In this reaction scheme, structures I, II, and III show the transition state complex structure in the reaction of reduced nickel and chlorosilane, i.e., I is the structure close to the reactant system, II is that dissociated in the silicon–chlorine bond, and III is that after one electron transfer has occurred. The substituents of methyl and chlorine groups in the methylchlorosilanes may control the importance of the transition state structures between II and III to determine the observed activity order.

If the monomers which do not polymerize cationically such as methyl methacrylate are present, the production of initiating radical by the reaction between the structure III and the monomer may become a probable way. Such consideration is in agreement with the observed reactivity order of the chlorosilanes which corresponds to the decreasing order in bond-dissociation energy of their silicon–chlorine bonds.

On the other hand, in the case where the monomers are polymerized cationically, such as styrene and isobutyl vinyl ether, the reaction of the monomer or trace water with the transition state structure II may become important. The observed reactivity order mentioned above supports the possibility of such a mechanism.

In this reaction mechanism, however, the possibility for a rapid reaction of the growing cation with the chloride anion existed as a counter ion must be eliminated. We consider that the chloride anion is located near the growing cation, but stabilized as the result of adsorption at the surface of reduced nickel. Such a hypothesis is supported by our recent observations that the cationic polymerization of isobutyl vinyl ether with hydrogen chloride takes place to give a high polymer in the presence of some metals and metal oxides,[11] and that the *cis*-1,4 polymerization of butadiene is induced with these initiator systems.[12]

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Heterogeneous Copolymerization of Acrylamide with Maleic Acid in Dioxane

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Synopsis

Heterogeneous copolymerization of acrylamide with maleic acid has been investigated. The process was carried out at 70°C in 1,4-dioxane. The polarographic method of analysis was applied. The analysis of the experimental and theoretical composition distribution curves has shown an anomalously large composition polydispersion for the experimental distribution curves. This is attributed to the heterogeneity of the copolymerization process.

INTRODUCTION

A considerable increase of research on copolymerization introduces the problem of the proper theoretical explanation of the accumulating experimental data.[1-3] In many recent publications the authors when dealing with the data apply, as a rule, the formal procedure of determining the copolymerization constants r_A and r_B. Less common are the attempts to explain the obtained values of r_A and r_B with the help of the Alfrey and Price Q–e scheme. An increased number of available combinations of monomer pairs, the comparative simplicity of applying the Mayo-Lewis equation[4] to the data obtained, as well as the increasing number of copolymerization control methods may result in poorly compatible data in current investigations. In connection with this, poor agreement of r_A and r_B values established by different investigations for the same systems should be mentioned.[5] The exceeding of admissible error due to not taking into consideration "doubtful" experimental points is also hardly justifiable. A recent publication[6] stresses the danger of formal interpretation of anomalous systems with the help of the classical Mayo-Lewis equation. At the same time good prospects of investigating the heterogeneity of copolymer composition are emphasized. The latter provides for far more reliable information on the copolymerizing system as compared with the common procedure of analyzing the copolymer composition as a function of the substrate composition. It may be pointed out that in case of anomalous systems the information on the composition polydispersion becomes more important. Moreover, to judge the anomalies of the system, information on the composition distribution curves is indispensable.

This paper gives an analysis of the composition distribution curves for the anomalous system of acrylamide (AA)–maleic acid (MA). The anomalous character of copolymerization is caused by the heterogeneity of the copolymerization.

EXPERIMENTAL STUDIES AND RESULTS

Copolymerization was carried out in 5% solutions at 70°C in dioxane solvent with the use of α,α-azobisisobutyronitrile as initiator in an atmosphere of nitrogen. Samples were taken from the reaction vessel at given time intervals.[7] Vigorous stirring provided for uniformity of the composition of the sample as well as of the bulk mixture. The samples were analyzed for residual monomers by the polarographic method described previously.[8,9] In Figure 1 some polarograms obtained during the copolymerization process are shown. In Figure 2 calibration curves for acrylamide and maleic acid are given. Figure 3 shows an example of comonomer consumption curve for one composition of the substrate in the process of copolymerization. The kinetic curves were dealt with according to the procedure described in an earlier report[10,11] and this led to the integral curves of composition distribution (Fig. 4). In Figure 4, X_i is the integral

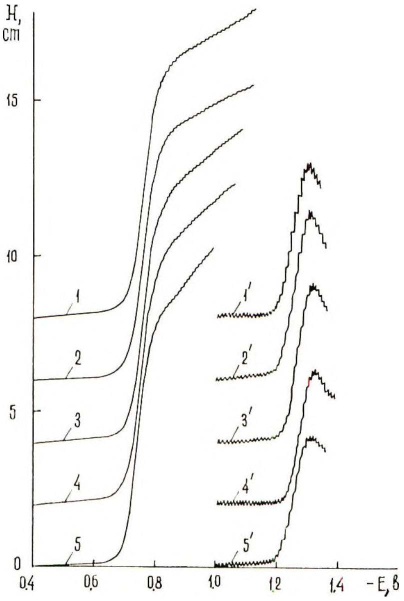

Fig. 1. Polarograms of maleic acid (MK) (integral curves *1–5*) and acrylamide (AA) (differential curves *1'–5'*) recorded in the process of copolymerization: (*1, 1'*) stock monomer mixture with $m_1 = 0.0158$ g; (*2, 2'*) in 12 min, with $m_2 = 0.0167$ g; (*3, 3'*) in 40 min, with $m_3 = 0.0174$ g; (*4, 4'*) in 110 min, with $m_4 = 0.0175$ g; (*5, 5'*) in 170 min, with $m_5 = 0.0179$ g. Polarograms *1–5* were recorded at sensitivity 6×10^{-8} A/mm, and polarograms *1'–5'* at sensitivity 3×10^{-8} A/mm. The composition of the initial substance was 4:6 (AA–MK). The initiator concentration was 0.2 wt-%.

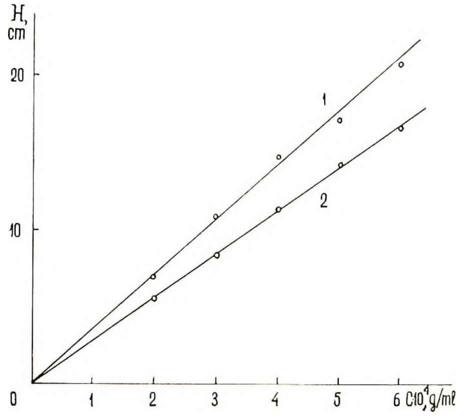

Fig. 2. Calibrated curves for determining (*1*) AA and (*2*) MK (4:6): (*1*) against derivative polarograms at sensitivity 3 × 10^{-8} A/mm; (*2*) against ordinary polarograms at sensitivity 5 × 10^{-7} A/mm.

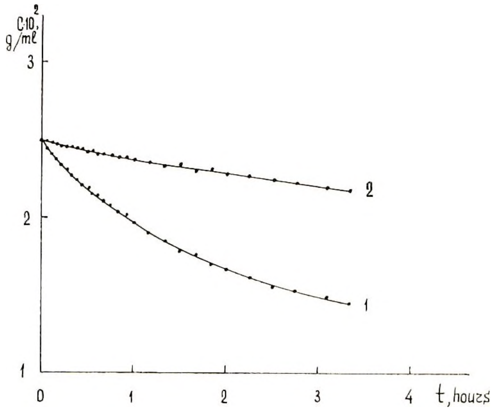

Fig. 3. Monomer flow curves in the process of copolymerization of (*1*) AA with (*2*) MK (1:1). Initiator concentration, 0.2 wt-%.

weight part of the *i*th fraction, γ is the weight content of maleic acid in copolymer, and ψ is the conversion (by weight). Figure 5 gives differential curves of composition distribution for the studied copolymer systems.

DISCUSSION

Papers limited to a study of copolymerization in heterogeneous media are few in number. Some earlier publications[12,13] should be mentioned. We shall discuss, however, only two recent publications[14,15] in which the experiments were carried out in a most thorough way. The aim of the above papers was to establish a correlation between the compositions of copolymer and of substrate for the case of radical copolymerization of acrylonitrile with acrylate, the objective being to find a dependence between

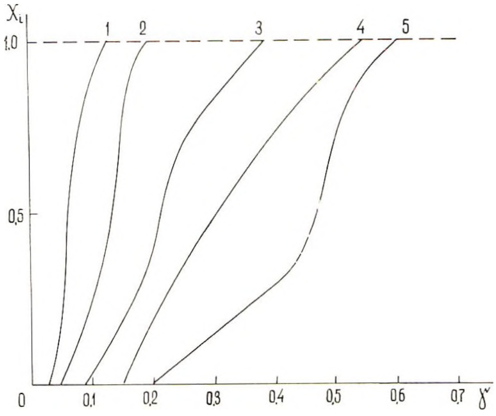

Fig. 4. Integral composition distribution curves, according to the experimental data at various initial compositions: (*1*) AA:MK = 9:1, ψ = 0.69; (*2*) AA:MK = 4:1, ψ = 0.37; (*3*) AA:MK = 5:5, ψ = 0.39; (*4*) AA:MK = 2:3, ψ = 0.37; (*5*) AA:MK = 3:7, ψ = 0.34. ψ denotes conversion per acrylamide.

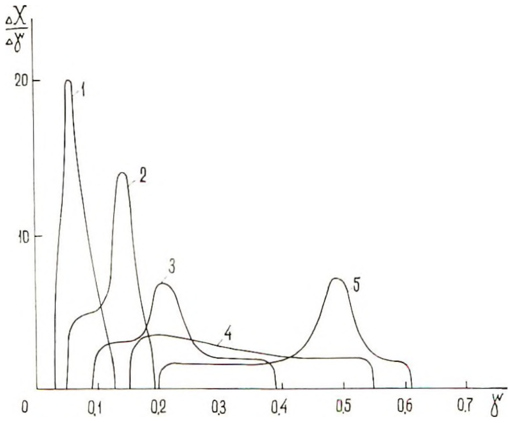

Fig. 5. Differential composition distribution curves, according to the experimental data at various initial AA:MK compositions: (*1*) 9:1; (*2*) 4:10 (*3*) 5:5; (*4*) 2:3; (*5*) 3:7.

the kind of copolymerization (emulsion, suspension, homogeneous) and the relative reactivity of comonomers in copolymerization. The papers simply postulate the applicability of Mayo-Lewis equations to heterogeneous copolymerization. Some investigators[3,4,16] think however, that this approach lacks validity. In the present study we show that it is justified only for some particular cases of heterogeneous copolymerization.

We consider a model of copolymerization in which the system is homogeneous at the initial moment of the process and on attaining a certain critical degree of copolymerization N_{cr}, the macroradicals coagulate to form a heterogeneous stage. Let C_A, C_B and C_A', C_B' be volume-weight concentrations of monomers A and B in solutions and suspension, respectively.

If N is the mean degree of polymerization of the copolymer macromolecules and $N > N_{cr}$, the composition of the substrate in solution will differ, in general, from that of the microsubstrate in suspension, i.e.,

$$\beta_A = \frac{C_A}{C_A + C_B} \neq \beta_A{}' = \frac{C_A{}'}{C_A{}' + C_B{}'} \tag{1}$$

It follows that the macroscopic mean value

$$\beta_A{}'' = \frac{C_A + C_A{}'}{C_A + C_B + C_A{}' + C_B{}'} \tag{2}$$

used by an investigator cannot account for the whole of the copolymerization process in a heterogeneous system, because copolymerization develops as if two systems having different compositions of the substrate were involved.

It should be pointed out that at low degrees of conversion,

$$\beta_A{}'' \cong \beta_A \tag{3}$$

Furthermore, particular cases of

$$\beta_A \cong \beta_A{}' \cong \beta_A{}'' \tag{4}$$

are possible, where one should not expect a considerable complication of copolymerization due to heterogeneity in the system. This probably, was the case in the studies of Brandrup[14] and Izumi and Kitagawa.[15] Nevertheless, complications are possible, even if eq. (4) is fulfilled, due to the difference in values of diffusion ratios for comonomers in suspension and in solution.[6]

In actual systems there is a number of reasons for considerable complications in the scheme. We shall mention only a few: (*1*) continuous change of β_A, $\beta_A{}'$, $\beta_A{}''$ parallel to the increase of ψ in the system; (*2*) the presence of molecular weight polydispersion in the system; (*3*) the presence of nonpolymerized monomer units in the "dead" suspension particles; (*4*) the presence of side reactions.

Nevertheless, the general case is

$$\beta_A{}' \neq \beta_A \neq \beta_A{}'' \tag{5}$$

and the formal dependence between γ and β does not lead to strict judgment about relative reactivity ratios for the comonomers in heterogeneous copolymerization process. In order to confirm the statement, let us turn to the integral curves of composition distribution (Fig. 4). It is natural that the $C_A(t)$ and $C_B(t)$ relation (see Fig. 3) absorb all the anomalies of heterogeneous copolymerization process. The two-stage nature of radical copolymerization causes anomalies to appear on changing the monomer concentration during the process. This accounts for anomalous widening of the composition distribution curves (Figs. 4 and 5). It may be shown that for the acrylamide–maleic acid system the experimental curves of composition distribution differ considerably from the theoretical ones. The theoretical curves have been calculated in accordance with a modified method of Skeist for weight concentrations,[6,9] r_A and r_B being varied within reasonable limits $1 \leq r_A \leq 3$, $0 \leq r_B \leq 0.2$.

This is illustrated by Figures 6 and 7, which give the curves calculated for a model with $r_A = 2.2$ and $r_B = 0$. In analyzing the curves it is essential to take into consideration not only the position and form of the curves (especially helpful is comparison of the differential curves in Figs. 5 and 7), but also their width which characterizes composition polydispersion.

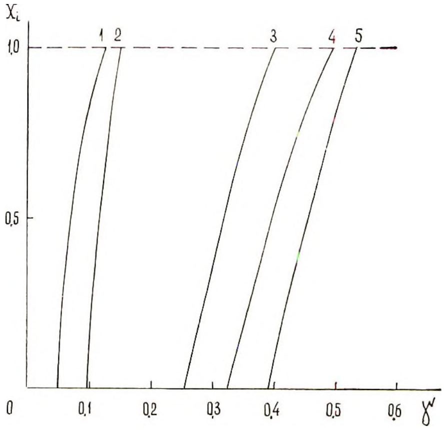

Fig. 6. Integral composition distribution curves, according to Skeist, (for weight concentrations) for $\Delta\psi = 0.01$ and $r_A = 2.2$; $r_B = 0$ at various initial compositions: (*1*) AA:MK = 9:1, $\psi = 0.69$; (*2*) AA:MK = 4:1, $\psi = 0.37$, (*3*) AA:MK = 5:5, $\psi = 0.39$; (*4*) AA:MK = 2:3, $\psi = 0.37$; (*5*) AA:MK = 3:7, $\psi = 0.34$.

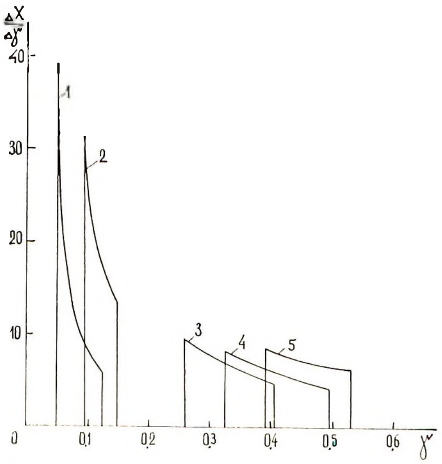

Fig. 7. Theoretical differential composition distribution curves at various initial compositions: (*1*) AA:MK = 9:1; (*2*) AA:MK = 4:1; (*3*) AA:MK = 5:5; (*4*) AA:MK = 2:3; (*5*) AA:MK = 3:7.

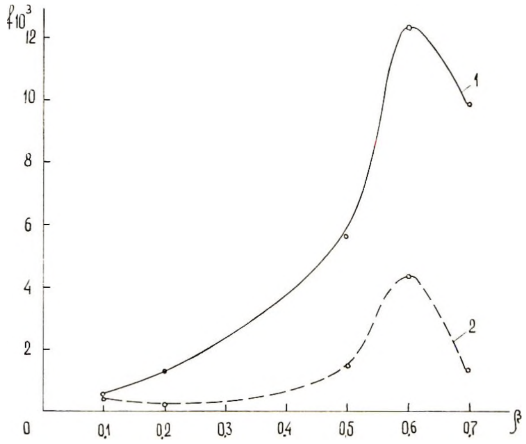

Fig. 8. Dependence f of the initial composition β; (*1*) experimental; (*2*) theoretical.

Comparison of the curves in Figures 4 and 5 and 6 and 7 shows that the experimental curves are characterized by a greater polydispersion than the corresponding theoretical curves. Thus, composition distribution curves are most indicative of heterogeneity in the system.

There are good grounds to believe that the anomalous widening of the composition distribution curves in heterogeneous copolymerization may be detected by means of preparative fractionation. Furthermore we must note that a clear S-shaped curve should not be expected of the experimental integral curves of composition distribution, since the stages in heterogeneous systems are continuously interacting. In order to illustrate the above statements, we give in Figure 8 the values of quantitative estimation of the composition distribution $f = f(\beta)$:[6]

$$f = (\bar{\alpha}_z - \bar{\alpha}_B)\bar{\alpha}_B = \left(\sum_{i=1}^{k} W_i\gamma_i^2 \Big/ \sum_{i=1}^{k} W_i\gamma_i - \sum_{i=1}^{k} W_i\gamma_i\right) \sum_{i=1}^{k} W_i\gamma_i \quad (6)$$

where W_i is the weight portion of the fractions with composition γ_i. From Figure 8 it is seen that $f_{\text{expl}} > f_{\text{theor}}$ for all $\beta/_{t=0}$. The qualitative estimation of the above may be made by comparing the curves in Figures 4 and 6.

It must be pointed out that the anomalous widening of the composition distribution curves cannot be accounted for by the influence of the penultimate and farther links on the comonomer reactivity[17,18] or realization in the system of a chain scission reaction.[19,20] The effect is too great to account for "instantaneous" composition heterogeneity as well,[3] since the obtained copolymers were of sufficiently high molecular weight.

SUMMARY

On the basis of calculations from the kinetic data, curves of composition distribution for acrylamide–maleic acid copolymers have been plotted. The copolymerization process is heterogeneous. From the analysis of the

theoretical and experimental composition distribution curves, an "anomalous" widening of the experimental curves has been established. It has been related to the heterogeneity of the copolymerization.

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Copolymerization of Trialkylvinylgermane

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Synopsis

The polymerization of trimethylvinylgermane (TMGeV) with the use of γ-ray, radical, and ionic initiator was attempted, but homopolymer was not obtained. This monomer did not undergo polymerization by itself, but polymerized with high concentration of *n*-BuLi. Copolymerization of TMGeV with styrene (St) and methyl methacrylate (MMA) was carried out by using radical initiator. From the results obtained by the copolymerization, monomer reactivity ratios and Q–e values were obtained as follows: for the system St(M_1)–TMGeV (M_2), $r_1 = 24.4$, $r_2 = 0.009$, $Q_2 = 0.0049$, $e_2 = 0.43$; for the system MMA (M_1)–TMGeV (M_2), $r_1 = 19.98$, $r_2 = 0.05$; $Q_2 = 0.037$, $e_2 = 0.43$., The polymerizability of TMGeV is discussed on the basis of the Q and e values obtained.

INTRODUCTION

Recently, a number of studies for the polymerization of vinylmetal, allylmetal, and styrylmetal, have been reported.[1–5] The majority of the works[1,2,4] dealt with silicon as the metal in the vinylmetal compound. In some studies, germanium[3,5] and tin[3,6] have been used. Korshak and coworkers[3] carried out the polymerization of trialkylvinyltin under a pressure of 600 atm at 120°C for 6 hr, and obtained an oily colorless product which was found to be the trimer.

In a previous study,[6] homopolymerization and copolymerization of timethylvinyltin and tributylvinyltin were carried out, and the Q and e values from results of copolymerization were reported. In this work the synthesis, homopolymerization, and copolymerization of trimethylvinylgermane (TMGeV) were carried out, and the monomer reactivity ratios obtained for radical copolymerization of TMGeV with styrene and methyl methacrylate were: St(M_1)–TMGeV(M_2), $r_1 = 24.4$, $r_2 = 0.009$; MMA(M_1)–TMGeV(M_2), $r_1 = 19.98$, $r_2 = 0.05$, respectively. Moreover, the polymerizability of this monomer was discussed.

EXPERIMENTAL

Synthesis of Trialkylvinylgermane

TMGeV was prepared by a Grignard method[7] according to the reactions (1)–(5).

$$CH_3Br + Mg \rightarrow CH_3MgBr \tag{1}$$

$$4CH_3MgBr + GeCl_4 \rightarrow (CH_3)_4Ge + 2MgBr_2 + 2MgCl_2 \tag{2}$$

$$3(CH_3)_4Ge + GeCl_4 \rightarrow 4(CH_3)_3GeCl \tag{3}$$

$$CH_2{=}CHCl + Mg \rightarrow CH_2{=}CHMgCl \tag{4}$$

$$CH_2{=}CHMgCl + (CH_3)_3GeCl \rightarrow CH_2{=}CHGe(CH_3)_3 + MgCl_2 \tag{5}$$

Methyl magnesium bromide was prepared by passing methyl bromide into tetrahydrofuran containing 110 g (4.53 mole) of magnesium ribbon. Then, 203 g (0.93 mole) of tetrachlorogermane (IV) was added dropwise to the Grignard solution. The reaction mixture was reflexed for 10 hr and was permitted to stand for 24 hr in ice water. Tetramethylgermane was obtained by distillation on a steam bath, the fraction boiling in the range 41–45°C (lit. bp 43.5°C) was collected; 76 g of tetramethylgermane was obtained (61.4% yield). Trimethylchlorogermane was prepared with 50 g (0.25 mole) of tetrachlorogermane and 100 g (0.76 mole) of tetramethylgermane in an autoclave at 220°C for 24 hr in the presence of 9.5 g (0.07 mole) of trichloroaluminum as a catalyst. The reaction mixture was distilled in the range 97–99°C (lit. bp, 98°C); the yield of trimethylchlorogermane was 87 g (58%). Vinylmagnesium chloride was prepared from vinyl chloride and 31.3 g (1.29 mole) of magnesium ribbon (31.3 g, 1.29 mole) in diethylene glycol dimethyl ether. After the end of the Grignard reaction, TMGeV was obtained by dropwise addition of trimethylchlorogermane (67 g, 0.46 mole) dissolved in 100 ml of monoglyme, refluxing of the reaction mixture for 5 hr, and standing for 24 hr. TMGeV was distilled at 67–72°C. The yield was 100 g (61.5%).

Other Materials

Styrene and methyl methacrylate used as comonomers were purified by conventional methods.

Azobisisobutyronitrile (AIBN) used as a initiator was recrystallized from ethanol.

Boron trifluoride–diethyl etherate was distilled before use. A hexane solution of *n*-BuLi was supplied commercially and its concentration was determined by usual double titration method of Gilman and Haubein.[16] Benzene was distilled before use.

Polymerization

Homopolymerization was carried out by using γ-irradiation from a ^{60}Co source or radical or ionic initiation in sealed ampoules containing 5 ml of monomer.

Copolymerization was carried out in sealed ampoules of 20 ml capacity. The required amounts of both monomers, initiator (AIBN), and solvent (benzene) were placed in the ampoule, and the ampoule was sealed off. The copolymerization was carried out in a constant temperature bath (50 ± 0.01°C). After 10% conversion had been reached, the contents of the ampoule were poured into a large amount of methanol to precipitate the product. The precipitate was washed thoroughly, filtered off, dried under vacuum at room temperature, and weighed. The composition of the copolymer was determined by elementary analysis for C and H.

Viscosity Measurement

Viscosity of the copolymer was measured in benzene solution at 30°C by using an Ubbelohde viscometer.

Infrared Spectra

Infrared spectra of the products were measured with a Perkin-Elmer 337 instrument.

Molecular Weight

The molecular weight of the polymer was measured in benzene solution at 60°C by using a Knauer vapor pressure osmometer.

RESULTS AND DISCUSSION

Homopolymerization

The results of the homopolymerization of TMGeV with γ-ray, radical, and ionic initiations are summarized in Table I. This monomer could not be homopolymerized under the experimental condition, but as shown in Table I, in case of the high concentration of *n*-BuLi (20% based on monomer TMGeV), this monomer could be homopolymerized to an oily colorless product which was found to have $[\eta] = 0.008$ and a molecular weight of 1298. The infrared spectrum of the polymer obtained is shown in Figure 1.

TABLE I
Homopolymerization of TMGeV

Initiator	Temp, °C	Time, hr.	Catalyst concn, mole/l.	Polymer formed
BPO	80	200	5×10^{-2}	None
AIBN	80	200	"	None
$BF_3 \cdot O(C_2H_5)_2$	−78 to 0	200	"	None
BuLi	−78 to 0	300	"	None
BuLi	Room Temp.	360	0.5	Present ($\bar{P}_n = 9$)
γ-rays[a]	Room Temp.	50	—	None

[a] Co^{60} source, 3×10^4 r/hr.

ANAL Calcd: for polyTMGeV: C, 41.49%; H, 8.29%. Found: C, 42.35%, H, 8.42%.

From these results, the oily colorless product was confirmed to be the oligomer of TMGeV having $P_n = 8.97$.

The difference in the reaction between the low and high concentration of BuLi is not yet known with certainty.

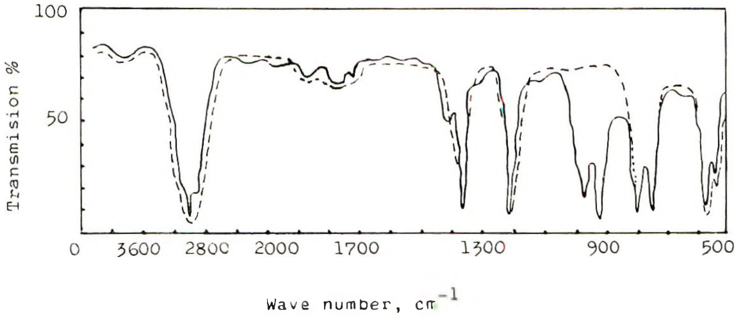

Fig. 1. Infrared spectra of TMGeV monomer and homopolymer: (——) monomer; (- - -) polymer ($P_n = 10.5$) obtained at high *n*-BuLi concentration.

Copolymerization

The results obtained by the copolymerization of the St–TMGeV and MMA-TMGeV systems are shown in Tables II and III. The effects of monomer composition on rate of copolymerization R_p are shown in Figure 2. From Figure 2, it was found that the rate of copolymerization decreased with increasing molar ratio of the vinylgermane compound to the comonomer for all systems. The viscosities of the polymers obtained are shown in Table II and III. The intrinsic viscosity also decreased with increasing molar ratio of the vinylgermane compound to comonomer. For the case viscosity $[\eta] = 0.13$, if the polymer consisted of only polystyrene, $\bar{P}_n$ of this polymer would be 106 from the viscosity equation ($\log \bar{P}_n = 3.248 + 1.4 \log [\eta]$) for polystyrene.[8] The ratio of St to TMGeV in the copolymer, M_1/M_2 was 10. Therefore, the results suggested that the copolymer having $\bar{P}_n = 106$ contained about ten units of TMGeV. Similarly, in the case of experiment S-6, where $[\eta] = 0.57$ ($\bar{P}_n = 848$ for polystyrene) $M_1/M_2 = 86$. The copolymer chain having $\bar{P}_n = 848$ would thus contain about 10 TMGeV units. The copolymerization for all the systems followed almost the same trend, as shown in Figures 3 and 4. The copolymerization composition curves were obtained from the results shown in Tables II and III.

According to the Fineman-Ross method[9] and the curve-fitting method, the monomer reactivity ratios (r_1 and r_2) were calculated for these copolymerization systems (see Figs. 3 and 4). The results are summarized in Table IV. From the r_1 and r_2 values, Q and e values for the monomer was calculated by assuming the values $Q_1 = 1.0$, $e_1 = 0.80$ for St and $Q_1 = 0.74$, $e_1 = 0.40$ for MMA. These results indicate that r_1 values were very

TABLE II

Copolymerization of St–TMGeV System in Benzene at 50°C, [AIBN] = 5 × 10^{-2} mole/l.

	Monomer feed								
Expt.	TMGeV, g	St, g	TMGeV in comonomer, mole-%	Time, hr	Conversion, wt-%	R_p, wt-%/hr	C, %[a]	TMGeV in copolymer, mole-%	[η], dl/g
S-1	6.18	0	100	100	0	0			
S-2	4.99	0.81	80	60	4.23	0.05	86.12	8.86	0.13
S-3	3.69	1.81	60	19	4.63	0.21	88.47	5.32	0.28
S-4	3.09	2.26	50	15	5.44	0.34	89.12	4.36	0.36
S-5	2.49	2.72	40	11	5.18	0.45	90.20	2.78	0.42
S-6	1.20	3.53	20	7	5.18	0.69	91.38	1.07	0.57
S-7	0	4.43	0	3	5.26	1.05	91.87	0	—

[a] Results of elementary analysis for C. The copolymer composition was calculated from these C values.

TABLE III

Copolymerization of MMA–TMGeV System in Benzene at 50°C, [AIBN] = 5 × 10^{-2} mole/l.

	Monomer feed								
Expt.	TMGeV, g	MMA, g	TMGeV in comonomer, mole-%	Time, hr	Conversion, wt-%	R_p wt-%/he	C, %[a]	TMGeV in Copolymer mole-%	[η] dl/g
M-1	4.99	0	100	100	0	0			
M-2	4.99	0.84	80	46	27.5	0.59	55.58	17.64	0.16
M-3	3.69	1.68	60	12.5	6.18	0.49	58.58	5.22	0.18
M-4	3.09	2.11	50	5.5	14.10	2.64	58.89	4.32	0.25
M-5	2.49	2.53	40	4	16.64	4.16	58.92	3.89	0.28
M-6	1.20	3.37	20	1.5	5.93	4.56	59.22	2.74	0.45
M-7	0	4.31	0	1	4.85	4.85		0	—

[a] Results of elementary analysis for C. The copolymer composition was calculated from these C values.

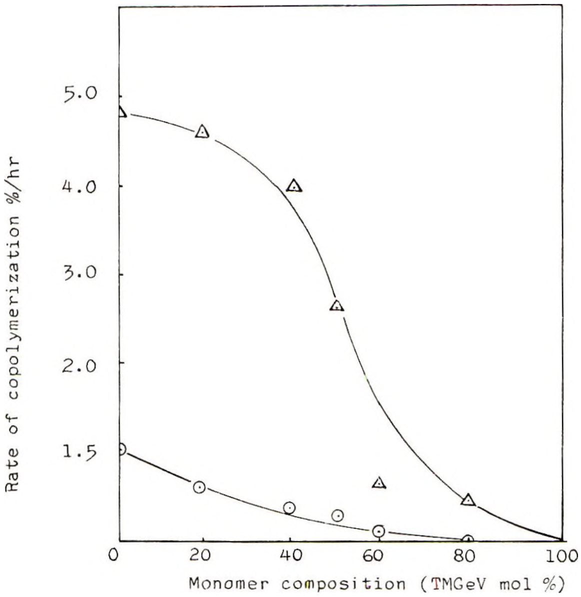

Fig. 2. Relationship between the rate of copolymerization and monomer feed composition: (○) St–TMGeV system; (△) MMA–TMGeV system.

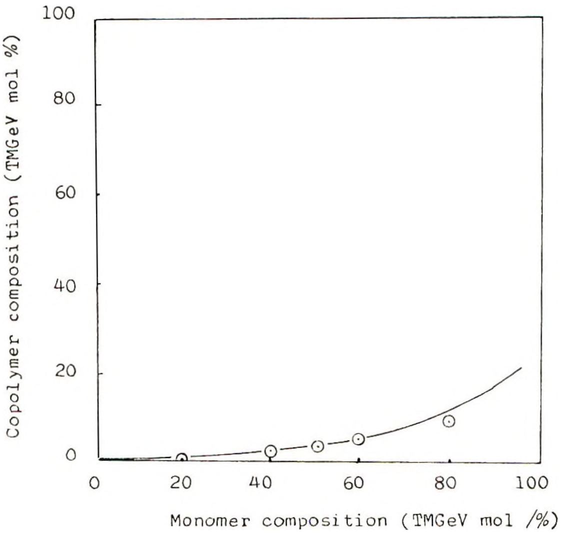

Fig. 3. Composition curve for St(M_1)–TMGeV copolymer: (○) experimental results; (—) theoretical curve for r_1 = 24.4, r_2 = 0.009.

much greater than r_2 values in all systems. Therefore, the rate of addition of styrene and methyl methacrylate monomer to its own radical was greater than that of the organogermanium compound (TMGeV) monomer unit to its own radical.

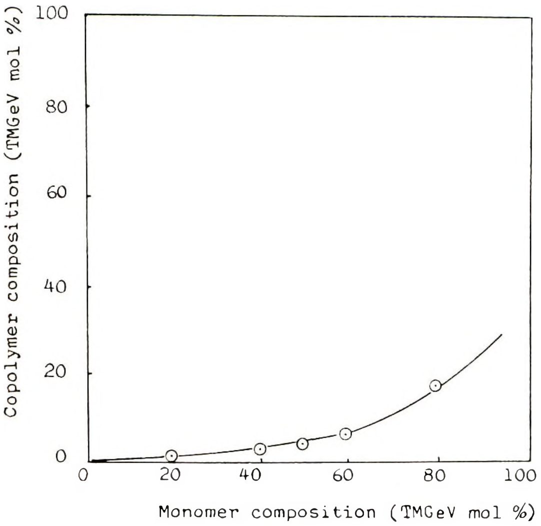

Fig. 4. Composition curve of MMA (M_1)–TMGeV copolymer: (○) experimental results; (——) theoretical curve for $r_1 = 19.98$, $r_2 = 0.05$.

TABLE IV

Q_2–e_2 Value of TMGeV

M_1	M_2	r_1	r_2	Q_2	e_2
St	TMGeV	24.4	0.009	0.0049	0.43
MMA	TMGeV	19.98	0.05	0.037	0.43

TABLE V

Q–e Values and Hammett Constants for $CH_2{=}CHR$

R in $CH_2{=}CHR$	e	Q	Hammett constant σ_p		Reference
$C(CH_3)_3$	−0.63	0.007[a]	−0.197	±0.02	11
$Si(CH_3)_3$	−0.14	0.035[a]	−0.07	±0.1	1,12
	−0.10	0.031[b]			1,12
$Ge(CH_3)_3$	+0.431	0.005[a]	0.0	±0.1	This paper
	+0.430	0.037[b]			
$Sn(CH_3)_3$	+0.962	0.005[a]	0.0	±0.1	6
	+0.933	0.036[b]			6

[a] Copolymerization with styrene.

[b] Copolymerization with methyl methacrylate.

The Q–e values for *tert*-butylethylene,[10] trimethylvinylsilane,[10] and trimethylvinyltin[6] having structures similar to TMGeV are listed in Table V for comparison with those of TMGeV. The second column in Table V shows that the e value changes from negative to positive as the atomic number in Group IV in the periodic table increases. This phenomenon may be explained as follows. The bond orbitals of carbon and silicon have $2s$, $2p$ and $3s$, $3p$, respectively, while these of germane and tin have $4s$, $4p$ and $5s$, $5p$ with larger orbital radius than those of $2s$, $2p$ and $3s$, $3p$. Generally, in the case of silicon, germanium, and tin, there is a contribution of the *d* orbital to bonding. Consequently, the mesomeric effect increases in the order, C < Si < Ge < Sn.

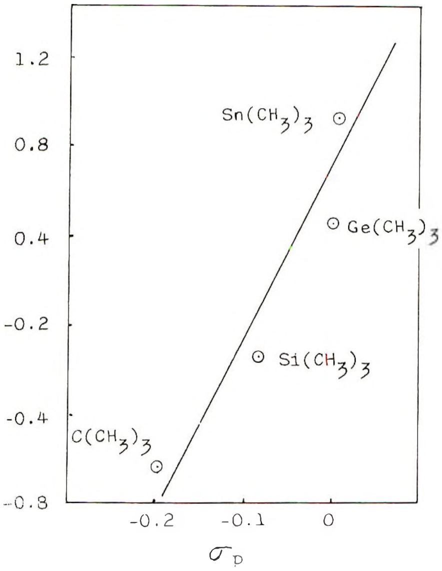

Fig. 5. Relationship between *e* values and σ_p constants for $CH_2{=}CHC(CH_3)_3$, $CH_2{=}CHSi(CH_3)_3$, $CH_2{=}CHGe(CH_3)_3$, and $CH_2{=}CHSn(CH_3)_3$.

In general, both the *e* value and the Hammett constant σ_p are terms which are related to the polarity. Furukawa and Tsuruta[13] and Price[14] have found a linear relationship between them. In order to check this point, *e* was plotted against the Hammett constant (σ_p).[15] The results are shown in Figure 5. An approximately linear relationship was observed between, σp and *e*, and the *e* value of TMGeV obtained in this work is therefore thought to be appropriate.

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Decomposition of Peroxycarbamates and their Initiation of Vinyl Polymerization

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Synopsis

A review is given of the synthesis, physical properties, and decomposition kinetics of organic peroxycarbamates. The activity of these compounds in initiating free-radical vinyl polymerization is discussed. The decomposition of hexamethylene N,N'-bis-(α-cumyl peroxycarbamate) has been measured in different solvents between 65 and 95°C and found to be a first-order reaction governed by the specific rate constant $k_d = 2.21 \times 10^{16} \exp \{-34\,100/RT\}$. The initiator exhibits normal free-radical polymerization kinetics and in polymerization of styrene at 80°C shows an initiating efficiency of 0.53. Cobalt naphthenate can act as both accelerator and retarder of styrene polymerization, depending upon its concentration and the temperature of the polymerization.

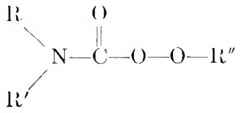
INTRODUCTION

There are many examples of the synthesis and thermal decomposition of peroxycarbamates. Several of these peroxycarbamates have been used as free-radical initiators of vinyl polymerization. This publication combines a review of the literature on the subject with a report on some new decomposition kinetics of hexamethylene N,N'-bis(α-cumyl peroxy-carbamate) and its initiation of styrene and methyl methacrylate polymerization.

Peroxycarbamates

Kinetic studies of radical-initiated vinyl polymerization have been devoted mainly to symmetrical peroxides and azo compounds. Among unsymmetrical compounds capable of initiating vinyl polymerization alkyl perbenzoates[1] and alkyl and aryl hydroperoxides[2,3] have been examined. In this review peroxycarbamates are considered in terms of their preparation, stability and initiation of vinyl polymerization.

Organic peroxycarbamates are esters derived from the unknown peroxycarbamic acids and may be represented by the general formula:



$$\mathrm{RR'N{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}O{-}R''}$$

The first report of such compounds were given by Davies and Hunter,[4] who synthesized *tert*-butyl peroxycarbamate and four of its *N*-monosubstituted derivatives [phenyl, α-naphthyl, *p*-xenyl, (−)-methyl] by three methods: (a) RNCO + t-C_4H_9OOH with pyridine as catalyst; (b) RNHCOCl + t-C_4H_9OOH with pyridine as acid acceptor; (c) RNH_2 + t-$C_4H_9OOCOCl$.

Additional peroxycarbamates synthesized by applications of these methods are shown in Table I together with related physical properties and decomposition data. Expressions for the rate constants (k_d) of ring-substituted *tert*-butyl *N*-phenyl-substituted peroxycarbamates were calculated from the data of Mesrobian and co-workers[7] by the method of least squares.

The peroxycarbamates, especially the liquid ones, possess a characteristic odor which is a disagreeable combination of the odors of peroxides and amines. They are colorless unless they contain a chromophoric group and liberate iodine quantitatively from acidified potassium iodide.

Peroxycarbamates are relatively unstable to heat and most decompose rapidly in the range 80–140°C yielding carbon dioxide as a major product. Examination of Table I shows that α-cumyl *N*-substituted peroxycarbamates are less stable than the corresponding *tert*-butyl derivatives.

The nature and rate of decomposition of peroxycarbamates can vary markedly with structure and changes in external environment. For example thermal decomposition of crystalline *tert*-butyl *N*-methyl-*N*-*p*-nitrophenyl peroxycarbamate at room temperature proceeds by a combination of a nonradical intramolecular concerted reaction involving a six-membered transition state and a homolytic scission of the O-O bond.[10] In cumene solution, however, it is probable that the decomposition is solely by homolysis, as the configuration favorable for the concerted reaction is less readily attained. The greater stability of crystalline *tert*-butyl *N*-*p*-nitrophenyl, *tert*-butyl *N*-ethyl, and hexamethylene *N*,*N′*-bis(*tert*-butyl) peroxycarbamates is attributed to their inability to form the six-membered transition state and also to the possibility of intermolecular hydrogen bonding between the hydrogen atom linked to the nitrogen and the carbonyl oxygen atom. It is suggested that the stability of *tert*-butyl *N*,*N*-dimethyl peroxycarbamate is associated with its higher electron density on the nitrogen atom attached to two methyl groups and to its liquid state which diminishes the tendency for a concerted reaction.

Thermal decomposition of ring-substituted *tert*-butyl *N*-phenyl peroxycarbamates in solution has been followed by iodometric titration and shown to be first order.[7] Rate constants increase with the electron releasing power of the substituents according to the Hammett σ–ρ relationship.[11] It is observed from Table I that both the energy of activation and the frequency factor are in general affected in a systematic manner by the substituents such that higher activation energies correlate with higher frequency factors. The Hammett equation is exact only for those series of reactions for which potential energy terms alone are affected by the change of substituents.[12] This requires that the frequency factor of the rate constants be the same for all members of the series and hence the Hammett equation is only approximate for peroxycarbamates. This behavior is also observed for substituted benzoyl peroxides[12] and substituted *tert*-butyl perbenzoates[1,13-15]

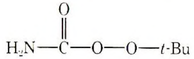
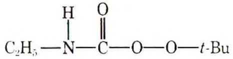
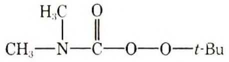
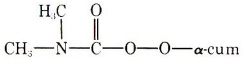
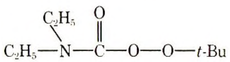
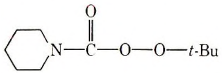
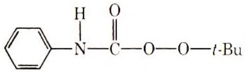
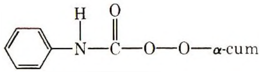
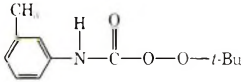
The *tert*-butyl *N*-α-naphthyl peroxycarbamate exhibits induced decomposition. The decrease in stability in the series *tert*-butyl *N*-ethyl peroxycarbamate, *tert*-butyl *N*-phenyl peroxycarbamate, and *tert*-butyl *N*-α-naphthyl peroxycarbamate suggests that resonance stabilization of the amino radical formed in the decomposition process may be an important factor in governing the rate of decomposition of the peroxycarbamates.[7] This idea differs from conclusions deduced from the decomposition of phenyl substituted benzoyl peroxides where the stability of the radicals formed after cleavage is not an important factor in determining the rate of spontaneous cleavage. In this latter case inductive effects have been invoked to explain the change in rate of decomposition.[16]

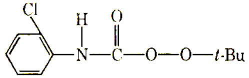
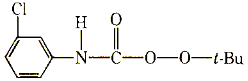
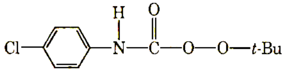
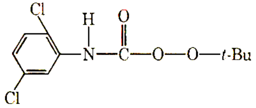
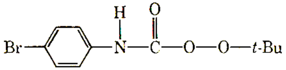
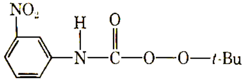
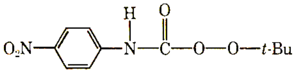
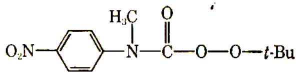
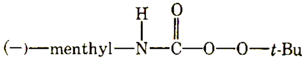
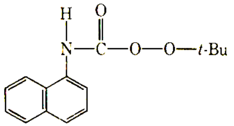
Thermal decomposition of peroxycarbamates can be utilized to initiate vinyl polymerization. The similar rates of bulk polymerization of styrene at 30°C by equimolar quantities of *tert*-butyl *N*-*p*-nitrophenyl peroxycarbamate and *tert*-butyl *N*-methyl *N*-*p*-nitrophenyl peroxycarbamate indicated to Pedersen[10] that the *N*-disubstituted derivative is an effective radical initiator and does not undergo the concerted decomposition reaction in styrene but homolytically decomposes at the 0-0 bond. In addition, *tert*-butyl *N*-*p*-nitrophenyl peroxycarbamate decomposes much faster in styrene solution than would be expected from the relative stability of the crystalline compound and cumeme solution. Both compounds may also undergo induced decomposition by the growing styryl radical.

Mesrobian and co-workers[6] have shown that *tert*-butyl and α-cumyl *N*-phenyl peroxycarbamates exhibit normal free-radical polymerization kinetics in styrene with rate of polymerization proportional to the first power of monomer concentration and to the half power of initiator concentration. In both cases transfer to initiator is negligible at lower initiator concentration. Initiating efficiencies of 0.95 and 0.73, respectively, demonstrate that the radicals formed from *tert*-butyl *N*-phenyl peroxycarbamate efficiently initiate chains while the radicals from the α-cumyl derivative are less efficient. The *tert*-butyl *N*-α-naphthyl peroxycarbamate, however, exhibits induced decomposition and consequently a strong dependence of initiating efficiency with initiator concentration.

The decomposition products of peroxycarbamates in solution appear to be carbon dioxide, an imino radical, and an alkoxy or aralkoxy radical. This is supported by the evidence of hydrazo and azo compound formation in decomposition studies.[6] The absence of a carbonyl absorption in the infrared spectrum of polystyrene initiated by *tert*-butyl *N*-phenyl peroxycarbamate indicates that carbon dioxide in lost simultaneously with the peroxide cleavage or that decarboxylation of the carbamate free radical is more rapid than addition to styrene. These observations suggest that the

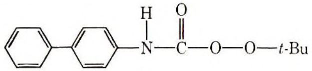
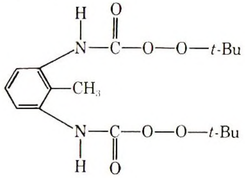
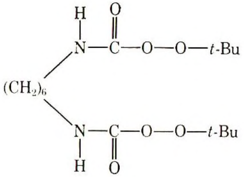
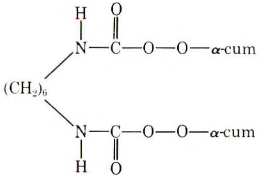
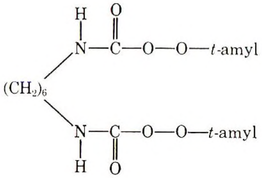
TABLE I
Properties of Organic Peroxycarbamates

Peroxy-carbamate	Formula	Yield, %	Mp, °C	Stability		First-order decomposition kinetics	Reference
				Temp, °C	Half-life, days		
tert-Butyl	 $H_2N-\overset{\overset{O}{\|}}{C}-O-O-t\text{-Bu}$	8	47–48	—	—	—	4
tert-Butyl *N*-ethyl	 $C_2H_5-\overset{\overset{H}{\vert}}{N}-\overset{\overset{O}{\|}}{C}-O-O-t\text{-Bu}$	18	39–40	24–28	600–800	—	5
tert-Butyl *N*,*N*-dimethyl	 $CH_3-\overset{\overset{H_3C}{\vert}}{N}-\overset{\overset{O}{\|}}{C}-O-O-t\text{-Bu}$	54	Liq.	24–28	57–65	—	5
α-Cumyl *N*,*N*-dimethyl	 $CH_3-\overset{\overset{H_3C}{\vert}}{N}-\overset{\overset{O}{\|}}{C}-O-O-\alpha\text{-cum}$	40	60	24–28	32	—	5
tert-Butyl *N*,*N*-diethyl	 $C_2H_5-\overset{\overset{C_2H_5}{\backslash}}{N}-\overset{\overset{O}{\|}}{C}-O-O-t\text{-Bu}$	43	Liq.	24–28	57–65	—	5
tert-Butyl *N*,*N*-pentamethylene		81	Liq.	30	2–4	—	5
tert-Butyl *N*-phenyl		70	83	25	349	$k_d = 1.52 \times 10^{16}e^{-32\,500/RT}$	4, 6, 7
α-Cumyl *N*-phenyl		—	72	25	25.3	$k_d = 1.26 \times 10^{14}e^{-28\,100/RT}$	6, 8
tert-Butyl *N*-(*m*-methylphenyl)		—	54–57	25	24.9	$k_d = 1.13 \times 10^{12}e^{-25\,300/RT}$	7

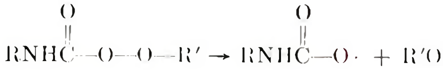
tert-Butyl *N*-(*o*-chlorophenyl)		—	71	—	—	—	7
tert-Butyl *N*-(*m*-chlorophenyl)		—	78–79	25	696	$k_d = 1.33 \times 10^{14} e^{-30\,100/RT}$	7 7
tert-Butyl *N*-(*p*-chlorophenyl)		—	71–72	25	91.5	$k_d = 2.47 \times 10^{13} e^{-27\,900/RT}$	7 7
tert-Butyl *N*-(2,5-dichlorophenyl)		—	46–47	25	2314	$k_d = 6.64 \times 10^{13} e^{-30\,400/RT}$	7
tert-Butyl *N*-(*p*-bromophenyl)		—	82–84	25	288	$k_d = 2.89 \times 10^{15} e^{-31\,400/RT}$	7
tert-Butyl *N*-(*m*-nitrophenyl)		—	80	25	4253	$k_d = 1.25 \times 10^{15} e^{-32\,500/RT}$	7
tert-Butyl *N*-(*p*-nitrophenyl)		59	93	24–28 25	600–800 959	$k_d = 3.91 \times 10^{12} e^{-28\,200/RT}$	5 7
tert-Butyl (*N*-methyl-*N*-*p*-nitrophenyl)		68	66	30	2–4	—	5, 14
tert-Butyl *N*-(−)-menthyl	 $(-)\text{—menthyl—}\overset{\text{H}}{\underset{}{\text{N}}}\text{—}\overset{\text{O}}{\overset{\Vert}{\text{C}}}\text{—O—O—}t\text{-Bu}$	—	101	—	—	—	4
tert-Butyl *N*-α-naphthyl		54	80	—	—	—	4, 6

(continued)

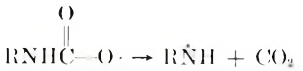
TABLE I (*continued*)

Peroxy-carbamate	Formula	Yield, %	Mp, °C	Stability		First-order decomposition kinetics	Reference
				Temp, °C	Half-life, days		
tert-Butyl *N*-(*p*-diphenyl)		38	85	—	—	—	4
2,6-Toluyl *N*,*N*′-bis-(*tert*-butyl)		93	135	—	—	—	9
Hexamethylene *N*,*N*′-bis(*tert*-butyl)		89	100	24–28	600–800	—	5,9
Hexamethylene *N*,*N*′-bis-(α-cumyl)		57	105	24–28	250	—	5,8
Hexamethylene *N*,*N*′-bis-(*t*-amyl)		93	60	—	—	—	9

decomposition of peroxycarbamates in solution in the presence of vinyl monomers can be represented as shown in eqs. (1)–(7).[7]



$$\mathrm{RNH}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}-\mathrm{O}-\mathrm{O}-\mathrm{R}' \rightarrow \mathrm{RNH}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}-\mathrm{O}\cdot + \mathrm{R'O}\cdot \tag{1}$$



$$\mathrm{RNH}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}-\mathrm{O}\cdot \rightarrow \mathrm{R\dot{N}H} + \mathrm{CO_2} \tag{2}$$

$$\mathrm{R\dot{N}H} + \mathrm{R'O}\cdot \rightarrow \mathrm{RNHOR'} \tag{3}$$

$$2\mathrm{R\dot{N}H} \rightarrow \mathrm{RNHNHR} \xrightarrow{-2\mathrm{H}} \mathrm{RN{=}NR} \tag{4}$$

$$\mathrm{R\dot{N}H} + \underset{\text{(solvent)}}{\mathrm{HS}} \rightarrow \mathrm{RNH_2} + \mathrm{S}\cdot \tag{5}$$

$$\mathrm{R\dot{N}H} + \mathrm{CH_2{=}CHX} \rightarrow \mathrm{RNHCH_2\dot{C}HX} \tag{6}$$

$$\mathrm{R'O\cdot CH_2{=}CHX} \rightarrow \mathrm{R'OCH_2\dot{C}HX} \tag{7}$$

Russian workers[8] have compared the reactivity of peroxycarbamates in vinyl polymerization with related compounds. It was found that compounds containing the group $>N-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-$ are generally more active than the corresponding peroxides with the grouping $>N-CH_2-O-O-$. Other limited data have shown that at lower temperatures *tert*-butyl *N*-pentamethylene peroxycarbamate is a more effective initiator of styrene polymerization than benzoyl peroxide but at higher temperatures benzoyl peroxide is more effective.[5] At 50°C both *tert*-butyl and α-cumyl *N*-phenyl peroxycarbamates are more effective initiators of styrene and methyl methacrylate polymerization than benzoyl peroxide.

The initiating activity of peroxycarbamates has been utilized by Tobolsky and Rembaum[17] in the synthesis of block copolymers. Industrially available polyether and polyester "prepolymers" containing one or several isocyanate groups per chain react with *tert*-butyl hydroperoxide to yield long-chain peroxycarbamates. These initiate polymerization of a wide variety of vinyl monomers and dienes leading to a class of block copolymers with very interesting physical properties.

Decomposition of Hexamethylene *N,N'*-Bis(α-cumyl peroxycarbamate) and Its Efficiency as an Initiator in Vinyl Polymerization

Detailed examination of the decomposition kinetics of peroxycarbamates and their activity as initiators of free radical vinyl polymerization has been restricted to *N*-aryl substituted peroxycarbamates. Mesrobian and coworkers[6] have studied *tert*-butyl *N*-phenyl peroxycarbamate, α-cumyl *N*-

phenyl peroxycarbamate and *tert*-butyl *N*-α-naphthyl peroxycarbamate. There have been only a few other limited accounts of initiation of vinyl polymerization by peroxycarbamates.

This paper describes some decomposition kinetics of an *N*-alkyl-substituted peroxycarbamate. In particular, a report is given of the decomposition of hexamethylene *N*,*N*′-bis (α-cumyl peroxycarbamate) in various solvents and its efficiency as an initiator of styrene and methyl methacrylate polymerization.

EXPERIMENTAL

Cumene hydroperoxide was purified by isolation of the sodium salt and regeneration of the hydroperoxide.[18] A purity of 97–98% was shown by iodometric titration.[19]

Styrene was free from inhibitor by fractional distillation under reduced pressure of nitrogen. Methyl methacrylate was purified by washing with 10% caustic soda solution and then with water. It was dried over molecular sieves (Linde Type 5A) and distilled under reduced pressure of nitrogen. Monomers were stored at −10°C and redistilled under high vacuum immediately before use.

Solvents were carefully purified by drying over molecular sieves (Linde Type 5A), followed by fractional distillation.

Hexamethylene *N*,*N*′-bis(α-cumyl peroxycarbamate) was synthesized from hexamethylene diisocyanate and cumene hydroperoxide in the presence of triethylamine.[5] Iodometric analysis indicated a purity of 80% which was not improved by reprecipitations.

All other reagents were of highest available purity and were used as received.

For decomposition experiments, solutions (10 ml) of the peroxycarbamate were sealed in ampoules. After specific time intervals in the water bath, the contents of each ampoule were analyzed iodometrically to determine the concentration c of undecomposed peroxycarbamate.

Low-conversion polymerizations were carried to about 5% conversion in the complete absence of air in dilatometers at 80°C for styrene and 60°C for methyl methacrylate with the use of hexamethylene *N*,*N*′-bis(α-cumyl peroxycarbamate) as initiator. Polymers were recovered by precipitation in methanol to which petroleum were recovered by precipitation in methanol to which petroleum ether (30–60°C) and dilute hydrochloric acid (0.1*N*) had been added to aid coagulation. Purification was performed by reprecipitation from benzene and prolonged drying in vacuum. For high-conversion polymerizations, aliquots (5 ml) of peroxycarbamate initiator and monomer from which oxygen had been removed by addition of solid carbon dioxide were sealed in ampoules. After specific time intervals in a water bath, polymer was recovered as previously described for the low-conversion polymerizations.

RESULTS AND DISCUSSION

Decomposition Kinetics of Hexamethylene *N*,*N*′-Bis(α-cumyl Peroxycarbamate)

The rate of decomposition of hexamethylene *N*,*N*′-bis(α-cumyl peroxycarbamate) in benzene was studied at four temperatures and first-order kinetics were observed (Fig. 1). Experiments at 75°C were performed

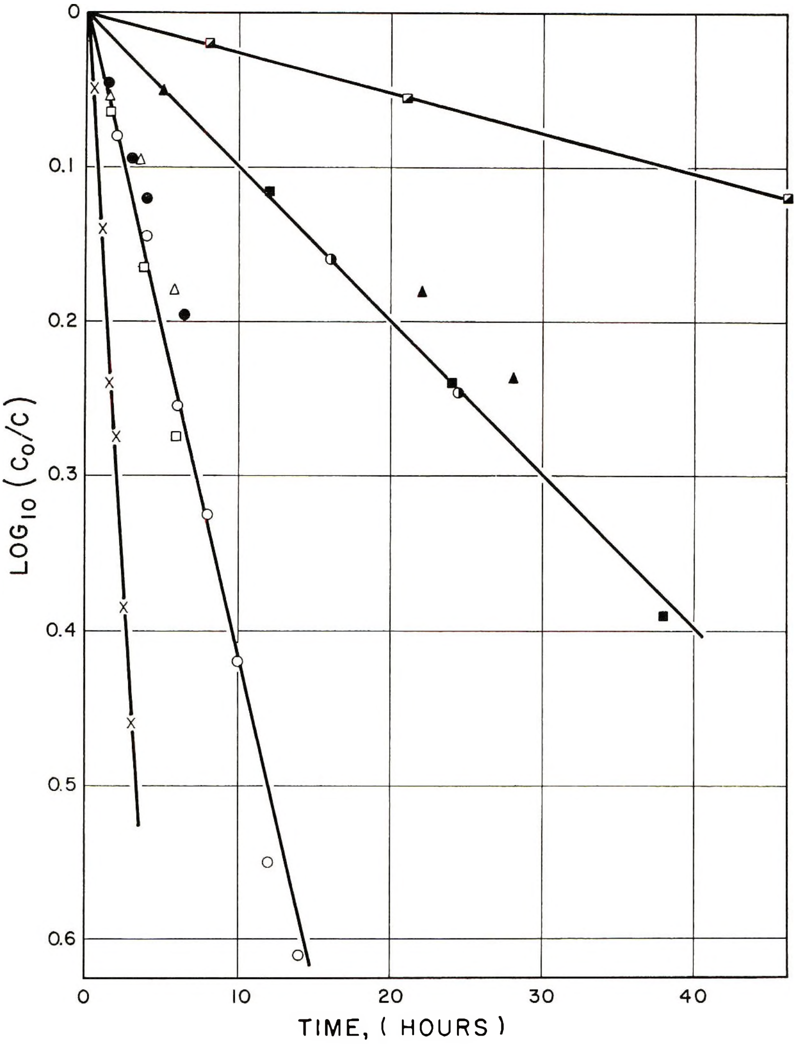


Fig. 1. Decomposition of hexamethylene *N*,*N*′-bis(α-cumyl peroxycarbamate) in solvents at several temperatures and initial molar peroxycarbamate concentrations: (◪) 65°C, 9.50 × 10^{-3}; (■) 75°C, 5.80 × 10^{-3}; (◑) 75°C, 1.00 × 10^{-3}; (▲) 75°C, 5.00 × 10^{-3}, [T8] = 4.30 × $10^{-3}M$; (○) 85°C, 1.03 × 10^{-2}; (□) 85°C, 9.90 × 10^{-3} (acetonitrile); (△) 85°C, 9.90 × 10^{-3} (ethyl acetate); (●) 85°C, 9.90 × 10^{-3} (chlorobenzene); (×) 95°C, 1.06 × 10^{-2}.

at two different initial peroxycarbamate concentrations and showed the rate constant was independent of concentration. Comparison of runs at 85°C in benzene, ethyl acetate, acetonitrile, and chlorobenzene demonstrated that solvent polarity did not significantly affect the decomposition rate. The data of Figure 1 give the rare expression (8) for the temperature dependence of the unimolecular rate constant (k_d) in benzene:

$$k_d = 2.21 \times 10^{16}\, e^{-34.100/RT} \tag{8}$$

The frequency factor and activation energy are both higher than the values reported for aromatic peroxycarbamates. The absence of a concentration or solvent effect suggests that induced decomposition by peroxycarbamate radicals formed in the decomposition is insignificant under the conditions employed in this study.

The presence of dibutyltin di-2-ethylhexoate (T8) catalyst had very little influence upon the rate of decomposition of the peroxycarbamate (Fig. 1). Similar experiments with cobalt naphthenate were unsatisfactory as colored side products masked the iodometric titration.

Low-Conversion Polymerization of Styrene and Methyl Methacrylate

Low-conversion homopolymers of styrene and methyl methacrylate were prepared at 80°C and 60°C, respectively, with the use of hexamethylene *N*,*N'*-bis (α-cumyl peroxycarbamate) as initiator. Summaries of the experimental conditions are shown in Tables II and III.

TABLE II
Polymerization of Styrene (8.21 mole/l.) with Hexamethylene *N*,*N'*-Bis(α-cumyl Peroxycarbamate) at 80°C

[Initiator] $\times 10^3$, mole/l.	$R_p \times 10^4$, mole/l.-sec	$R_i \times 10^8$, mole/l.-sec	f
16.00	2.47	52.80	0.51
10.40	2.02	35.40	0.51
8.00	1.72	25.60	0.50
3.20	1.14	11.30	0.54
1.60	0.81	5.68	0.66
0.52	0.47	1.91	0.58

Polymerizations exhibited normal free-radical kinetics with rate of polymerization proportional to the half power of initiator concentration (Fig. 2).

True rates of initiation R_i are related to the measured rate of polymerization R_p by eqs. (9) and (10):[20]

$$R_i(1 + x) = R_i' = 2A'R_p^2/[M]^2 \tag{9}$$

$$x = k_{td}/(k_{tc} + k_{td}) \tag{10}$$

TABLE III
Polymerization of Methyl Methacrylate (8.96 mole/l.) with Hexamethylene N,N'-Bis(α-cumyl peroxycarbamate) at 60°C

[Initiator] × 10^3, mole/l.	$R_p \times 10^4$, mole/l.-sec	$R_i' \times 10^8$, mole/l.-sec	f'
16.00	1.66	4.69	0.84
10.40	1.26	2.70	0.74
8.00	1.13	2.17	0.78
3.20	0.79	1.06	0.94
1.60	0.48	0.39	0.70
0.80	0.39	0.26	0.93

where [M] is the monomer concentration, k_{tc} and k_{td} are the rate constants for termination by combination and disproportionation, respectively; x is the fraction of chains terminating by disproportionation. A' for styrene is governed by the relation:[21]

$$A' = 5.68 \times 10^{-6}\, e^{12,460/RT} \tag{11}$$

and A' for methyl methacrylate is governed by the relation:[21]

$$A' = 5.02 \times 10^{-5}\, e^{9,350RT} \tag{12}$$

For styrene polymerization it is well established that $x = 0$ at all temperatures and $R_i = R_i'$. For methyl methacrylate polymerization the value of

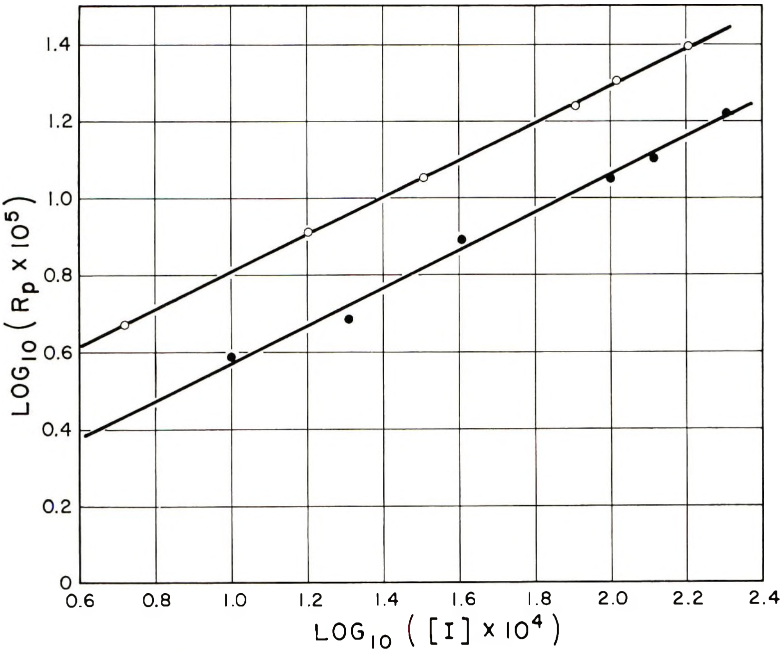


Fig. 2. Polymerization of styrene at 80°C and methyl methacrylate at 60°C initiated by hexamethylene N,N'-bis(α-cumyl peroxycarbamate): (○) styrene, slope 0.48; (●) methyl methacrylate, slope 0.49.

x is less certain[22] and strongly dependent upon temperature. In this case rates of initiation are expressed by R_i' (Table III).

Initiator efficiency (f) is defined by the relation:[20]

$$R_i = 2\,fk_d[\text{initiator}] \tag{13}$$

Inasmuch as values of R_i' rather than R_i were computed for methyl methacrylate, a quantity f' is defined and it is directly calculated as follows:

$$f' = f(1 + x) = R_i'/2\,k_d[\text{initiator}] \tag{14}$$

It should be remembered in all cases that [initiator] is twice the molar concentration, as there are two peroxycarbamate functions in each molecule of initiator. The efficiency of initiation of styrene at 80°C is 0.53 and for methyl methacrylate at 60°C is 0.82. These high efficiencies also suggest that induced decomposition is not of major importance.

Initial rates of polymerization of styrene were measured at different temperatures. Use of eqs. (2) and (4) enabled the absolute magnitudes of R_i/[initiator] produced by hexamethylene N,N'-bis(α-cumyl peroxycarbamate) to be obtained (Table IV).

TABLE IV

Polymerization of Styrene and Various Temperatures

[Initiator] $\times 10^3$, mole/l.	[Styrene], mole/l.	$R_p \times 10^6$, mole/l.-sec.	Temp, °C	$\dfrac{R_i \times 10^7}{[\text{initiator}]}$, sec^{-1}
1.60	8.46	4.23	50	2.37
15.7	8.38	33.4	60	8.60
15.2	8.29	88.3	70	36.5
15.0	8.21	240	80	166
3.20	8.21	114	80	177
1.55	8.21	82.2	80	193

Of more interest is a plot of log R_1/[initiator] versus the reciprocal of absolute temperature (Fig. 3). A good straight line is obtained which corresponds to:

$$R_i/[\text{initiator}] = 2\,fk_d = 2.28 \times 10^{15}\,e^{-32\,600/RT} \tag{15}$$

It has already been shown that the specific rate of spontaneous decomposition of the initiator does not vary significantly in different solvents. The plot in Figure 3 shows further that the efficiency of initiation exhibits dependence upon temperature. From eqs. (8) and (15) the calculated efficiency for initiation of styrene in the temperature range 50–80°C is 0.53–0.44. The value of 0.44 at 80°C compares with the value of 0.53 previously found. Similar evaluations of the efficiencies of initiation by azobisisobutyronitrile and substituted benzoyl peroxides have been described by Tobolsky and Baysal.[20]

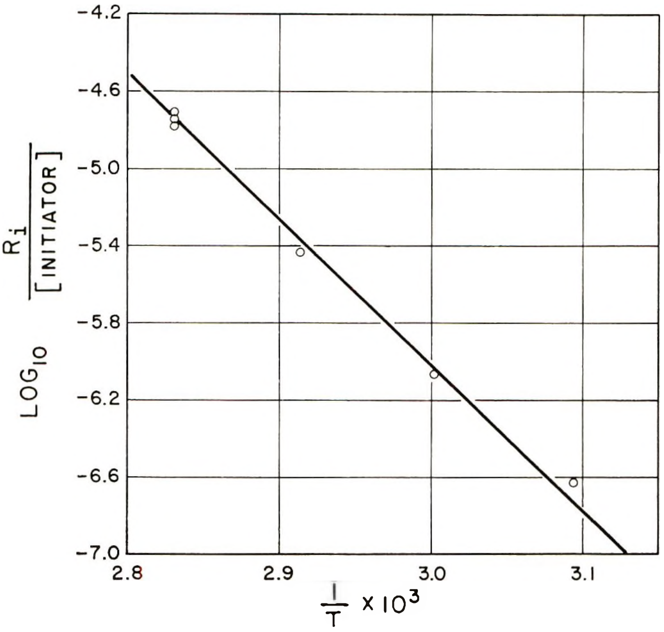


Fig. 3. Plot of log R_i/[initiator] vs. 1/T for the polymerization of styrene initiated by hexamethylene *N*,*N*′-bis(α-cumyl peroxycarbamate).

The efficiency of initiation by the aliphatic hexamethylene *N*,*N*′-bis-(α-cumyl peroxycarbamate) is lower than the values of 0.73 and 0.95 found for α-cumyl and *tert*-butyl *N*-phenyl peroxycarbamates, respectively.[6]

High-Conversion Polymerization of Styrene

The polymerization of styrene was examined further at three temperatures over the entire range of conversion. Complete kinetic curves are shown in Figure 4. There is evidence for a Trommsdorff[23] effect at higher conversions. It would be expected that the onset of autoacceleration would occur at lower conversions for hexamethylene *N*,*N*′-bis(α-cumyl peroxycarbamate) than for benzoyl peroxide or other monofunctional initiators. This would be the result of formation of higher molecular weight polystyrene by the difunctional initiator, higher viscosities, and earlier restriction of the termination reaction.

Effect of Accelerators on Polymerization Rate

Different concentrations of cobalt naphthenate and dibutyltin di-2-ethylhexoate (T8) were added to the bulk polymerization of styrene by hexamethylene *N*,*N*′-bis(α-cumyl peroxycarbamate) (2.0×10^{-3} mole/l.) to determine the possible effect of these accelerators upon the initial rate of polymerization. Runs were performed at 50 and 80°C, and the results are illustrated in Figure 5. At both temperatures T8 has little or no effect upon the polymerization rate. In the case of cobalt naphthenate at 50°C there is an enhanced rate for addition of low concentrations of accelerator. This effect is reduced at higher concentrations and a decreased rate is observed for accelerator concentrations exceeding about 0.25% by volume. At 80°C the initial rate of polymerization becomes slower as the concentration of cobalt naphthenate increases.

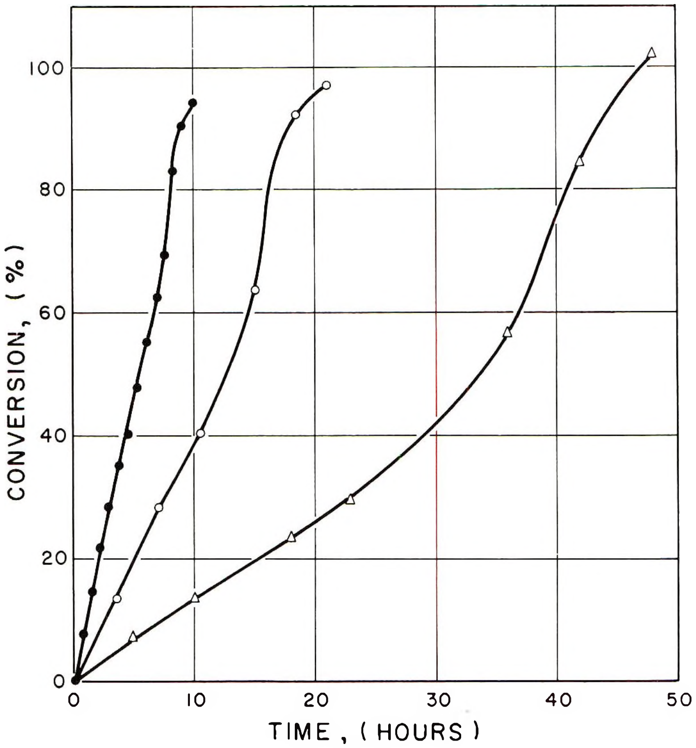


Fig. 4. Variation of the degree of conversion of styrene with the time of polymerization at various temperatures using hexamethylene N,N'-bis(α-cumyl peroxycarbamate) (1.53×10^{-2} mole/l. as initiator: (△) 60°C; (○) 70°C; (●) 80°C.

The effect of accelerators upon the decomposition of initiators in vinyl polymerization is often unpredictable and is dependent upon the type and concentration of both initiator and accelerator and the temperature of the reaction. In some cases, additives normally considered to be accelerators can show a reversal of their activity and inhibit polymerization.[24] For example, for 0.2% additive and a concentration of peroxide equivalent to 1% benzoyl peroxide, dimethylaniline accelerates polymerization in the order benzoyl peroxide > acetyl peroxide > *tert*-butyl hydroperoxide > methyl ethyl ketone peroxide. For cobalt naphthenate the order is methyl ethyl ketone peroxide > *tert*-butyl hydroperoxide; there is no effect upon benzoyl peroxide and for acetyl peroxide there is a slight inhibition.

Stannous octoate accelerates polymerization initiated by benzoyl peroxide more than acetyl peroxide, but for methyl ethyl ketone peroxide the same polymerization rate is observed and for *tert*-butyl hydroperoxide a slight inhibition occurs.

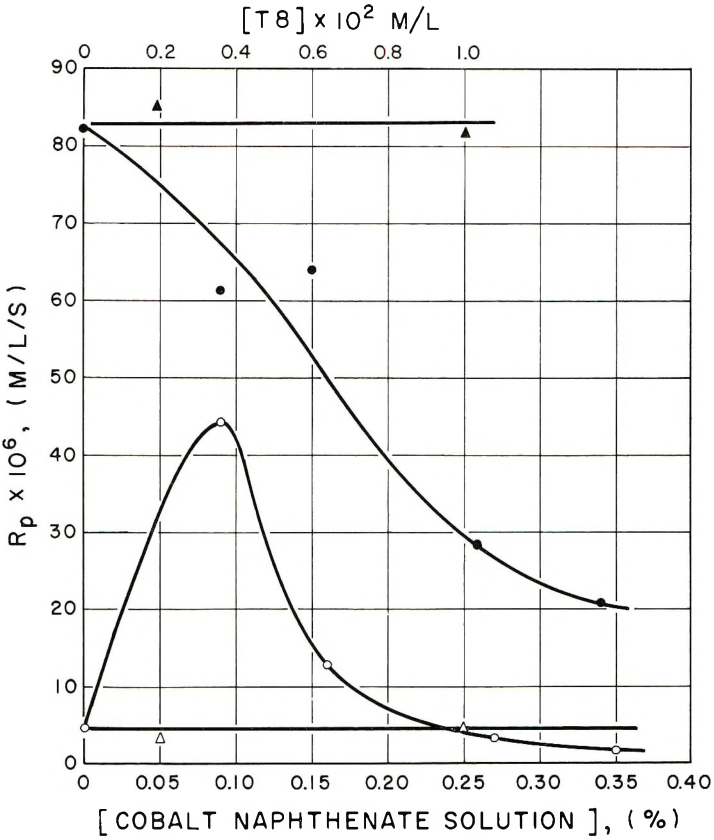


Fig. 5. Effect of cobalt naphthenate and dibutyltin di-2-ethylhexoate (T8) catalyst upon the initial rate of polymerization of styrene by hexamethylene N,N'-bis(α-cumyl peroxycarbamate): (○) cobalt naphthenate at 50°C; (●) cobalt naphthenate at 80°C; (△) T8 at 50°C; (▲) T8 at 80°C.

The data for the polymerization of styrene initiated by hexamethylene N,N'-bis(α-cumyl peroxycarbamate) in the presence of cobalt naphthenate (Fig. 5) suggest that there may be two competing effects produced by the additive. The additive may catalyze the decomposition of the initiator and increase the production of initiating radicals. At the same time, other competing reactions which decrease the rate of polymerization may be taking place. The overall effect upon the polymerization rate depends upon the temperature and concentration of the cobalt naphthenate.

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Acid-Catalyzed Polycondensation of Bisdiazoalkanes

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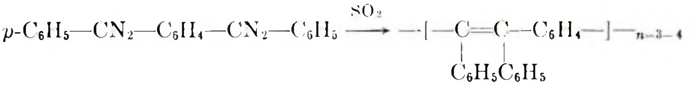
Synopsis

Dimerization reactions of diphenyldiazomethane have been applied to the polycondensation of six bisdiazobenzyl arylenes, namely 1,4- and 1,3-bis(α-diazobenzyl)-benzenes $C_6H_5CN_2—(C_6H_4)—CN_2C_6H_5$; 1,4- and 1,3-bis($\alpha$-diazo-$p$-methoxybenzyl)-benzenes, p,p'-$MeO—C_6H_4—CN_2—(C_6H_4)—CN_2C_6H_4—OMe$; 4,4′-bis($\alpha$-diazobenzyl)-diphenylmethane, $C_6H_5CN_2—(C_6H_4CH_2C_6H_4)—CN_2C_6H_5$; and 4,4′-bis($\alpha$-diazobenzyl)-diphenyl ether, $C_6H_5CN_2—(C_6H_4—O—C_6H_4)CN_2C_6H_5$. Depending on the nature of the catalysts, polyene-arylenes $(—C(Ar)=C(Ar)—C_6H_4)_n$, and polyazine-arylenes, $(—C(Ar)=N—N=C(Ar)—C_6H_4—)_n$, can be obtained selectively by acid-catalyzed decomposition of these bisdiazoalkanes at room temperature. With perchloric acid and with arylsulfonic acids in strong polar media, polyene-arylenes are formed. On the other hand, boron trifluoride and arylsulfonic acids in solvents of low dielectric constant afford polyazine-arylenes. Less selective is the thermal decomposition at 75°C in toluene solution; it gives a polymer containing about 90% azine and 10% olefinic groups. All these polymers are soluble in common solvents. Their molecular weight vary from 3 200 to 5 000, i.e., $\bar{X}_n$ from 12 to 20. The polyene-arylenes are very stable and decompose only around 500°C; the polyazine-arylenes are less stable and decompose around 370°C by losing nitrogen.

INTRODUCTION

Recently Nagai, Namikoshi and Tokura[1] described the polymerization of 1,4-bis(α-diazobenzyl)benzene in the presence of sulfur dioxide. This condensation method is based on the well known dimerization reaction of diphenyldiazomethane to tetraphenylethylene which takes place under similar experimental conditions, with accompanying formation of some benzophenone.



$$p\text{-}C_6H_5—CN_2—C_6H_4—CN_2—C_6H_5 \xrightarrow{SO_2} —[—\underset{C_6H_5}{\underset{|}{C}}=\underset{C_6H_5}{\underset{|}{C}}—C_6H_4—]—_{n=3-4} \quad (1)$$

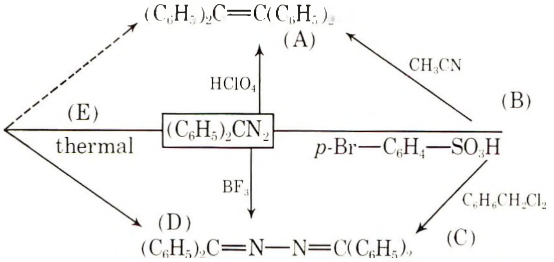
$$(C_6H_5)_2CN_2 \xrightarrow{SO_2} (C_6H_5)_2C=C(C_6H_5)_2 \quad (2)$$

Other dimerization reactions of diphenyldiazomethane have also been reported in the literature, and the present paper deals with the polycondensation of several bisdiazo compounds, as an application of these reactions on bifunctional systems.

Tetraphenylethylene is formed in nearly quantitative yield (95–96%) on treatment of diphenyldiazomethane with a catalytic amount of perchloric acid independently of the reaction medium, anhydrous acetonitrile,[2,3] benzene, methylene chloride. With arene sulfonic acids as catalysts, e.g., *p*-toluenesulfonic acid, *p*-bromobenzenesulfonic acid, it was found that the structure of the reaction product depends strongly from the polarity of the solvent. In a solvent of high dielectric constant, as acetonitrile and nitromethane, *p*-bromobenzenesulfonic acid affords 95% tetraphenylethylene,[3] while in methylene chloride 85% benzophenone azine, $(C_6H_5)_2$-$C{=}N{-}N{=}C(C_6H_5)_2$, is obtained.

Dimerization of diphenyldiazomethane to benzophenone is also obtained in 91% yield in the presence of boron trifluoride with benzene as solvent.[4,5]

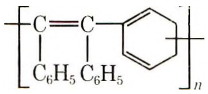
The thermal decomposition of diphenyldiazomethane results in the formation of benzophenone azine (in about 90% yield) and a small amount of tetraphenylethylene, provided the reaction has been carried out in the absence of oxygen and in a solvent inert to radical hydrogen abstraction.[6] These dimerization reactions can be summarized in eq. (3).



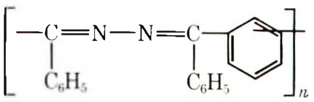
(3)

POLYCONDENSATION OF BISDIAZOBENZYL COMPOUNDS

Six different bisdiazobenzyl derivatives have been synthesized, namely: (I) 1,4-bis(α-diazobenzyl)benzene, *p*-$C_6H_5{-}CN_2{-}C_6H_4{-}CN_2{-}C_6H_5$; (II) 1,3-bis($\alpha$-diazobenzyl)benzene, *m*-$C_6H_5{-}CN_2{-}C_6H_4{-}CN_2{-}C_6H_5$; (III) 4,4′-bis($\alpha$-diazobenzyl)diphenylmethane, $C_6H_5{-}CN_2{-}C_6H_4{-}CH_2{-}C_6H_4{-}CN_2{-}C_6H_5$; (IV) 1,3-bis($\alpha$-diazo-*p*-methoxybenzyl)benzene, $CH_3O{-}C_6H_4{-}CN_2{-}C_6H_4{-}CN_2{-}C_6H_4{-}OCH_3$; (V) 1,4-bis($\alpha$-diazo-*p*-methoxybenzyl)benzene; (VI) 4,4′-bis(α-diazobenzyl)diphenyl ether, $C_6H_5{-}CN_2{-}C_6H_4{-}O{-}C_6H_4{-}CN_2{-}C_6H_5$. The treatment of these compounds under the same reaction conditions as those used for diphenyldiazomethane will result in the formation of a polymer. Thus, in the case of compound II, reaction paths A and B produce mainly a polyene-arylene

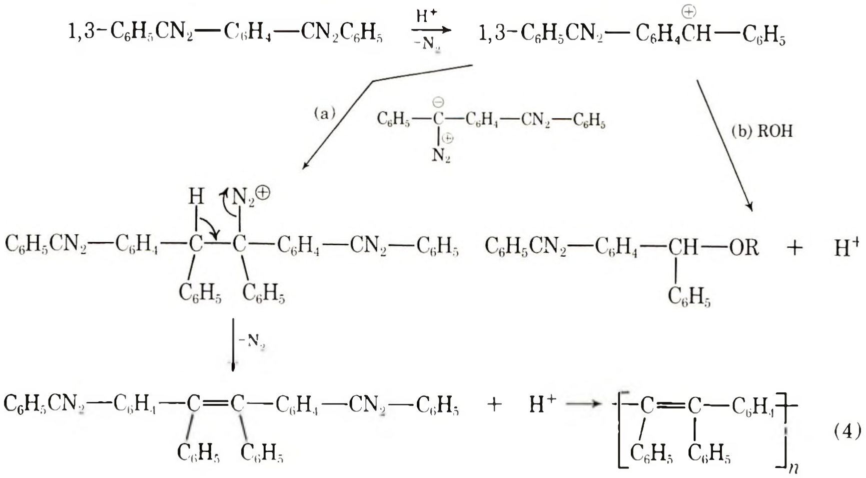


in which aromatic nuclei alternate regularly with double bonds, whereas reaction paths C, D, and E give rise to a polyazine-arylene:



Polyene-Arylenes

In analogy with the dimerization reaction of diphenyldiazomethane, it is assumed that the polymerization of bis(diazobenzyl)-benzenes proceeds by protonation of one of the diazoalkane groups, followed by nitrogen evolution. The diarylcarbonium which is formed will react with another diazoalkane giving rise to a polymer [eq. (4a)] or react with any nucleophile present in the medium [eq. (4b)]. In the case of the 1,3-α-diazobenzyl compound the polycondensation reaction will be written:



(4)

The presence of electron-releasing groups in the diazobenzyl groups will stabilize the intermediary carbonium ion, and increases the nucleophilic reactivity of the diazoalkane.[3] Therefore compounds V and VI were synthesized in which a methoxyl group is introduced in *para* position with respect to the diazoalkane group. On the other hand, molecular models show a very rigid structure and high stiffness of these polyene-arylene chains; these effects are much more pronounced for the polymers than for diphenyldiazomethane itself. Therefore compounds III and IV carrying in the main chain a methylene group and an oxygen atom respectively were also synthesized.

Polycondensations with perchloric acid were carried out in benzene at room temperature and went to completion within 2 min or less; a maximum of 1 mole-% catalyst with respect to the bisdiazo compound is required. As the solubility of the bisdiazo compounds is rather low (1–2 wt-%) the reactions have to be conducted in dilute solutions (1 to 5 × $10^{-2}M$).

With *p*-bromobenzenesulfonic acid, a mixture of nitromethane (or acetonitrile) and methylene chloride is required in order to dissolve the bisdiazo compounds. It was ascertained by preliminary experiments that in the case of diphenyldiazomethane the reaction course is not altered by the addition of 50 vol-% of benzene or methylene chloride to nitromethane or acetonitrile, and that 95% conversion to tetraphenylethylene is still obtained.

The polycondensation with sulfonic acids lasted about 1 hr, and about 4 mole-% catalyst with respect to the bisdiazo compound is needed.

In the particular case of 1,4 bis(α-diazobenzyl)benzene(I), pure polymer could only be obtained at low temperature with *p*-bromobenzenesulfonic acid as catalyst (see Experimental section).

The reaction conditions for the synthesis and the properties of the polyene-arylenes are given in Table I, where the first column refers to the different bisdiazobenzyl derivatives mentioned above.

As far as we are aware, these polyene-arylenes, in which aryl-disubstituted olefinic groups alternate with aryl groups, have not been previously described in the literature. However, analogous polymers were already obtained (1) by Wittig reaction of a dialdehyde with a bisphosphonium ylide,[7–10] (2) by dehydrohalogenation or dehalogenation of di- or tetrahalo *p*-xylylenes,[11–15] (3) by condensation of an aromatic dialdehyde with compounds carrying two active methylene groups,[16–20] (4) by decomposition of a bissulfonium ylide,[21] or (5) by reduction of a bisdiazonium salt in the presence of acetylene derivatives.[22] The degree of polymerization of these polymers varied; generally they were either only slightly soluble or insoluble, probably as a result of chain branching and crosslinking.

On the contrary, the polyene-arylenes described in the present paper are all soluble in the common solvents as benzene, chloroform, dioxane. Although their melting points are relatively low (200–250°C), nevertheless they are stable up to 420°C; on thermogravimetric analysis under nitrogen, polyolefin II loses only 9% weight between 430–560°C (16°C/min); above 560°C the decomposition becomes rapid.

Evidence for the structure of these polyene-arylenes comes from their mode of synthesis, the correct elemental analysis, and the similarity of their infrared and ultraviolet spectra with those of the model substance tetraphenylethylene (Figs. 1 and 2). With tetracyanoethylene they give electron-donor acceptor complexes; in dichloromethane, II and tetraphenylethylene are both green in color and absorb at 647 and 598 mμ, respectively.

Polyazine-arylenes

The formation of polyazines instead of polyolefins in the presence of boron trifluoride as catalyst results from the steric hindrance in the intermediate betaine, $\overset{-}{\text{C}}\text{—}\overset{+}{\text{B}}\text{F}_3$ due to the BF_3 group, which makes the carbonium ion less accessible to the second molecule of diazoalkane. Similarly in solvents of low dielectric constant, such as benzene or dichloromethane, the reaction with arylsulfonic acids would produce an ion-pair at which the second diazoalkane molecule adds only with its terminal nitrogen atom, which is less hindered than the diazoalkane carbanion:

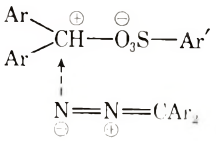
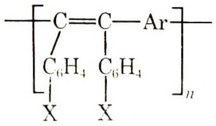


TABLE I
Synthesis and Properties of Polyene-arylenes



Bisdiazo-benzyl	Reaction conditions[a]				Polymer structure		Reaction product			
		Catalyst								
	[Diazo] × 10,² mole/l.	Concn × 10⁴, mole/l.	Type	Solvent	X	Ar	Yield, % (b)	$\overline{M}_n$	x_n	Mp, °C
I	2.4	48	$HClO_4$	Benzene	H	*p*-C_6H_4	34			
II	3.9	3.9	$HClO_4$	Benzene	H	*m*-C_6H_4	53	4 950	19	215–235
III	2.3	29	$HClO_4$	Toluene	H	*p,p'*-C_6H_4—CH_2—C_6H_4	92	2 400	7	
IV	1.8	2.3	$HClO_4$	Benzene	*p*-MeO	*m*-C_6H_4	50	4 550	15	225–240
VI	2.7	1.2	$HClO_4$	Benzene	H	*p,p'*-C_6H_4—O—C_6H_4	60	4 500	13	200–215
I_{bis}[d]	1.1	4.3	BrBS[c]	C_6H_6–CH_2Cl_2 (2:1)	H	*p*-C_6H_4	70	4 500	18	255–275
II_{bis}	1.7	6.4	BrBS	Nitromethane–CH_2Cl_2 (1:2)	H	*m*-C_6H_4	65	3 900	15	*e*

[a] The reactions were carried out at room temperature except as otherwise noted.

[b] Amount in per cent, isolated after three reprecipitations.

[c] *p*-Bromobenzenesulfonic acid.

[d] At −35°C.

[e] Polymer II_{bis} is completely identical with polymer II (infrared and elemental analysis).

The third method of azine synthesis is based on the thermal decomposition of the diaryldiazoalkanes; the reaction proceeds through a diarylcarbene.[6,23,24] This reaction must be carried out in the absence of oxygen and in an inert solvent.

The results of the three preparation methods are summarized in Table II. The easiest synthesis of these polyazines is the BF_3-method, as the reactions go to completion within 5 min and give an analytically pure polymer. With *p*-bromobenzenesulfonic acid, about 5 mole-% of the catalyst is necessary to complete the reaction within one day. Thermal decomposition of the bisdiazo compounds was carried out in vacuum sealed tubes to prevent the reaction of oxygen with the carbene intermediates. The duration of the thermolysis was about one week. The thermal polyazines are less pure than those prepared with BF_3 catalyst, as shown on infrared analysis.

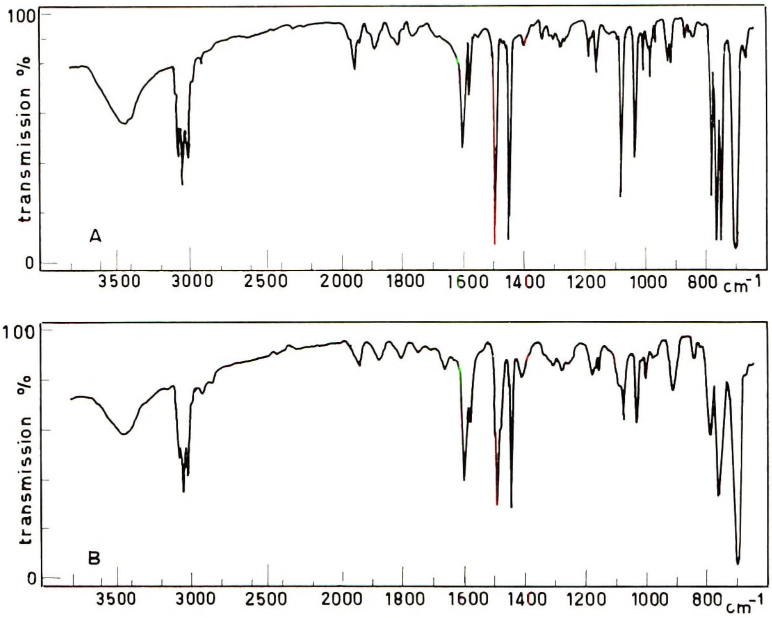


Fig. 1. Infrared absorption spectra of (*A*) tetraphenylethylene and (*B*) polyenearylene II.

Some analogous polyazines were previously described and prepared by condensation of dicarbonyl derivatives with hydrazine;[25–32] in the case of benzyl a degree of polymerization of 25 was obtained.[33]

For these polyazines, the structure was also demonstrated on the basis of the elemental analysis, their ultraviolet and infrared spectra (Figs. 3 and 4). The strong absorption peak at 1300 cm^{-1}, typical of benzophenone azine, is observed in the spectra of all polyazines obtained. These polyazine-arylenes have all a melting range between 150 and 200°C, i.e., noticeably lower than the polyene-arylenes. Thermogravimetrically they are also less stable; polyazine II starts to decompose at 370°C, and loses 63% of its weight at 475°C under inert atmosphere.

In the presence of tetracyanoethylene in dichloromethane solution these polyazines develop a red color; its absorption however interferes with that of the free azine.

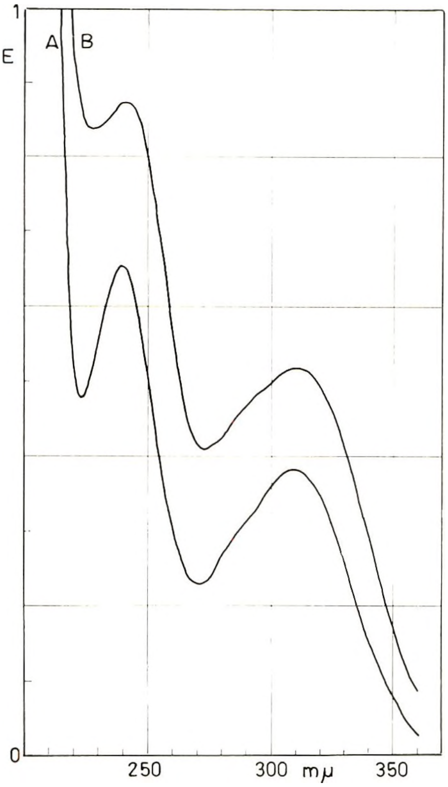
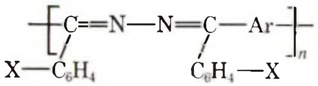


Fig. 2. Ultraviolet absorption spectra of (*A*) tetraphenylethylene (λ_{max} 240, 310, mμ, ϵ_{max} 24 600, 14 300 l./mole-cm) and (*B*) polyene-arylene II (λ_{max} 310 mμ, ϵ_{max} 11 800 l./mole-cm); in dioxane solution.

The acid-catalyzed decomposition has also been applied to bisdiazomethyl instead of bisdiazobenzyl derivatives. In these cases two major difficulties lie in the impurity of the starting bisdiazo compounds and in their unstability at room temperature. Thus 1,3- and 1,4-bis diazomethylbenzenes were decomposed in toluene solution (0.15*M*) in the presence of boron trifluoride, perchloric acid, and *p*-bromobenzenesulfonic acid (0.015*M*). Only insoluble polymers were obtained in all the experiments; all of these show an infrared absorption band at 1 620 cm^{-1} due to the C=N double bond, but no olefinic C=C absorption.

TABLE II
Synthesis and Properties of Polyazine-arylenes



	Reaction conditions[a]									
		Catalyst			Polymer structure			Reaction product		
Bisdiazo benzyl	[Diazo] $\times 10^2$, mole/l.	Concn., mole/l. $\times 10^4$	Type	Solvent	X	Ar	Yield, %[b]	$\bar{M}_n$	x_n	Mp, °C
I	3.0	3.8	BF_3	Benzene	H	p-C_6H_4	68			190–205
II	3.5	3.6	BF_3	Benzene	H	m-C_6H_4	36	3 370	12	165–80
III	2.3	2.5	BF_3	Toluene	H	p,p'-C_6H_4—CH_2—C_6H_4	88			
IV	2.1	2.4	BF_3	Benzene	p-MeO	m-C_6H_4	62			170–190
V	1.4	4.8	BF_3	Benzene	p-MeO	p-C_6H_4	85			185–200
VI	5.1	3.6	BF_3	Benzene	H	p,p'-C_6H_4—O—C_6H_4	72	4 100	11	185–230
I	3.0	19	BrBS[c]	CH_2Cl_2	H	p-C_6H_4	68			
II	3.3	13	BrBS	CH_2Cl_2	H	m-C_6H_4	40			
I	6.8		Thermal	Benzene	H	p-C_6H_4	90			
II	14		Thermal	Toluene	H	m-C_6H_4	70			

[a] The reactions were carried out at room temperature except for the two thermolysis experiments (at 75°C).

[b] Amount in percent, isolated after three reprecipitations.

[c] BrBS indicates p-bromobenzenesulfonic acid.

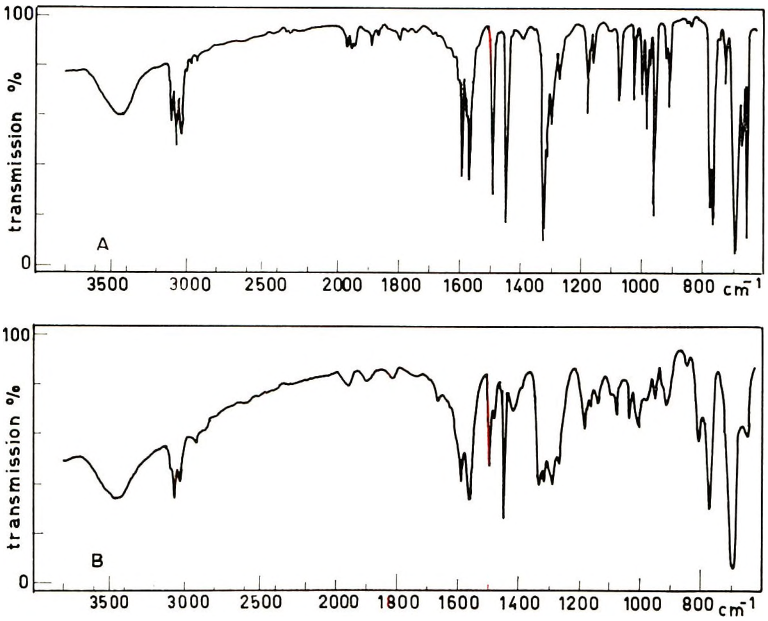


Fig. 3. Infrared absorption spectra of (*A*) benzophenone azine and (*B*) polyazine-arylene.

EXPERIMENTAL

Several compounds used as starting materials were already described in the literature. Besides the 1,4- and 1,3-bisdiazobenzylbenzenes (I and II) more recently reported by Murray and Trozzolo,[34] four other bisdiazo compounds have been synthesized by manganese dioxide oxidation of the corresponding dihydrazone.

Synthesis of Bishydrazones

4,4′-Dibenzoyldiphenylmethane Dihydrazone. 4,4′-Dibenzoyldiphenylmethane[35] (31 g 0.082 mole) were refluxed with 58 ml (1.16 mole) hydrazine hydrate in 230 ml *n*-propanol for 8 hr. After cooling, the reaction mixture was extracted with 2 l. diethyl ether and 8 l. water. On evaporation of the ethereal layer, the residual viscous oil was redissolved in 100 ml diethyl ether. After a short time the dihydrazone separated as a yellow powder. The yield was 9.3 g (28% conversion). It was recrystallized three times from *n*-butanol (to which a few drops of hydrazine hydrate have to be added to prevent disproportionation into azine) mp 174–179° (dec). N—H absorption bands were seen at 3 380, 3 240, and 3 180 cm^{-1}; there was no residual carbonyl absorption.

ANAL. Calcd: C, 80.18%; H, 5.98%; N, 13.84%. Found: C, 80.35%; H, 5.95%; N, 13.75%.

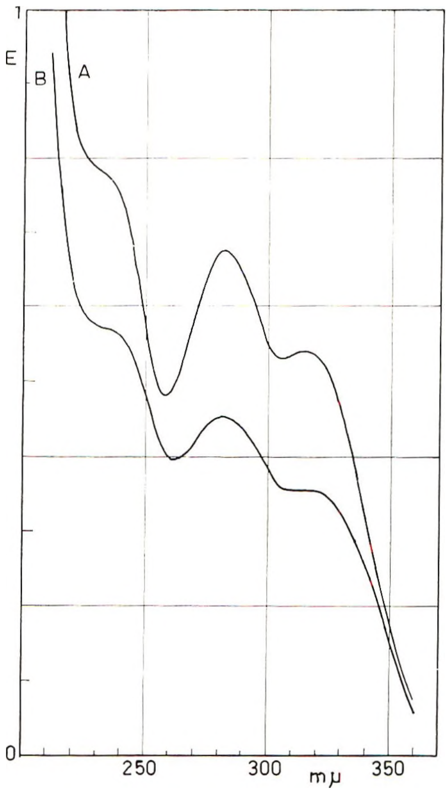


Fig. 4. Ultraviolet absorption spectra of (*A*) benzophenone azine (λ_{max} 280, 315 mμ, ϵ_{max} 18800, 15700 l./mole-cm) and (*B*) polyazine-arylene II (λ_{max} 280, 320 mμ, ϵ_{max} 16600, 14100 l./mole-cm).

1,3-Dianisoylbenzene Dihydrazone. This compound was prepared by refluxing 20 g (0.058 mole) of the bisketone[36] and 120 ml (2.4 mole) hydrazine hydrate in 120 ml *n*-propanol for 12 hr; 17 g (85%) of the bishydrazone was isolated in the form of a white powder. Recrystallization was from *n*-propanol; mp 121–124°C. N—H absorption bands were noted at 3 350, 3 260, and 3 200 cm^{-1}; absorption due to the ether link at 1 255 (arom.) and 1 030 (aliph.) cm^{-1} was also present. Carbonyl C=O absorption was absent.

Anal. Calcd: C, 70.57%; H, 5.89%; O, 8.56%; N, 14.98%. Found: C, 70.15%; H, 5.95%; O, 8.70%; N, 14.70%.

1,4-Dianisoylbenzene Dihydrazone. This was prepared in the same way with 20 g (0.058 mole) of the bisketone,[36] 125 ml (2.5 mole) hydrazine hydrate, and 250 ml *n*-butanol. The reaction time was 18 hr. After two recrystallizations from *n*-butanol the yield was 22%; mp 200–205°C. N—H absorption bands were at 3420, 3360, 3280, and 3200 cm^{-1}; ether absorption was at 1250 and 1025 cm^{-1}; absorption due to residual ketonic impurity was observed at 1640 cm^{-1}.

4,4′-Dibenzoyldiphenyl Ether Dihydrazone. This dihydrazone was prepared by refluxing 31 g (0.082 mole) of the bisketone[37] with 58 ml (1.16 mole) hydrazine hydrate in 230 ml *n*-propanol for 15 hr. By the same procedure, 24.5 g (73%) of the bishydrazone was isolated as a yellow powder. Recrystallization was from *n*-propanol; mp 171–174°C. N—H absorption bands in the infrared were at 3410, 3260, and 3200 cm^{-1}; aromatic ether absorption was seen at 1 240 cm^{-1}. Carbonyl absorption was absent.

ANAL. Calcd: C, 76.82%; H, 5.43%; O, 3.97%; N, 13 78%. Found: C, 77.02%; H, 5.50%; O, 3.85%; N, 13.72%.

Synthesis of Bisdiazobenzyl Compounds

4,4′-Bis(α-diazobenzyl)diphenylmethane (III). The bishydrazone (1.49 g, 3.7 mmole) was mixed with 3.3 g (37 mmole) active manganese dioxide[38] in 130 ml toluene for 15 min. The compound was not obtained in a crystalline state; the reaction solution was used after filtration. The yield of diazo compound was 94%.[39] Infrared analysis showed strong absorption at 2040 cm^{-1}, absence of N—H absorption, and the presence of a C=O impurity at 1655 cm^{-1}.

1,3-Bis(α-diazo-*p*-methoxybenzyl)benzene (IV). Bishydrazone (6 g, 16 mmole) and MnO_2 (16 g, 0.184 mole) were mixed for 2 hr in 1.2 l. methylene chloride. After filtration the solution was concentrated under reduced pressure at room temperature to a final volume of 20 ml. Crystals (5.7 g) were filtered off, redissolved in CH_2Cl_2 at ambient temperature, and the solution concentrated. After five recrystallizations 3.6 g (60%) of pure compound is obtained, mp 131–132°C. CN_2 absorption at 2040 cm^{-1} and ether absorption at 1250 (arom) and 1035 cm^{-1} (aliph.) were present; absorption due to N—H and C=O were absent.

ANAL. Calcd: C, 71.38%; H, 4.86%; N, 15.12%; O, 8.64%. Found: C, 71.65%; H, 4.90%; N, 15.05%; O, 8.55%.

1,4-Bis(α-diazo-*p*-methoxybenzyl)benzene (V). This compound was prepared by the same method by use of 5.7 g (15 mmole) bishydrazone, 16 g (0.184 mole) MnO_2, and 1.5 l. methylene chloride. Recrystallization was from benzene. After two recrystallizations a yield of 23% of bisdiazo compound was obtained (97% purity). Infrared analysis showed strong CN_2 absorption at 2 040 cm^{-1}, ether absorption at 1255 and 1030 cm^{-1}, absorption due to carbonyl impurity (1640 cm^{-1}). The N—H absorption band was absent.

4,4′-Bis(α-diazobenzyl)diphenyl Ether (VI). Bishydrazone (6 g, 15 mmole), dissolved in 1.2 l. CH_2Cl_2, was mixed for 1 hr with 18 g MnO_2; the resulting 5.5 g crude diazo compound was twice recrystallized from cyclohexane and affords 3.5 g of 98% pure compound. After recrystallization four times from a CH_2Cl_2–cyclohexane mixture (7/12, v/v), 1.7 g (28%) pure product was obtained; mp 126–128°C, purity 99.5%. Infrared absorptions of CN_2 at 2 050 cm^{-1} and of aromatic ether at 1250 cm^{-1} were found. N—H and carbonyl bands were absent.

ANAL. Calcd: C, 77.62%; H, 4.48%; N, 13.92%; O, 3.98%. Found: C, 77.70%; H, 4.60%; N, 13.95%; O, 4.15%.

Bisdiazomethyl benzenes. 1,3- and 1,4-bisdiazomethylbenzenes were prepared by mixing 0.5 g (3.1 mmole) of isophthalaldehyde and terephthalaldehyde, respectively, with 1.2 g (1.4 mmole) MnO_2 for 1 hr in 70 ml dichloromethane. After filtration and evaporation of the solvent, 1,3-bisdiazomethylbenzene was a red oil which could not be crystallized; 1,4-bisdiazomethylbenzene was a red crystalline product, mp 73°C (dec.); diazo content, 73%.

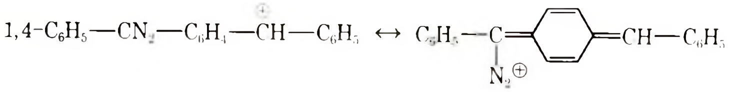
Table III summarizes the ultraviolet and visible light absorption maxima and infrared data of these diazo compounds. The spectrum of 1,3-bisdiazomethylbenzene (VIII) corresponds to that of phenyldiazomethane; 1,4-bisdiazomethyl benzene (VII) absorbs at much higher wave length on account of the strong interaction between the two diazomethyl groups. Similarly II shows the same spectral characteristics as diphenyldiazomethane, while I is again bathochromic and shows a doublet in the ultraviolet and infrared regions; in the KBr pellet, however, only a single infrared band is shown.

Polymerization

The polymerization procedure will be exemplified by the conversion of 1,3-bis(α-diazobenzyl)benzene to the corresponding polyene-arylene in the presence of perchloric acid.

In a 100-ml glass tube provided with a narrow neck and closed with a rubber cap, dry benzene (80 ml) was added to 0.963 g bisdiazo compound by means of a syringe. After dissolution of the diazo compound, 1 mole-% perchloric acid was introduced in the same way. Evolution of nitrogen occurred and after 1 min the color of the solution had changed from red to yellow. The catalyst was destroyed with a few drops of methanol and ammonia, the solution concentrated to about 25 ml, and the polymer precipitated in 150 ml methanol. It was isolated as a yellow powder in 87% yield (0.691 g). After three reprecipitations from benzene, twice in methanol and finally in pentane, the yield of recovered product was still 53%; $M_n = 4950$.

Some peculiarities and difficulties were encountered in the polycondensation of 1,4-bis(α-diazobenzyl)benzene (I). Its protonation at -80°C in dichloromethane solution ($10^{-3}M$) in the presence of perchloric acid causes a very deep blue colour (λ_{max} 560 mμ; $\epsilon \gg 11000$ l./mole-cm); simultaneously the diazo absorption band decreases. Considering that this blue coloration is absent for the 1,3-derivative, this color must be related to the resonance:



For a complete decomposition, 20 mole-% $HClO_4$ was required.

TABLE III

Ultraviolet, Visible Light, and Infrared Absorption Maxima of Diazoalkanes

Diazoalkane	Solvent	Ultraviolet		Visible		Infrared	
		$\lambda_{\max}$, mμ	$\epsilon_{\max}$, mμ	$\lambda_{\max}$, mμ	$\epsilon_{\max}$,	Solvent	cm^{-1}
Phenyldiazomethane	Pentane	274	27 500	490	29	Hexane	2062
1,3-Bisdiazomethylbenzene, *m*-$CHN_2—C_6H_4—CHN_2$ (VIII)	CH_2Cl_2	279	64 000	486	63	CH_2Cl_2	2060
1,4-Bisdiazomethylbenzene, *p*-$CHN_2—C_6H_4—CHN_2$ (VII)	Hexane	313	46 000	505	112	Hexane	2050
Diphenyldiazomethane	Dioxane	285	20 800	525	101	CH_2Cl_2	2043 (ϵ 1610)
						KBr	2036
1,3-Bisdiazobenzylbenzene, *m*-$C_6H_5—CN_2—C_6H_4—CN_2—C_6H_5$ (II)	Dioxane	290	44 600	525	203	KBr	2043 (3160)
1,3-Bis(diazo-*p*-methoxybenzyl)-benzene (IV), $MeO—C_6H_4—CN_2—C_6H_4—OMe$	Dioxane	290	42 000	525	196		
4,4′-Bis(diazobenzyl)diphenyl ether, $C_6H_5—CN_2—C_6H_4—O—C_6H_4—CN_2C_6H_5$ (VI)	Dioxane	285	47 000	525	234		
1,4-bisdiazobenzylbenzene, *p*-$C_6H_5—CN_2—C_6H_4—CN_2—C_6H_5$ (I)	Dioxane	330	24 750	535	330	KBr	2026
		300	27 900			CH_2Cl_2	2044 (2080) 2024 (2540)

TABLE IV
Analysis of Polymers

	C, %		H, %		N, %		O, %	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Polyene-arylenes								
I	94.45	94.60	5.55	5.60				
II	94.45	94.45	5.55	5.60				
III	94.15	89.83	5.85	5.80				
IV	84.05	83.85	5.77	5.80			10.18	10.25
VI	90.14	90.45	5.24	5.24			4.62	4.75
Polyazine-arylenes								
I	85.08	85.25	4.99	4.75	9.93	10.00		
II	85.08	84.90	4.99	5.40	9.93	9.95		
III	87.07	84.55	5.41	5.58	7.52	7.07		
IV	77.18	76.80	5.30	5.35	8.18	8.25	9.34	9.60
V	77.18	77.10	5.30	5.40	8.18	8.20	9.34	9.40
VI	83.40	83.55	4.85	5.10	7.48	7.40	4.27	4.45

The low molecular weight polymer, isolated in poor yield was impure. Elemental analysis showed the presence of chlorine (1.6%) while a diaryl ketone group was detected in its infrared spectrum by absorption at 1655 cm^{-1}. Apparently, during the polymerization reaction, the catalyst was consumed by oxidation of the bisdiazo compound. A pure polymer sample could be obtained by treatment of the diazo compound with *p*-bromosulfonic acid in a methylene chloride–acetonitrile mixture at −35°C. This low temperature was needed in order to prevent incorporation of solvent molecules in the polymer.

Elemental Analysis of the Polymers

The polyene-arylenes were obtained with perchloric acid, except for I, which was obtained by use of *p*-bromobenzenesulfonic acid. The polyazines-arylenes were prepared in the presence of boron trifluoride. Results of analyses are shown in Table IV.

The catalysts were added as one of the following solutions: $BF_3.Et_2O$, 0.48*M* in toluene; *p*-bromobenzenesulfonic acid, 0.1*M* in benzene; perchloric acid, 0.1*M* solution of the anhydrous acid in methylene chloride.[40]

All solvents used were thoroughly dried: benzene and toluene over calcium hydride; methylene chloride, nitromethane, and acetonitrile over phosphorus pentoxide.

Infrared spectra were obtained with Perkin-Elmer infrared spectrophotometers, models 21 and 521; ultraviolet spectra on a Cary UV 14 spectrophotometer. Molecular weights were determined on a Mechrolab vapor pressure osmometer, 301 A.

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Polymerization of Methyl Methacrylate with Dimethylbenzylanilinium Chloride

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Synopsis

In order to clarify the mechanism of initiation by dimethylbenzylanilinium chloride (DMBAC), the polymerization of methyl methacrylate with DMBAC has been investigated at 60–80°C. From the results of kinetic and tracer studies, it was found that this polymerization proceeded via a radical mechanism and benzyl radical was not an initiating species. However, it was also noted that DMBAC easily dissociated into dimethylaniline and benzyl chloride under the present conditions, and the overall activation energy for the methyl methacrylate polymerization was 14.6 kcal/mole. These observations indicate that initiating radicals other than benzyl radical, i.e., phenyl or methyl radicals, may be produced through a redox interaction between DMBAC and dimethylaniline dissociated from DMBAC.

INTRODUCTION

The reaction of tertiary amines with alkyl halides to give a quaternary salt is known as the Menschutkin reaction. Previously, Fueno et al.[1] found that the binary system of dimethylaniline and benzyl chloride and their quaternary salt, dimethylbenzylanilinium chloride, could serve as radical initiator for the polymerization of methyl methacrylate. In these cases, the methyl radical, not the benzyl radical, produced through homolysis of the carbon-nitrogen bonds in the quaternary salt was considered to be an initiating species.

Recently, Horner and co-workers[2] reported that, if trace oxygen was presented in these systems, the hydroperoxide of dimethylaniline, $C_6H_5N(CH_3)CH_2OOH$, was easily formed, and this peroxide was significant in the step of initiating radical production. Thus there are some unsolved problems regarding the exact initiation mechanism in these systems. The present paper describes the results obtained by using dimethylbenzylanilinium chloride (DMBAC) as initiator of the polymerization of methyl methacrylate (MMA).

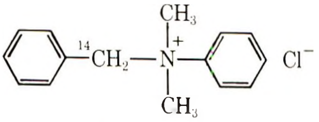
EXPERIMENTAL

Synthesis of DMBAC

DMBAC was prepared by mixing an equimolar amount of freshly distilled dimethylaniline solution with benzyl chloride in ethyl acetate, followed by recrystallization several times from a mixture of ethyl acetate and alcohol. The resulting DMBAC was a monohydrate, mp 108°C in closed tube.

ANAL. Calcd for $C_{15}H_{20}NOCl$: C, 67.78%; H, 7.59%. Found: C, 67.58%; H, 7.73%.

DMBAC labeled on the benzylic carbon atom with ^{14}C (^{14}C-DMBAC) was prepared similarly, except that ^{14}C-benzyl chloride was used.



^{14}C-DMBAC

The activity of ^{14}C-DMBAC obtained was 23250 cpm when oxidized by the van Slyke and Floch method and then measured by the Geiger-Müller method.[3]

Other Reagents

Commercially obtained methyl methacrylate (MMA) and styrene were purified by ordinary methods and distilled just before use. Other reagents were used after ordinary purification.

Polymerizations

Polymerizations were carried out in a sealed glass tube without external light. The required amounts of initiator, monomer, and solvent were charged into a glass tube and degassed by repeated freezing and thawing in order to eliminate dissolved oxygen as much as possible. The tube was then sealed under vacuum. After polymerization for a given time, the tube was opened and its contents poured into a large amount of methanol to precipitate the polymer. The resulting polymers were then purified by reprecipitation from benzene solution into methanol. Especially, in the polymers obtained by using ^{14}C-DMBAC, this reprecipitation was repeated until the activity of the polymer became constant.

Decomposition of DMBAC

Decompositions of DMBAC in various solvents were carried out in a sealed glass tube. After reaction for a given time, the reaction mixture was diluted with dilute $NaHCO_3$ aqueous solution and extracted fully with a definite amount of benzene at room temperature to separate the unreacted

DMBAC. The resulting dimethylaniline and benzyl chloride, which were the main products under the present conditions, were determined by gas-chromatographic analysis of the extracted benzene solution.

RESULTS

Kinetic Study

As was described by Fueno et al.,[1] DMBAC was confirmed to act as an excellent radical initiator of the polymerization of MMA (see Table 1). In order to estimate overall activation energy for the polymerization by DMBAC, the rates of polymerization R_p of MMA were plotted logarithmically against reciprocal polymerization temperature. The result is shown in Figure 1.

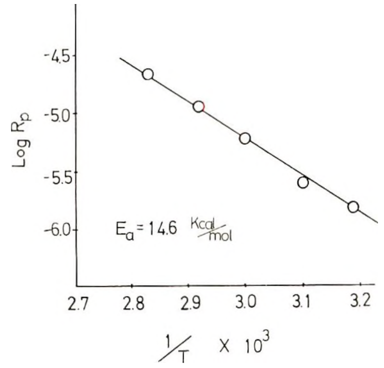


Fig. 1. Relationship between log R_p and $1/T$ in the polymerization of MMA with DMBAC in ethyl alcohol; [MMA] = 4.68 mole/l.; [DMBAC] = 1.50×10^{-2} mole/l.

From the slope of the straight line in Figure 1, the overall activation energy was obtained as 14.6 kcal/mole. The activation energy of initiation by DMBAC was calculated to be 19.4 kcal/mole, by using the reported activation energies for propagation (6.3 kcal/mole) and termination (2.8 kcal/mole).[4] This value was considerably smaller than that reported for benzoyl peroxide (29.6 kcal/mole),[5] but close to that for redox initiators such as benzoyl peroxide and dimethylaniline (15.6 kcal/mole).[6]

Figure 2 shows the plot of R_p against initial concentration of DMBAC initiator at 60°C. R_p was found to be proportional to the square root of concentration of DMBAC initiator. The correlation between R_p and MMA concentration is shown in Figure 3; R_p was directly proportional to the monomer concentration. Accordingly, the equation for R_p in the MMA polymerization by DMBAC was formulated as follows:

$$R_p = k[\mathrm{MMA}][\mathrm{DMBAC}]^{1/2}$$

The obtained activation energy and rate equation indicate that DMBAC induces radical polymerization of MMA. Similar conclusions were re-

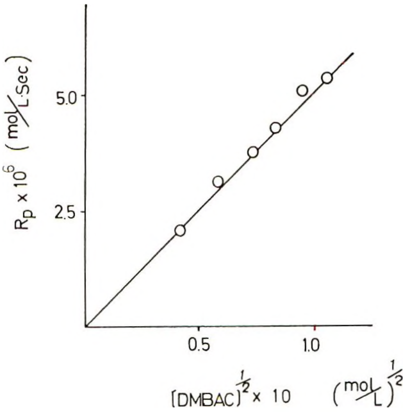


Fig. 2. Relationship between R_p and the initiator DMBAC concentration at 60°C; [MMA] = 4.68 mole/l. in ethyl alcohol.

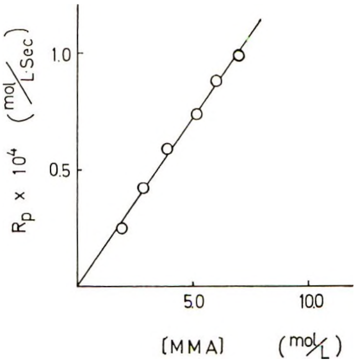


Fig. 3. Relationship between R_p and the MMA concentration in the polymerization with DMBAC at 70°C; [DMBAC] = 3.76 × 10^{-2} mole/l.; [C_2H_5OH] = 1.73 mole/l. in benzene.

ported by Fueno et al.[1] from the results of copolymerization with styrene and the effect of radical inhibitor.

Tracer Study

In order to clarify the exact nature of the initiating species in this polymerization, MMA was polymerized with ^{14}C-DMBAC initiator at 80°C. The results are shown in Table I.

Table I shows the activities of all the resulting polymers to be identical within experimental error with that of the reference polymer which was obtained by inactive DMBAC. If one ^{14}C-benzyl group was incorporated into the polymer of P_n = 442, the activity of 175 cpm would be detected empirically. Accordingly, it was concluded that the benzyl radical was not the initiating radical in the polymerization by DMBAC.

TABLE I
Analysis of Polymers Obtained by the Polymerization of MMA by ^{14}C-DMBAC[a]

[^{14}C-DMBAC] × 10^2, mole/l.	Conversion, %	$\bar{P}_n$[b]	Activity of polymer, cpm
1.88	8.3	1800	18.0
3.76	13.5	956	18.4
5.64	18.8	645	17.6
7.52	22.9	422	18.2
0	—	—	18.0

[a] Conditions: [C_2H_5OH] = 3.46 mole/l.; [MMA] = 4.68 mole/l.; in benzene; 80°C; 30 min.

[b] Number-average degree of polymerization determined from viscosity measurement in benzene and calculated by the equation:[7] $[\eta] = 8.69 \times 10^{-5} \bar{M}_n^{0.76}$.

Decomposition of DMBAC

In order to analyze the decomposition products, the thermal decomposition of DMBAC was carried out in various solvents. The results are shown in Table II, from which dimethylaniline and benzyl chloride were found to be the main products in the decomposition in benzene at 80°C. However, the other minor products were uncertain at the present time.

TABLE II
Thermal Decomposition of DMBAC in Various Solvents[a]

Solvent	Temp, °C	Time, hr	Decomposition product, %	
			$C_6H_5N(CH_3)_2$	$C_6H_5CH_2Cl$
Benzene	40	5	0.73	0.68
"	60	"	18.6	11.4
"	80	0.5	24.0	17.2
"	"	2	66.9	49.3
"	"	5	91.7	78.2
Water	"	"	0.63	0
Ethyl alcohol	"	"	34.1	27.7
Ethyl acetate	"	"	88.1	77.9
Acetone	"	"	78.7	67.0
Acetonitrile	80	5	84.2	74.9
Dimethylformamide	"	"	75.5	64.0
Dimethyl sulfoxide	"	"	71.1	59.0

[a] Conditions: [DMBAC] = 0.15 mole/l.; [C_2H_5OH] = 6.86 mole/l. in solvent.

From Table II, it is clear that the yields of dimethylaniline and benzyl chloride during the decomposition in benzene increase with increasing reaction temperature and also with increasing reaction time. It was noted that a significant amount of these materials was produced, even in the early stages of the reaction. This finding might indicate that the presence of these materials, especially dimethylaniline, was important in the initiation mechanism of the polymerization by DMBAC.

It was also noted that the yields of these materials were markedly changed by the solvents used and increased in aprotic solvents. Although the yields decreased in protic solvents such as water and ethyl alcohol, more detailed investigations are now in progress.

Effect of Additives

From the result of the decomposition of DMBAC mentioned above, the effect of dimethylaniline and sulfuric acid on the rate of polymerization of MMA with DMBAC was investigated. The results are shown in Table III.

TABLE III
Effect of Additives on the Polymerization of MMA[a]

[DMBAC], mole/l.	Additive		Yield at 6 hr, %
	Type	Concn., mole/l.	
0.10	None		5.7
0.10	Dimethylaniline	0.10	12.4
0	Dimethylaniline	0.10	1.4
3.76×10^{-2}	Ferrocene	3.76×10^{-2}	6.0[b]
0	Ferrocene	3.76×10^{-2}	1.0[b]
0.10	Sulfuric acid	0.03	0.9
0	None		0.3

[a] Conditions: [MMA] = 4.68 mole/l., in C_2H_5OH.
[b] Polymerized for 3 hr.

Since a significant amount of dimethylaniline was not produced from the decomposition of DMBAC under the present conditions, the presence of dimethylaniline may be important in the initiation by DMBAC. A similar accelerating effect was observed in the addition of ferrocene as a reducing agent. The observed retardation by sulfuric acid, which neutralized the producing dimethylaniline, might also support the above conclusion.

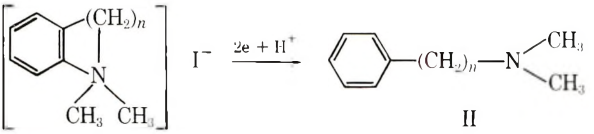
DISCUSSION

The results of kinetic and tracer studies show clearly that the polymerization of MMA with DMBAC proceeded by a radical mechanism and the benzyl radical was not a true initiating radical. Similar conclusions were pointed out by Fueno et al.[1] previously.

From the absence of graft polymer formation in polymerization of MMA with the mixture of dimethylaniline and partially chloromethylated polystyrene, Fueno et al.[1] concluded that the initiating species, of the various hydrocarbon radicals which would be produced from a homolysis of the N^+-C bonds in DMBAC, was the methyl radical. The present tracer result may be in agreement with this methyl radical initiation. From the standpoint of the bond-dissociation energies of the N^+-C bonds in DMBAC, production of a benzyl radical would be favored more than that of a methyl or phenyl radical. However, the fact that the benzyl radical was not the true initiating radical might indicate that the initiation with DMBAC did not proceed solely through a spontaneous decomposition of the N^+-C bond.

A possibility for forming true initiating radicals other than benzyl radical may be considered to proceed through a redox decomposition of DMBAC with dimethylaniline derived from dissociation of DMBAC. This mechanism may coincide with the facts that DMBAC dissociates into dimethylaniline and benzyl chloride at about 60°C in benzene, and that the addition of dimethylaniline and ferrocene accelerates the polymerization rate by DMBAC. Such a conclusion may also agree with the observed low activation energy, but the observed rate equation is not explained at the present time.

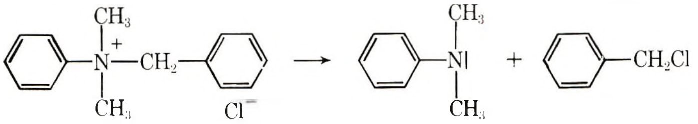
Similar redox mechanism was proposed for the reduction of dimethylbenzylanilinum chloride with dimethylaniline in the presence of light.[8] In the redox decomposition, if one electron of dimethylaniline transfers to the phenyl nucleus bonded to the N^+ of DMBAC, a phenyl radical would be produced. Emmert[9] and Horner et al.[10] reported that product II was obtained with high yields above 88% in the electrode reduction of I in the presence of acid, indicating predominant scission of the phenyl-N^+ bond in I as shown in eq. (1).



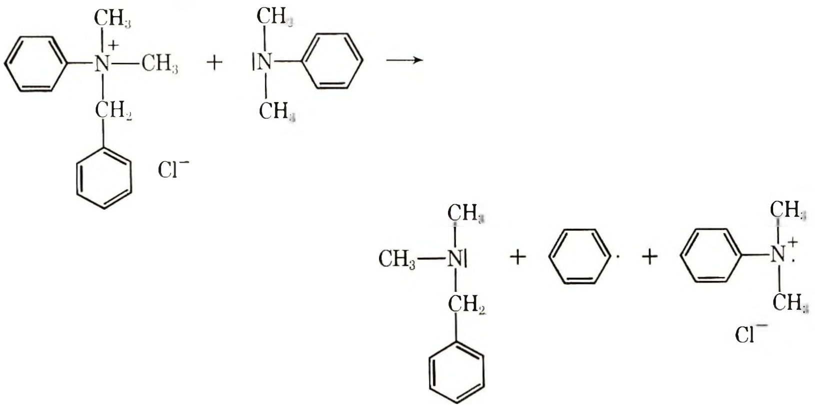
II

I, $n = 2, 3, 4$ (1)

From the above considerations, the initiation mechanism may be expressed as in eqs. (2)–(4).



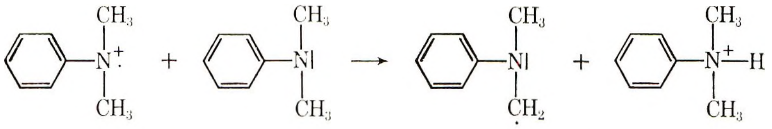
(2)



(3)

(4)

In the previous paper[11] we reported that the dimethylaniline cation radical derived from redox decomposition of benzoyl peroxide with dimethylaniline was not inactive for initiation of vinyl polymerizations. However, more recently, this cation radical produced from the reaction between dimethylaniline *N*-oxide and cobaltous nitrate was assumed to be able to induce the radical polymerization of MMA.[12] Accordingly, the possibility of initiation by this cation radical [eqs. (5) and (6)] ruled out would not be eliminated in the present case.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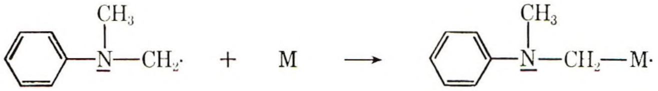
(6)

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New Polyimides via Hydrogen-Transfer Polymerization

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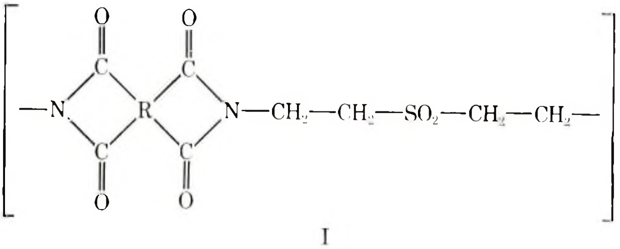
Synopsis

The synthesis and some properties of new linear polyimides obtained via hydrogen-transfer polymerization between divinyl sulfone and diimides of tetracarboxylic acids are described.

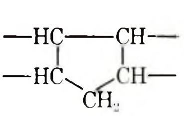
The synthesis and properties of linear polyimides have been described by several authors.[1-4] Most of these syntheses involve the formation of a poly-*o*-carboxyamide which subsequently undergoes a cyclodehydration reaction to polyimide. The synthesis of linear polyimides from benzalazine and bismaleimides, as a result of a double 1,3-addition across benzalazine,[5] and from pyromellitic diimide and dihalo compounds[6,7] are also described. Crosslinked polyimides were obtained by heating *N,N'*-bisimido derivatives of unsaturated dicarboxylic acids.[8]

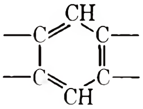
In this paper we report the synthesis via hydrogen-transfer polymerization of linear polyimides from a tetracarboxylic acid diimide and divinyl sulfone.* The linear polyimides obtained in this way, and not known from literature, consist of repeating units having the structure I;

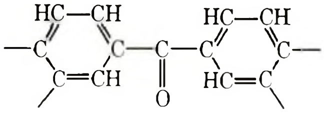


I

where R may be







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* After this work had been completed, we learned that a recent patent[9] described the synthesis of polyimides via hydrogen-transfer polymerization of alicyclic diimides with activated diolefins.

RESULTS AND DISCUSSION

Preparation of the Polymers

According to the known chemical reactivity of divinyl sulfones,[10] crystalline polymers are obtained by reacting diimides with divinyl sulfone in the presence of bases. Although no special studies were carried out to clarify the structure of these polyimides, the analytical data and physical properties support a linear structure.

Polymerizations were carried out in the presence of a solvent and under nitrogen, sodium *tert*-butoxide being used as catalyst. To prevent the radical homopolymerization of divinyl sulfone, *N*-phenyl-β-naphthylamine (0.15 wt-% with respect to the total monomers) was added to the reaction mixture.

Table I reports the polymerization conditions for hydrogen-transfer reaction of diimides with divinyl sulfone.

The inherent viscosity of the polymers does not increase markedly with increasing reaction time, the other operating conditions being the same. In the case of the cyclopentane-1,2,3,4-tetracarboxylic acid diimide, when the temperature is increased from 18°C to 100°C in dimethyl sulfoxide, the inherent viscosity does not change appreciably; on the contrary, some increase in inherent viscosity is obtained by use of pyridine as solvent instead of dimethyl sulfoxide.

Mechanism of Polymerization

The suggestion that polymerization occurs by hydrogen transfer from the imide groups to the vinyl groups of the divinyl sulfone is reasonable on the basis of the polymer structure and the catalytic action exerted by the bases.

The mechanism of hydrogen-transfer polymerization of unsaturated amides to linear polyamides, catalyzed by bases (in particular for the synthesis of nylon 3 from acrylamide) has been much debated. In particular, Breslow et al.[11] proposed two possible mechanisms of initiation [eqs. (1) and (2)],

$$CH_2{=}CHCONH_2 + \overset{\ominus}{B} \rightleftharpoons CH_2{=}CHCO\overset{\ominus}{N}H + BH \qquad (1)$$

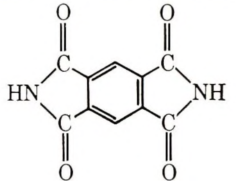
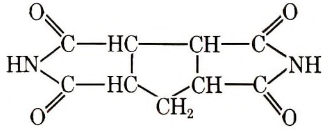
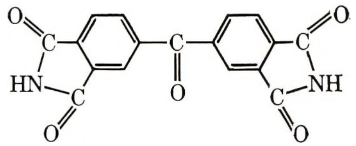
$$CH_2{=}CHCONH_2 + \overset{\ominus}{B} \rightleftharpoons B{-}CH_2{-}\overset{\ominus}{C}HCONH_2 \rightleftharpoons B{-}CH_2{-}CH_2{-}CO\overset{\ominus}{N}H \qquad (2)$$

but excluded mechanism (2) due to the presence of end unsaturation in the polymer and the isolation of the unsaturated dimer.

Ogata,[12] on the contrary, operating with an equimolar monomer/$\overset{\ominus}{O}R$ ratio, concluded that the mechanism is of type (2), as supported by the appearance of an infrared absorption band at 9.0μ which is attributed to the ether bond.

Finally, Trossarelli et al.[13] do not consider reaction (1) to be a real initiation reaction, in that it shows only the behavior of acrylamide as an acid. These authors state that the two possible initiation reactions are

TABLE I
Polymerization of Diimides with Divinyl Sulfone Catalyzed by *tert*-BuONa

Diimide	Solvent	[Catalyst], mole/mole monomer	Temperature °C	Time, hr	Procedure[a]	Yield, %	η_{inh}	Color
	Pyridine	9.4×10^{-2}	100	8	A	69	0.13	Tan
	Pyridine	9.4×10^{-2}	100	24	A	64	0.14	Brown
	Pyridine	9.4×10^{-2}	100	49	A	74	0.17	Brown
	Dimethyl sulfoxide	5.0×10^{-2}	18	24	B	72	0.09	White
	Dimethyl formamide	5.0×10^{-2}	18	24	B	62	0.11	White
	Dimethyl sulfoxide	5.0×10^{-2}	100	8	B	48	0.11	White
	Pyridine	5.0×10^{-2}	100	8	B	76	0.14	White
	Pyridine	5.0×10^{-2}	100	24	B	66	0.17	White
	Dimethyl formamide	1.2×10^{-1}	100	24	C	47	0.23	Brown

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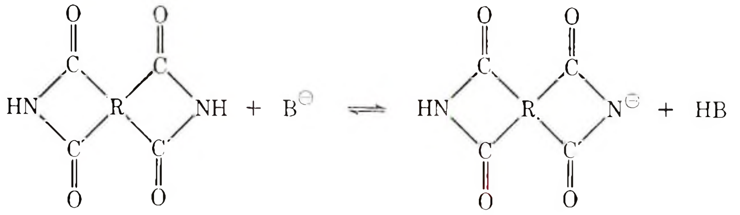
[a] Procedures A, B, and C differ by the concentration of reactants (see Experimental).

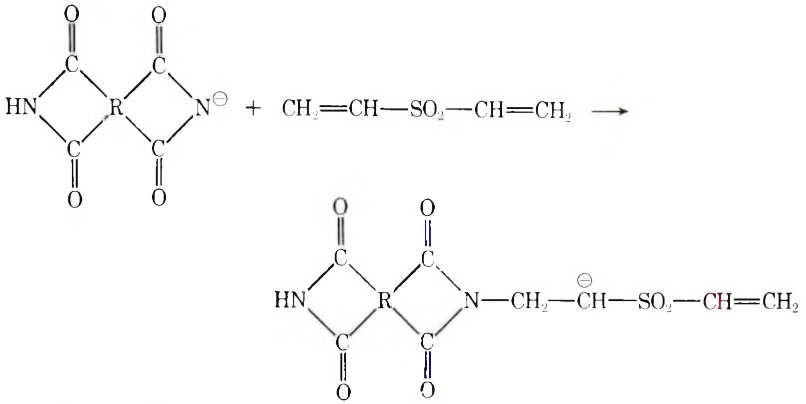
those shown in eqs. (2) and (3); the latter corresponds to the initiation from equilibrium (1). On the basis of the experimental results obtained with *tert*-butoxide, they conclude that the initiation reaction may occur, either through mechanism (3) or through mechanisms (2) and (3) simultaneously, depending on the solvents.

$$\mathrm{CH_2{=}CHCO\overset{\ominus}{N}H + CH_2{=}CHCONH_2 \rightarrow CH_2{=}CHCONHCH_2\overset{\ominus}{C}HCONH_2}$$
$$\rightleftarrows$$
$$\mathrm{CH_2{=}CHCONHCH_2CH_2CO\overset{\ominus}{N}H} \tag{3}$$

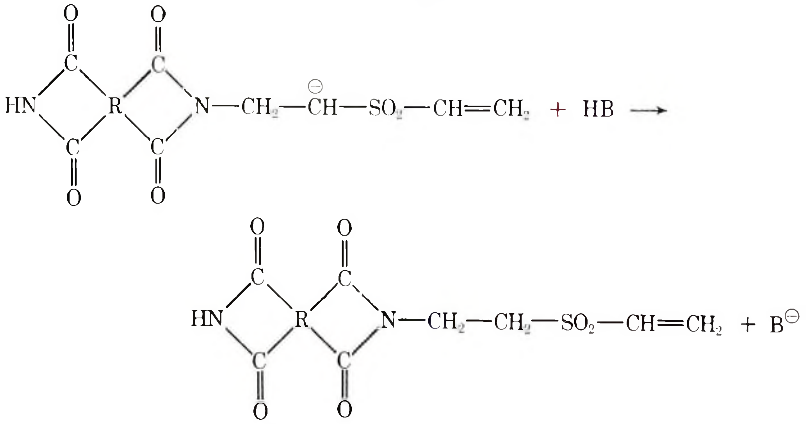
In our case, i.e., heteropolymerization to polyimides, since the first equilibrium between the diimide and the base is shifted considerably toward the right due to the acidity of the imidic hydrogen, the initiation of the hydrogen-transfer polymerization should proceed according to the mechanism shown in eqs. (4a)–(4c).



(4a)



(4b)



(4c)

The imidic anion attack occurs at the carbon atom β to the sulfonic group, in agreement with the known conjugative and inductive effect of the $-SO_2-$ grouping.

The infrared band at 9.1 μ cannot be attributed to the presence of ether bonds (direct attack of the catalyst on divinyl sulfone). In fact, a test carried out by procedure A (see Experimental Section) but in the absence of alkoxide catalyst yielded a polyimide having the same infrared spectrum as that of Figure 1.

Properties of Polyimides

The infrared absorption spectra of the polymers, as shown from Figures 1–3, are in agreement with the predicted polyimide structures. Polyimides A and B show absorption bands at 5.60 μ characteristic of the imide groups and at 7.65 and 8.85 μ characteristic of the sulfonic groups. Polyimide C, in addition to the bands of the imide (5.63 μ) and of the sulfonic groups (7.74 and 8.88 μ), also shows a band at 6.03 μ characteristic of the carbonyl groups.

The polyimides described here are infusible and, as seen from the spectrograms (Fig. 4), are crystalline by x-ray examination.

Those obtained from the benzene–1,2,4,5-tetracarboxylic acid diimide and from benzophenone-3,3′,4,4′-tetracarboxylic acid diimide, are soluble only in concentrated H_2SO_4.

The polyimides obtained from cyclopentane-1,2,3,4-tetracarboxylic acid diimide, on the contrary, are soluble in HCOOH, dimethylformamide, *N*-methyl-2-pyrrolidone, and dimethyl sulfoxide as well as in concentrated sulfuric acid.

Thermogravimetric analyses (Figs. 5–7) show that polyimides are stable up to about 300°C under dynamic vacuum (heating rate 2.7°C/min). As might be expected, these polyimides are far less stable than fully aromatic polyimides.

The three polyimides synthesized by us undergo thermal decomposition at about the same temperature, independent of the nature of the residual grouping of diimide: this fact might suggest that degradation affects the tetramethylenesulfonic group.

EXPERIMENTAL

Materials

Divinyl sulfone was purified by distillation as described in the literature.[14]

The diimide of benzene-1,2,4,5-tetracarboxylic acid was prepared according to the literature[15] by reaction of pyromellitic dianhydride (m.p. 284–286°C) with an aqueous solution of NH_4OH. The product obtained was purified by repeated crystallizations from anhydrous pyridine.

The diimide of cyclopentane-1,2,3,4-tetracarboxylic acid was synthesized as follows. Urea (30 g) and cyclopentane-*cis*,*cis*,*cis*,*cis*-1,2,3,4-tetracarboxylic acid dianhydride (94.5 g, mp 225–229°C, dec.) were introduced in a

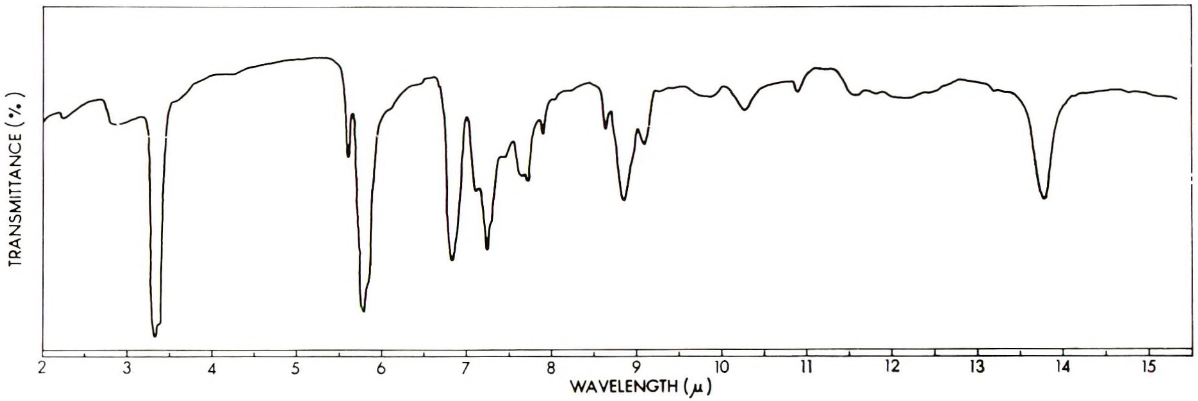


Fig. 1. Infrared absorption spectrum of the polyimide (polyimide A) obtained from the diimide of benzene-1,2,4,5-tetracarboxylic acid. Nujol mull.

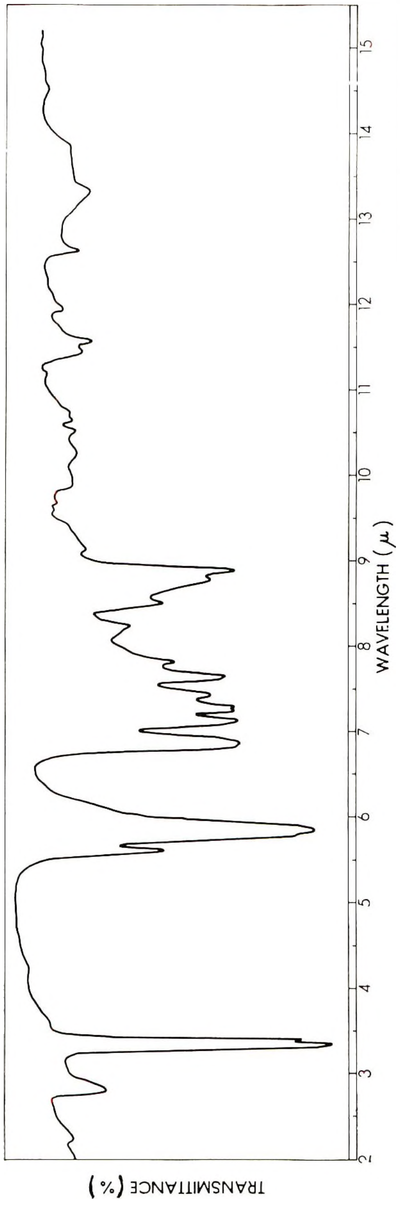


Fig. 2. Infrared absorption spectrum of the polyimide (polyimide B) obtained from the diimide of cyclopentane-1,2,3,4-tetracarboxylic acid. Nujol mull.

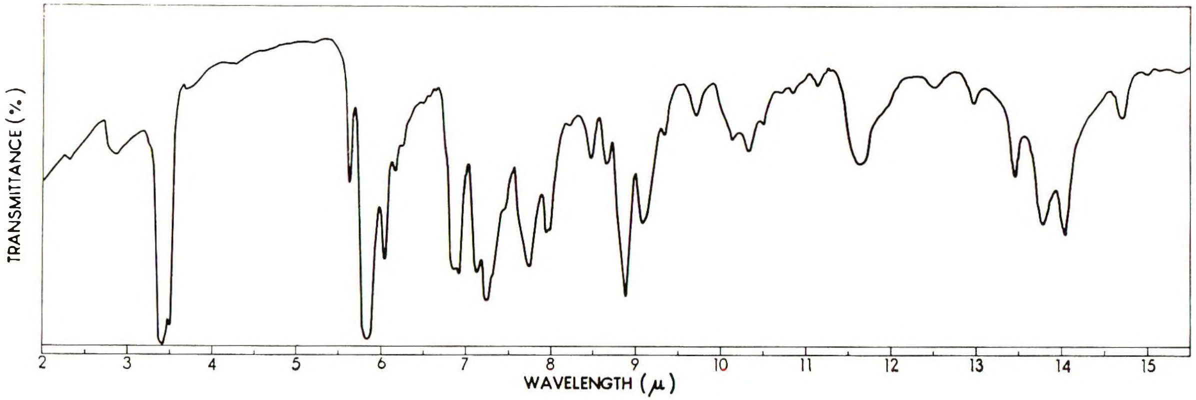


Fig. 3. Infrared spectrum of the polyimide (polyimide C) obtained from the diimide of benzophenone-3,3′,4,4′-tetracarboxylic acid. Nujol mull.

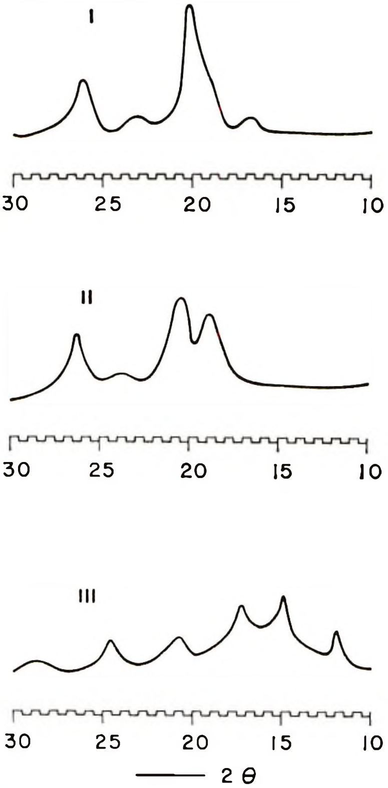


Fig. 4. Powder patterns obtained by high-angle spectrometer with CuKα radiation. (*I*) polyimide from the diimide of benzene-1,2,4,5-tetracarboxylic acid; (*II*) polyimide from the diimide of benzophenone-3,3′,4,4′-tetracarboxylic acid; (*III*) polyimide from the diimide of cyclopentane-1,2,3,4-tetracarboxylic acid.

flask equipped with a side arm, dipped into a bath at 200°C, and maintained at this temperature for about 1 hr. The solid mass formed was recovered; after crumbling it was placed into the flask for an additional 2 hr at 220–225°C. The greyish powder obtained in this way was put into water and ice; then it was filtered and washed thoroughly with water. After drying, a whitish product (57 g) was obtained, which was purified by repeated crystallization from water in the presence of active carbon. The melting point was 259–260°C.

ANAL. Calcd for $C_9H_8N_2O_4$: C, 51.94%; H, 3.84%; N, 13.47%. Found: C, 51.65%; H, 3.95%; N, 13.39%.

The diimide of benzophenone-3,3′,4,4′-tetracarboxylic acid was synthesized as follows. Urea (30 g) and benzophenone-3,3′,4,4′-tetracarboxylic acid dianhydride (145 g, mp 223–225°C) were introduced into a flask equipped with a side arm, dipped into an oil bath at 270°C, and maintained at this temperature for about 2 hr. After cooling, the solid mass formed was recovered; after grinding, it was again placed into the flask for an

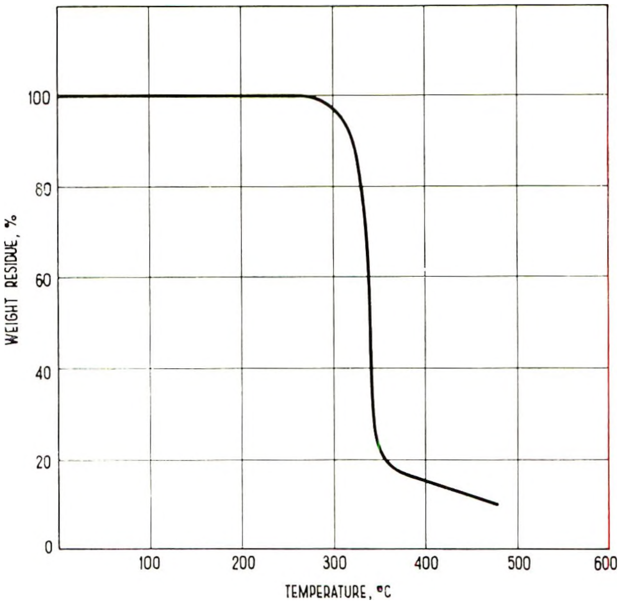


Fig. 5. Thermogravimetric analysis of the polyimide obtained from the diimide of benzene-1,2,4,5-tetracarboxylic acid.

additional 2 hr at 265–270°C. The greyish powder obtained in this way was put into water and ice, filtered, and thoroughly washed with water and ethanol. After drying, a white solid (135 g) was obtained, which was purified by repeated crystallizations from dimethylacetamide in the presence of active carbon. The diimide showed no melting up to 350°C.

ANAL. Calcd for $C_{17}H_8N_2O_4$: C, 63.77%; H, 2.50%; N, 8.74%. Found: C, 63.53%; H, 2.44%; N, 8.59%.

Pyridine was distilled over BaO.

Dimethyl sulfoxide was purified by distillation at reduced pressure (bp 66°C/5 mm Hg).

Dimethylformamide was purified by distillation on P_2O_5 at 20 mm Hg.

Polymerizations

Polymer from the Diimide of Benzene-1,2,4,5-tetracarboxylic Acid and Divinyl Sulfone. A solution of diimide of benzene-1,2,4,5-tetracarboxylic acid (5.0 g, 0.0231 mole) and *N*-phenyl-β-naphthylamine (0.012 g) in pyridine (200 cc) was introduced into a flask. To this solution, maintained at 100°C under mechanical stirring and under nitrogen, we added divinyl sulfone (2.72 g, 0.0231 mole) and a solution of *tert*-BuONa in *tert*-butyl alcohol, prepared from Na (0.1 g) dissolved in *tert*-butyl alcohol (7.75 g). A precipitate is immediately formed. The reaction mixture was allowed to stand for 49 hr at 100°C; the precipitate was separated by filtration and washed with hot water. After drying under vacuum at 70°C,

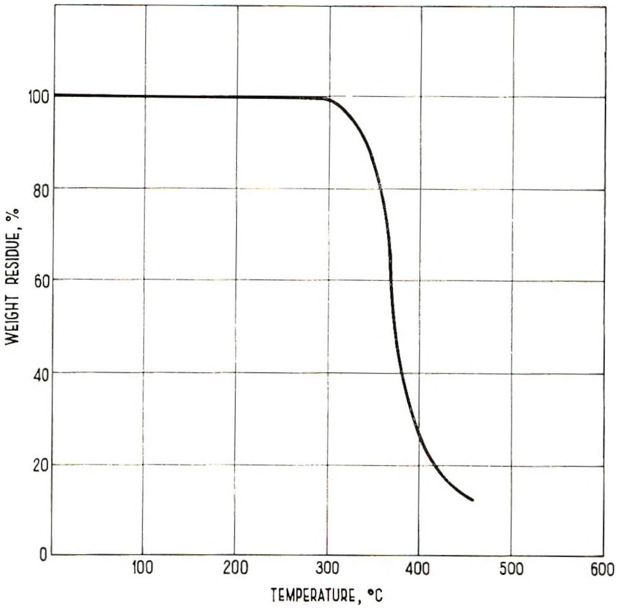


Fig. 6. Thermogravimetric analysis of the polyimide obtained from the diimide of cyclopentane-1,2,3,4-tetracarboxylic acid.

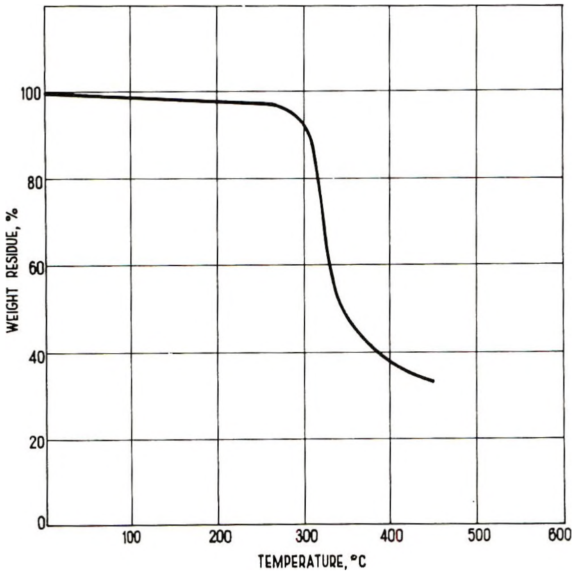


Fig. 7. Thermogravimetric analysis of the polyimide obtained from the diimide of benzophenone-3,3′,4,4′-tetracarboxylic acid.

a brown polymer (5.7 g) was obtained. The polymer was purified by dissolution in concentrated H_2SO_4 and by subsequent precipitation in H_2O. The polymer was found to be infusible and soluble only in concentrated H_2SO_4.

Figure 1 shows the characteristics of the infrared spectrum.

ANAL. Calcd for $(C_{14}H_{10}N_2O_6S)_n$: C, 50.31%; H, 2.99%; N, 7.12%; S, 8.52%. Found: C, 50.57%; H, 3.13%; N, 7.22%; S, 8.71%.

Polymer from the Diimide of the Cyclopentane-1,2,3,4-tetracarboxylic Acid and Divinyl Sulfone. A solution of *tert*-BuONa in *tert*-butyl alcohol prepared from Na (0.1 g) dissolved in *tert*-butyl alcohol (7.75 g) was added to a solution of diimide of cyclopentane-1,2,3,4-tetracarboxylic acid (9.0 g, 0.0433 moles), *N*-phenyl-β-naphthylamine (0.022 g), divinyl sulfone (5.1 g, 0.0433 mole), in dimethyl sulfoxide (200 cc), placed in a reaction flask as described above at a temperature of 18°C. After 24 hr, the solution was poured into acetone to precipitate the polymer, which was then washed with hot water. After drying under vacuum at 70°C, a white polymer (6.8 g) was obtained, which was found to be infusible and soluble in dimethyl sulfoxide, *N*-methyl-2-pyrrolidone, dimethylacetamide, formic and sulfuric acids. Figure 2 shows the characteristics of the infrared spectrum.

ANAL. Calcd for $(C_{13}H_{14}N_2O_6S)_n$: C, 47.86%; H, 4.29%; N, 8.58%; S, 9.83%. Found: C, 47.54%; H, 4.10%; N, 8.24%; S, 9.64%.

Polymer from Diimide of Benzophenone-3,3′,4,4′-tetracarboxylic Acid and Divinyl Sulfone. A solution of *tert*-BuONa in *tert*-butyl alcohol prepared from sodium (0.1 g) dissolved in *tert*-butyl alcohol (7.75 g) was added to a solution of diimide of benzophenone-3,3′,4,4′-tetracarboxylic acid (6.0 g, 0.0188 mole), *N*-phenyl-β-naphthylamine (0.013 g), divinyl sulfone (2.22 g, 0.0188 mole) in dimethylformamide (200 cc), placed in a reaction vessel at 100°C. The reaction mixture was allowed to stand 24 hr at 100°C; the precipitate was separated by filtration and washed with hot water. After drying under vacuum at 70°C, a brown polymer (4.2 g) was obtained, which was found infusible and soluble only in the concentrated H_2SO_4. Figure 3 shows the characteristics of the infrared spectrum.

ANAL. Calcd for $(C_{21}H_{14}N_2O_7S)_n$: C, 57.04%; H, 3.19%; N, 6.39%; S, 7.32%. Found: C, 56.34%; H, 3.10%; N, 6.11%; S, 6.91%.

The inherent viscosity of the polymers was measured at the concentration of 0.50 g of polymer/100 cc of H_2SO_4 (at 98 wt-%) at 30°C.

The authors wish to express their gratitude to Prof. Piero Pino for his kind interest in this work.

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Studies on the Biaxial Stretching of Polypropylene Film. V. Orientation Mechanism of the One-Step Biaxially Stretched Film

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Synopsis

The molecular orientation behavior during one-step biaxial stretching in air of a quenched, low crystalline film differs from that of a slightly crystallized, highly crystalline film. In the case of a quenched film a plot of $-\Delta n_{ss}$ versus $1/\sqrt{v_A}$ is composed of three intersecting straight lines with different slopes, Δn_{ss} and v_A being the birefringence with respect to the normal to the film surface and the degree of stretching in area, respectively. On the other hand, $-\Delta n_{ss}$ of crystalline film changes somewhat differently. It does not increase up to fairly high stretching ratio. When a film with surface layers of different crystallinity was stretched biaxially, the relations between $-\Delta n_{ss}$ and $1/\sqrt{v_A}$ for the two surface layers differ, that is, a surface layer of low crystallinity shows a change of $-\Delta n_{ss}$ like that of a quenched film type and the surface layer of higher crystallinity, follows the behavior typical of highly crystalline film. However, a commercial film having different crystallinities on the two surface layers exhibits another type of $-\Delta n_{ss}$ change, which may be ascribed to the stress remaining frozen in the film in the manufacturing process. In addition, it is found that an Abbé refractometer can give the refractive indices of both the upper and lower surface layers of a film when the film structure is not the same on both surface layers.

INTRODUCTION

As is well known, the deformation behavior of the spherulites as well as the orientation of the amorphous chains relate closely to the molecular orientation of the film. However, the orientation mechanism during the biaxial stretching has not been clear. In a preceding paper,[1] a comparatively simple relation was found between $-\Delta n_{ss}$ and $1/\sqrt{v_A}$ in the case of quenched film, where $-\Delta n_{ss}$ is the birefringence with respect to the *ss* axis[2] and v_A the degree of stretching in area.[3]

In this paper, as an approach to the mechanism of orientation of a film in biaxial stretching, the effects of crystallinity and isotacticity on the relation between $-\Delta n_{ss}$ and $1/\sqrt{v_A}$ were studied, and the morphological change of the spherulites on the surface of the film during the biaxial stretching was also investigated by electron microscopy and compared with the change in birefringence.

Especial attention was given to the measurement of the refractive index by an Abbé refractometer; further discussion of this given in detail elsewhere.[4]

EXPERIMENTAL

Preparation of Films

The characteristics of the sample used are presented in Table I.

TABLE I
Characteristics of the Samples

Polymer Sample[a]	$\bar{M}_v$[b]	Isotacticity, %[c]	Thickness, μ
B_2	3.4×10^5	98	400
B_3	3.6×10^5	96	400
C_4	2.7×10^5	80	110

[a] The symbol C denotes a sample supplied by Chisso Corp.; and sample B were commercial films from another company. The subscript indicates lot number. C_4 was a sample specially prepared by blending an atactic fraction with C_1.[3]

[b] Evaluated by the equation of Kinsinger and Hughes.[5]

[c] Extracted with boiling n-heptane.

The samples were melted and cooled in different ways in order to obtain films of various crystallinities.

Film Preparation

Film 1. A piece of sample B_3, about 12 cm × 12 cm, was placed on a stainless steel plate (S_1) 3 mm thick and melted at 190°C. After melting for 5 min, the sample, together with S_1, was immersed quickly in a poly(ethylene glycol) bath thermostatically controlled at 80°C for 5 min. and quenched in ice water. The upper surface of the film, not in contact with the plate, was unrestricted free surface.

Film 2. A piece of B_2 of the same size was placed between two stainless steel plates of 0.5 mm thickness (S_2) and, after melting at 200°C for 5 min, quenched in ice water together with (S_2).

Film 3. Eight sheets of sample C_4 were piled up and treated in the same manner as film 2.

Film 4. A piece of B_2, 12 cm × 12 cm, was melted between S_1 and a stainless steel plate (S_3) of 0.1 mm thickness at 200°C for 5 min and quenched in ice water.

Film 5. B_2, as received, was used.

The pressure applied to the hot press for preparing sample films 2–4 was about 10 kg/cm^2. Film 1 had a free surface, while in the other films, both surfaces were in contact directly with flat stainless steel plates. For films 2 and 3, the rate of cooling seemed to be equal on both surface layers of each film and larger than that of film 1 because S_1 was considerably thicker and of larger heat capacity than S_2. The cooling rates of the two surface layers of film 4 differed, and this brought about a difference in structure on the two surface layers of the film. Film 1 also had unequal cooling rates on the two surface layers, but the effect of this on the structure was likely to be small because the sample was crystallized at 80°C before quenching. Films 1 and 5 were about 400 μ thick and films 2–4 about 300–350 μ. The crystallinities calculated from the film densities for films 1, 2, 3, 4, and 5 were 54, 27, 26, 44, and 50%, respectively. The densities were measured in a water–ethanol density gradient column. On the free surface of film 1, spherulites were clearly observed by electron microscopy (replica method), but no spherulites were visible by electron microscopy on the surfaces of films 2–4 because of their contact with the smooth surfaces of stainless steel plates. However, as the low-angle light scattering (H_V) showed a distinct clover pattern in every film, it was expected that the films did contain spherulites.

In film 4, one surface layer which was in contact with the thicker plate (S_1) seemed to be highly crystalline compared to the opposite surface layer in contact with the thinner plate (S_3) because of the different rates of cooling. On one surface of film 5, many spherulites were observed by electron microscopy while on the opposite, smooth surface, no spherulites were seen.

Biaxial Stretching

The films 12 cm × 12 cm, were stretched biaxially in one step in air at 152°C at a rate of 3 mm/sec after preheating for about 10 min. The stretching apparatus was the same as that used in previous studies.[1,3]

Electron Microscopy

Morphological changes of the spherulites on stretching were studied by using an electron microscope (JEM—30 B, Japan Electron Optics Laboratory Co. Ltd.).

X-Ray Diffraction

X-Ray diffraction patterns were obtained by use of a Microflex B-3 instrument (Rigaku Denki Co., Ltd.). Cu$K\alpha$ radiation was used.

Measurement of Refractive Indices of a Film

The refractive indices normal and parallel to a film surface, n_{ss} and n_p, were measured by using an Abbé refractometer and were corrected to the values at $d = 0.900$ g/cm^3 as described in the previous studies. Recently we found the very interesting fact that the values of n_{ss} and n_p of "as received" film were often slightly different when one or the other surface faced the prism P_0 (Fig. 1). This is unreasonable if the film is of homogeneous structure and the ordinary principle of an Abbé refractometer is valid. In general, an Abbé refractometer can give the refractive index of a region

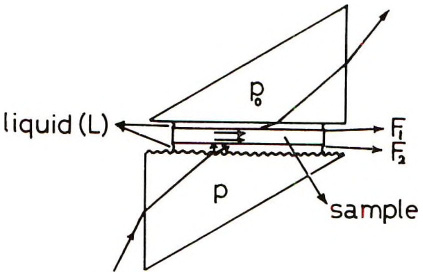


Fig. 1. Abbé refractometer: (P, P_0) glass prisms; (L) mounting material; (F_1, F_2) surface layers of film.

through which a light beam passes parallel to the film surface. In order to measure the refractive index n_{iso} of an isotropic and homogeneous film, the refractive index of the mounting material L must be larger than the refractive index of the film but smaller than the refractive index of the glass prism. If the film is composed of two layers (F_1 and F_2) having unequal refractive indices and their contact surface is an ideally optical plane, only the one smaller value of the refractive index should be read, irrespective of whether F_1 or F_2 faces P_0. The fact that two refractive indices can be read as described above, leads us to believe that some fraction of the light beam always passes parallel to the surface of the film facing the prism P_0, irrespective of whether the refractive index of the surface layer is larger or smaller than that of the opposite surface. This phenomenon is considered to be caused by the scattering of light beams passing through the film, in which crystallites disperse in amorphous phase, and the reflection of the incident light beam at the lateral surface of the film.

For films 1–4, refractive indices parallel to the film surface were nearly equal in all directions, but in the case of film 5, n_{pp} (refractive index along the machine direction in this case) and n_{ps} (refractive index along the cross direction in this case) were considerably different, and the differences, $n_{pp} - n_{ps}$, amounted to 4×10^{-3} and 12×10^{-3} on the upper and lower surfaces, respectively; hence n_p was expressed by $(n_{pp} + n_{ps})/2$.

RESULTS AND DISCUSSION

Plots of $-\Delta n_{ss}$ versus $1/\sqrt{v_A}$ for films 1–3 are shown in Figure 2, where $1/\sqrt{v_A} = 1$ means the unstretched state sustained only a preheating to 152°C for 10 min and $1/\sqrt{v_A} = 0$ corresponds to an infinitely stretched film. The plots for the quenched films (2 or 3) can be represented by three intersecting straight lines with different slopes, and regions 1 and 3 of these two films converge to one point, $-\Delta n_{ss} = 20 \times 10^{-3}$, when they are extrapolated to $1/\sqrt{v_A} = 0$. This behavior coincides with the results in the preceding paper.[1] The initial part of the same plot for film 1 differs considerably from that mentioned above, but the extrapolation of region 3 intersects the ordinate at the same point, $-\Delta n_{ss} = 20 \times 10^{-3}$. The dis-

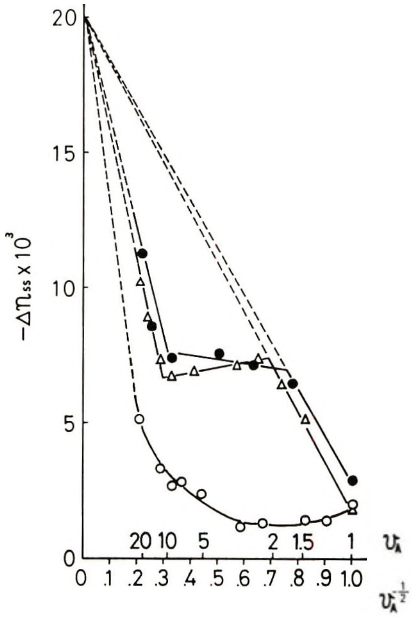


Fig. 2. Plots of $-\Delta n_{ss}$ vs. $1/\sqrt{v_A}$: (○) slightly crystallized film (film 1): (●) quenched film (film 2); (△) quenched film (film 3).

crepancy of the behavior of film 1 from that of quenched film in the initial stage of stretching seems to be due to its high crystallinity. It is considered that various elementary types of orientation occur during biaxial stretching of a film: *type 1:* orientation of the amorphous chains between lamellae or between spherulites. (Fig. 3*a*); *type 2:* inclination of the standing lamellae toward the film surface (Fig. 3*b*); *type 3:* inclination of the standing lamellae toward the film surface (Fig. 3*c*); *type 4:* tilting of the chain axis in the lamellae, which may occur concurrently with processes of types 2 and 3 (Fig. 3*d*); *type 5:* unfolding of chain molecules from lamellae (Fig. 3*e*).

Of these elementary processes, types 1, 4, and 5, contribute to an increase in $-\Delta n_{ss}$, and the effects of types 1 and 5 are especially marked, while types 2 and 3 make the opposite contribution. Type 3 may be rare because of the platelike shape of a lamella. Such various types of orientation occur in series and in parallel, but the detailed mode varies with the condition of stretching and the structure of the film due to the films thermal history. Orientation behavior of the films shown in Figure 2 will be explained qualitatively from the above point of view as follows. In the quenched films 2 and 3, although no spherulites are visible by electron microscopy because of their smooth surfaces, small and perhaps poorly developed spherulites are present as mentioned above. These spherulites seem to be dispersed within the amorphous phase and during the stretching in region 1, orientation of type 1 between the spherulites is considered to play a principal role. The spherulites also expand outward. When the amorphous chains are

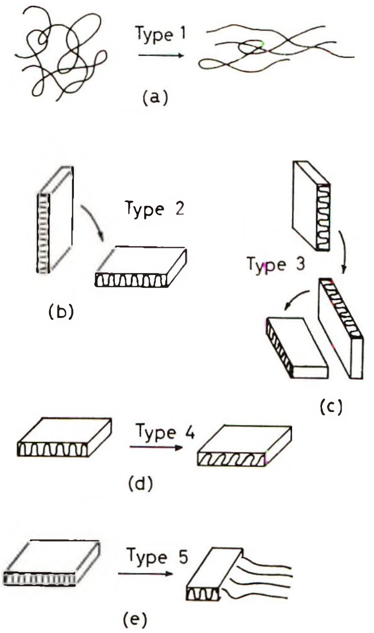
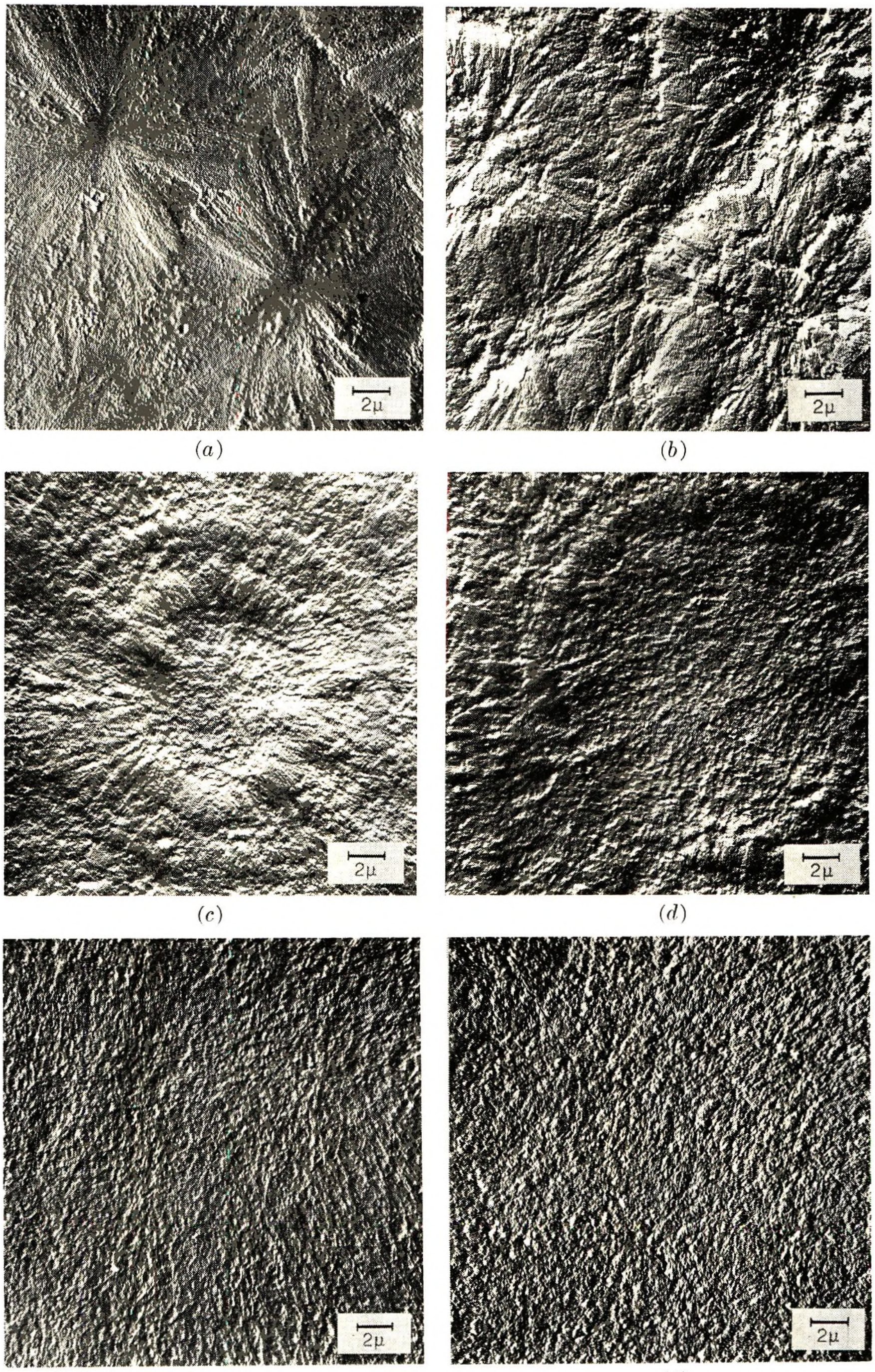


Fig. 3. Schematic representation of elementary deformation processes.

stretched to some extent the stretching load begins to act intensively on the spherulites and orientation of types 2, 3, and 4 will occur along with type 1. The breaking of lamellar crystals also occur in region 2. During this region an elementary process of type 2 is so prevalent that a smaller increase in $-\Delta n_{ss}$ (Fig. 8 in the preceding paper[1]) or even a decrease in $-\Delta n_{ss}$ appears, as seen in the case of film 3. Film 3 contains more atactic fraction than film 2. Hence a larger amount of amorphous fraction segregates between the lamellae in film 3 and more extensively weakens interlamellar forces. This is reflected in the extension of region 1 and negative slope of region 2 of film 3, where types 2 and 3 are more prevalent than in the case of film 2. In this range, breaking of the lamellae and unfolding from the ends of the fragments also occur; however, type 2 is predominant and type 5 is less apparent. Besides these changes of lamellae, inclination normal to the film surface of the amorphous chains, which may be caused by the inclination of lamellae, seems to occur,[6] and this also contributes to the decrease in $-\Delta n_{ss}$.

In the last stage of orientation, region 3, unfolding may be the main process, and $-\Delta n_{ss}$ increases most steeply. This assumption is confirmed to some degree in the case of film 1. The morphological change of the spherulites on the free surface was observed by electron microscopy (replica method) and the refractive index measurement was carried out on the opposite flat surface. Here, however, it must be taken into account that the difference in the cooling conditions of the two surface layers seems to bring about negligible change on the fine structure of the surface layers because the film was crystallized to some degree at 80°C before quenching.



(*a*) (*b*) (*c*) (*d*) (*e*) (*f*)

Fig. 4. Electron micrograph of the spherulites on the surface of film 1 stretched biaxially in one step in air at 152°C: (*a*) no stretching, preheating only for 10 min; (*b*) v_A = 1.4; (*c*) v_A = 2.2; (*d*) v_A = 5.3; (*e*) v_A = 12; (*f*) v_A = 21.

Thus, it seems not unreasonable to consider the change in $-\Delta n_{ss}$ to correspond with a morphological change in the film. In the relation between $-\Delta n_{ss}$ and $1/\sqrt{v_A}$ for film 1, $-\Delta n_{ss}$ decreases from the first. This is due to the orientation of types 2 and 3 occurring in the initial stage more prominently than type 1 because of the well developed spherulites in this sample. Figure 4*a* shows the spherulites after preheating. Figure 4*b* shows the spherulites which break from the center by slight stretching without change between the spherulites. In this stage, orientation of types 2 and 3 predominates and therefore $-\Delta n_{ss}$ decreases ($v_A = 1.2$). Orientation of type 1 also occurs along with types 2 and 3, but its effect on the increase in $-\Delta n_{ss}$ is less because of the high crystallinity of the sample. As the stretching proceeds further ($v_A = 2$–10), the spherulites expand concentrically with local breakage of the lamellae followed by unfolding of chains from the edges of the fragments (Figs. 4*c* and 4*d*). Orientation of type 5 becomes predominant and exceeds the effect of types 2 and 3: hence, $-\Delta n_{ss}$ increases gradually through a minimum value (Figure 2). This local breakage is nearly complete at $v_A = 10$ and thereafter $-\Delta n_{ss}$ increases very steeply by type 5 orientation as indicated in Figure 2 Figures 4*e* and 4*f* correspond to those states of region 3, where a net structure of fibrils can be clearly seen. (Morphological changes in the spherulites, are discussed in Part III of this series.[3])

In film 4 which was quenched at different cooling rates for the two surfaces, the density of each surface layer must be different; this was con-

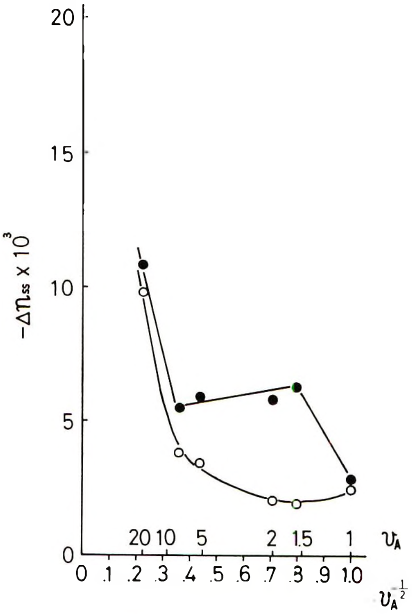


Fig. 5. Plots of $-\Delta n_{ss}$ vs. $1/\sqrt{v_A}$ for film 4: (○) upper surface of high density in contact with the thick plate (S_1); (●) lower surface of low density in contact with the thin plate (S_3).

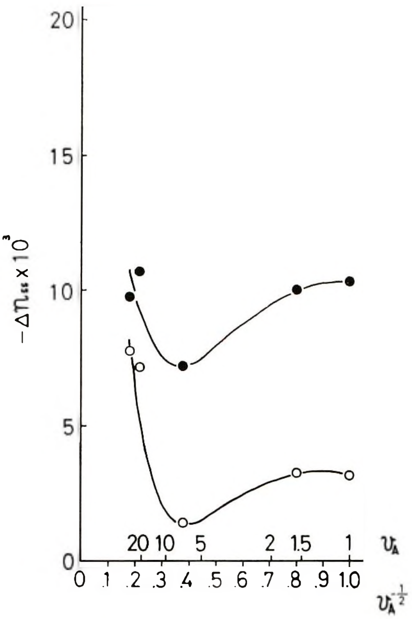


Fig. 6. Plots of $-\Delta n_{ss}$ vs. $1/\sqrt{v_A}$ for film 5: (○) upper surface of high density; (●) lower surface of low density.

firmed by measurement of the refractive index n_{iso} of the two surface layers of the film. The surface layer in contact with the thicker plate (S_1) is more highly crystalline than the opposite surface in contact with the thin plate (S_3). If this difference in the structure remains after preheating, a plot of $-\Delta n_{ss}$ versus $1/\sqrt{v_A}$ of the higher crystalline surface layer must be similar to the curve of film 1 and the plot of the opposite surface layer must follow the types shown in film 2 or 3 (Fig. 2). This conclusion is confirmed by Figure 5.

The refractive index (n_{iso}) values of the two surface layers of films 4 and 5 are nearly equal, but the relations between $-\Delta n_{ss}$ and $1/\sqrt{v_A}$ are quite different, shown in Figures 5 and 6. Film 5, which is a commercial product, seems to have frozen stress along the machine direction. When the film is preheated, the mobility of the chain segments increases and the stress is relaxed, followed by the orientation of crystallites (Figs. 7*a* and 7*b*) and amorphous chains (Fig. 6); $-\Delta n_{ss}$ increases markedly simply on preheating. As seen clearly in Figures 7*a* and 7*b*, the crystallites within a surface layer having low crystallinity before preheating, are oriented to the machine direction more highly than the other side, which was highly crystalline before preheating. In the case of film 4 such a stress is not frozen in, and this becomes clearer when Figures 7*a* and 7*b* are compared with Figures 8*a* and 8*b*. Figures 9 and 10 represent the positions at which the above mentioned micro-focus x-ray diffraction was made.

On taking account of the crystal orientation (Figs. 7*a* and 7*b*) and $-\Delta n_{ss}$

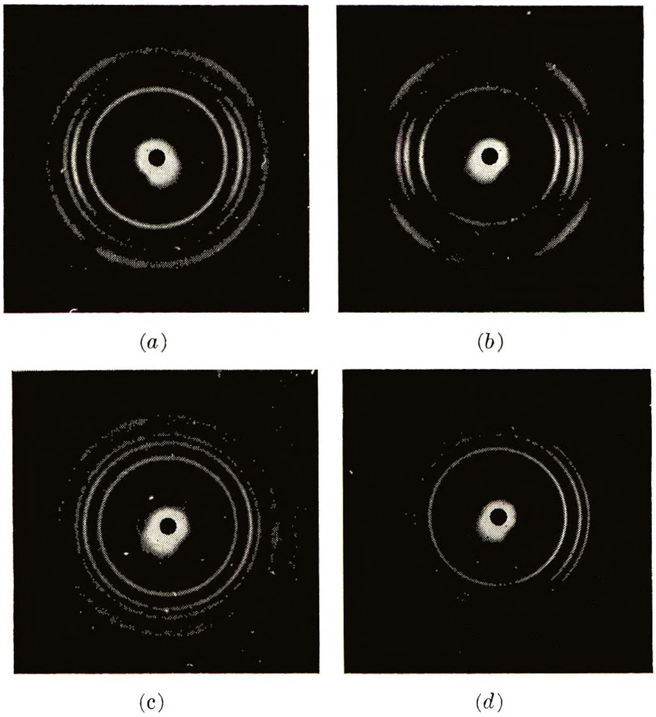


Fig. 7. Micro-focus x-ray diffraction pattern of film 5 after preheating. The equator of each photograph is perpendicular to the film surface. The position for each photograph is shown in Fig. 9. The x-ray beam is parallel to the film surface. The upper (lower) surface layer of this film was of high (low) crystallinity before preheating.

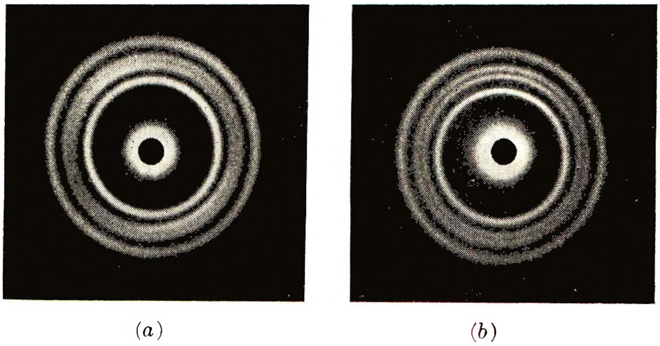


Fig. 8. Micro-focus x-ray diffraction pattern of film 4 after preheating. The equator of each photograph is perpendicular to the film surface. The position for each photograph is shown in Fig. 10. The x-ray beam is parallel to the film surface. The upper (lower) surface layer of this film was of high (low) crystallinity before preheating.

values after preheating (Fig. 6), film 5 has fairly oriented amorphous chains parallel to the film surface and crystalline chains, constituting the lamellae, normal to the film surface. Thus, when the film is stretched, the rotation of lamellae, an elementary process of type 2, begins to occur, resulting in the

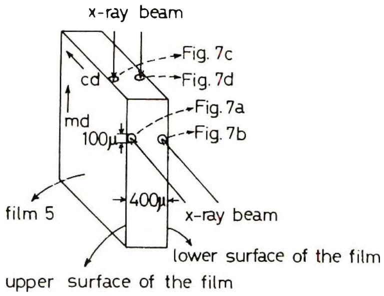


Fig. 9. Sketch of the film position for x-ray diffracting (film 5).

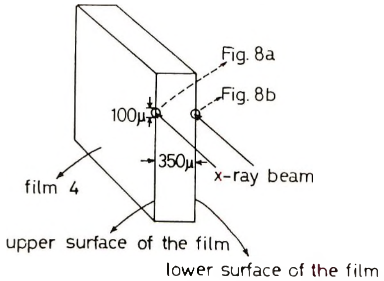


Fig. 10. Sketch of the film position for x-ray diffraction (film 4).

decrease of $-\Delta n_{ss}$ on stretching to some extent ($1/\sqrt{v_A} = 0.3$–0.4). Then deformation of type 5 occurs as previously stated in all cases. Further studies are required on the relationship between the orientation of molecular chains and that in the crystal.

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Vapor-Phase Graft Copolymerization of Vinyl Chloride and Vinylidene Chloride onto Polypropylene Fibers by Simultaneous Irradiation Technique

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Synopsis

The vapor-phase graft copolymerization of vinyl chloride and vinylidene chloride onto polypropylene fibers was studied by a simultaneous γ-irradiation technique. The weight increase during irradiation due to the grafting in monomers at constant vapor pressure was measured by a sensitive spring balance. The sorption of both monomers onto unirradiated polypropylene fibers was also measured. The graft copolymerization reaction was suppressed with increasing irradiation temperature, and the overall activation energies of grafting were negative in both monomers, -2.4 kcal/mole for vinyl chloride and -6.3 kcal/mole for vinylidene chloride. The initial rate of grafting increased linearly with the vapor pressure of monomers. The above dependence was found to parallel the sorption of monomers on polypropylene fibers. The reaction rates were proportional to the 0.9 power of the dose rate in both monomers. The relationship between the grafting and the sorption of monomers was discussed on the basis of kinetics.

INTRODUCTION

In recent years numerous studies on the radiation graft copolymerization of vapor-phase monomers have been reported. Both with simultaneous irradiation grafting and by preirradiation grafting techniques, the behavior of gaseous monomer toward a backbone polymer is thought to play an intrinsically important role; that is, the sorption and diffusion of monomer into the backbone polymer may affect and even control the graft copolymerization and may complicate the grafting process, depending on such experimental conditions as the dose rate, the reaction temperature, and the vapor pressure of monomer.

In addition, the vapor-phase graft copolymerization will be affected by the solubility of the grafted branch in its monomer.

Recently Kachan[1] has suggested a "shock mechanism" to explain the difference between the rate of sorption and the rate of grafting; Takamatsu et al.[2] also have discussed the kinetic feature of grafting reaction with respect to the sorption of monomer.

We have previously investigated the graft copolymerization of vinyl chloride and vinylidene chloride on γ-preirradiated polypropylene fibers by measuring the volume decrease of monomers continuously with the automatic recording device; we observed a parallel relationship between the sorption and the rate of grafting.[3] These systems seemed to be fairly simple, as the grafted branches have no ability to swell in their own monomers.

The present paper deals with simultaneous γ-irradiation graft copolymerization in the same monomer–polymer system. A spring balance method was used to elucidate the complicated features of vapor-phase graft copolymerization. The correlation between the grafting and sorption of monomers is discussed.

EXPERIMENTAL

Material

The polypropylene employed in the experiment was in the form of 5-den fibers (molecular weight, 45000), supplied by Toa Spinning Co. Ltd. The diameter of the monofilament was 0.025 mm and the surface area was calculated to be 0.15 m^2/g. The fibers were subjected to Soxhlet extraction with tetrahydrofuran for 8 hr, dried in air at room temperature, and stored over anhydrous calcium chloride.

Vinylidene chloride was obtained from Tokyo Kasei Industrial Co. Ltd. The gaseous monomer was condensed by the use of liquid nitrogen trap into a monomer reservoir attached to the vacuum line after being dried through anhydrous calcium chloride, and a freeze–thaw cycle was carried out to remove any contaminating air. The degassed monomer was run to an automatic pressure regulating apparatus (the reaction vessel, Fig. 1) for reaction.

Vinyl chloride was supplied by Toa Synthetic Co. Ltd. and treated by the same way as vinylidene chloride.

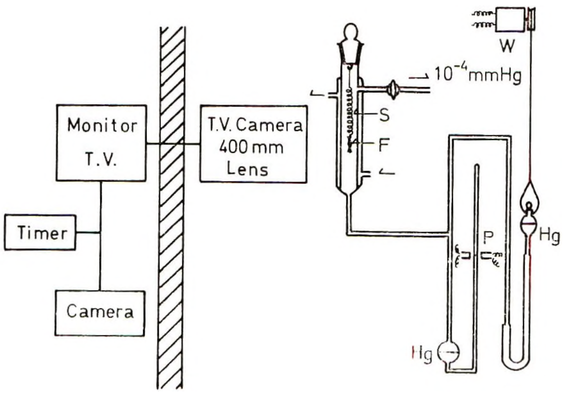

Fig. 1. Automatic measuring apparatus.

Simultaneous Graft Copolymerization in the Automatic Apparatus

The whole assembly used for simultaneous grafting with γ-radiation is shown diagrammatically in Figure 1. The graft copolymerization was carried out with a spring balance method. About a 70-mg bundle of polypropylene fibers (F) was suspended from a phosphor-bronze spring prepared as described below, and dried under reduced pressure for 15 min. Equilibrium of the balance was achieved in about 10 min. The monomer was then introduced into the apparatus and the system was allowed to stand for 20 min to complete the sorption of monomer before irradiation with γ-rays from a ^{60}Co source. The temperature of the irradiation cave was kept at 25 ± 0.5°C. The spring (S) used, a roll of 80 windings and a diameter of 13 mm, was made of 0.1 mm phosphor-bronze wire (Mitsubishi Electric Co. Ltd.) and had a sensitivity of 0.95 mg/mm. at 25°C.

The temperature of irradiation of polypropylene fibers was adjusted by circulating the thermoregulated water through the outer cylinder of the reaction tube. The monomer pressure was kept constant during the grafting reaction by controlling the height of mercury head by use of a combination of a photorelay (P) and a winch (W). In this device, the decrease in volume of monomer owing to the consumption by the grafting reaction and possible gas-phase homopolymerization was continuously compensated by the work of the winch, which diminished the internal volume of reaction system to restore the initial pressure by changing the level of the mercury reservoir.

The change in the length of the spring balance during the grafting was followed by use of a television camera which was equipped with a 400-mm telescopic lens. The image on the television monitor was photographed at given intervals. At the end of reaction, the reaction apparatus was again joined to the vacuum line, which removed all the unreacted monomers from the fibers. After 15 min evacuation, air was introduced and the weight of fibers was determined gravimetrically. The percentage of grafting was expressed as the ratio of the weight increase to the weight of the original polymer P_0.

$$\text{Percentage of grafting} = 100(P - P_0)/P_0$$

In several instances the occluded homopolymers were eliminated from the grafted fibers by extraction with hot tetrahydrofuran for 12 hr; results are shown in Table I. The vinylidene chloride-grafted polymers were discolored light-brown by hot tetrahydrofuran extraction. The sorption of monomers on unirradiated and grafted polypropylene fibers was measured by using cathetometer under the same conditions in the above apparatus. The percentage of sorption was calculated as the ratio of the weight increase to the weight of the original polymer:

$$\text{Percentage of sorption} = 100\ (A - A_0)/A_0.$$

TABLE I
Occluded Homopolymer Determined by Extraction with Hot Tetrahydrofuran

Monomer	Irradiation temperature, °C	Dose rate × 10^{-4}, rad/hr	Irradiation time, hr	Weight increase, %	Percentage of occluded homopolymers in total weight increase, %
Vinyl chloride	40	3.2	23.0	11.6	39.7
	50	3.2	20.5	7.7	27.7
	55	3.2	19.5	4.5	23.1
	25	2.6	22.4	42.0	29.6
Vinylidene chloride	40	0.66	19.6	16.6	28.1
	50	1.2	20.3	8.7	14.7

RESULTS

Sorption of Monomers by Polypropylene

The sorption of monomers by unirradiated polypropylene fibers at different temperatures is shown in Figure 2. In both monomers the amount sorbed approached an equilibrium value within about 20 min, whereas the equilibrium sorption decreased with increasing temperature. In spite of the fact that the pressure of vinyl chloride monomer is higher than that of vinylidene chloride the rate of sorption as well as the equilibrium percentage of sorption is lower for vinyl chloride.

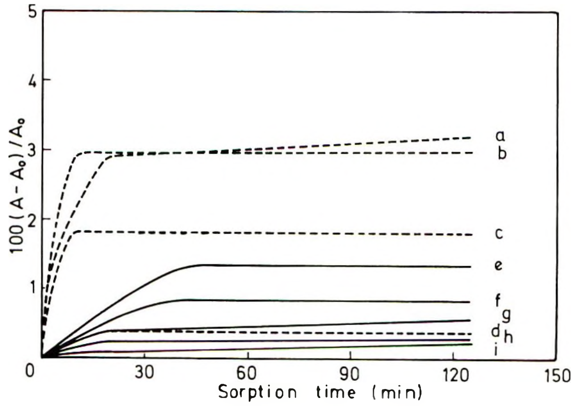

Fig. 2. Sorption of monomers (——) vinyl chloride at 560 mm Hg and (– –) vinylidene chloride at 210 mm Hg on polypropylene fibers at various temperatures: (*a*), (*f*) 25°C; (*b*), (*g*) 40°C; (*c*), (*h*) 50°C; (*d*), (*i*) 70°C; (*e*), 0°C.

Monomer absorbed into polymer can be easily removed under vacuum and the original weight recovered. The rough figures for diffusion coefficients and activation energies of diffusion are shown in Table II.

TABLE II
Sorption and Diffusion of Monomers into Polypropylene Fibers

Monomer	Vapor pressure, mm Hg	Temperature °C	Initial rate of sorption, %/min	Diffusion coefficient $\times 10^9$, cm²/min[a]	E_D, kcal/mole	Initial rate of grafting %/min
Vinyl chloride	560	0	0.06	5.4	9.7	—
	560	25	0.15	33		0.023
Vinylidene chloride	210	16	0.44	9.4	8.1	
	210	25	0.59	20		0.015
	210	50	0.41	33		0.0049

[a] Calculated from the tables prepared by Crank.[9]

Effect of Grafting Temperature

Figures 3 and 4 show the results of grafting at various irradiation temperatures. The rate of grafting decreased with increasing irradiation temperature. At high irradiation temperatures in vinylidene chloride a slight acceleration was observed with increasing irradiation time. The initial rates of sorption and those of grafting obtained from Figures 2–4 are compared in Table II. The initial rate of sorption of monomers is much more rapid than the initial rate of grafting. Consequently, under the conditions of this experiment the monomer is rapidly supplied into polypropylene fibers at a rate much greater than the consumption by grafting. An Arrhenius plot of initial rates of grafting and the amounts of monomer sorbed at equilibrium at constant pressures (560 mm Hg for vinyl chloride and 210 mm Hg for vinylidene chloride) are shown in Figure 5. The equilibrium sorption showed behavior similar to the initial rate of grafting regarding the temperature dependence.

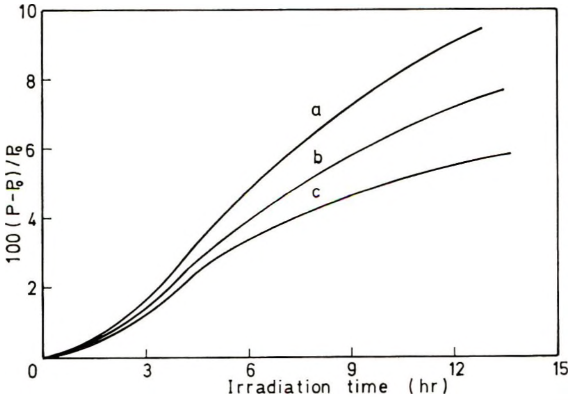

Fig. 3. Grafting of vinyl chloride at various temperatures: (*a*) 30°C; (*b*) 40°C; (*c*) 50°C. Vinyl chloride, 560 mm Hg; dose rate, 3.2×10^4 rad/hr.

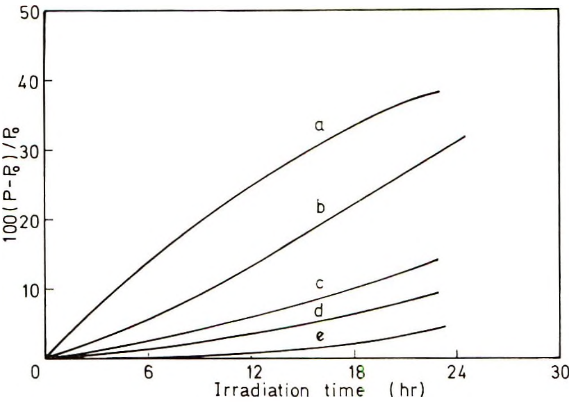

Fig. 4. Grafting of vinylidene chloride at various temperatures: (*a*) 0°C; (*b*) 25°C; (*c*) 39°C; (*d*) 50°C; (*e*) 70°C. Vinylidene chloride, 210 mm Hg; dose rate, 1.2×10^4 rad/hr.

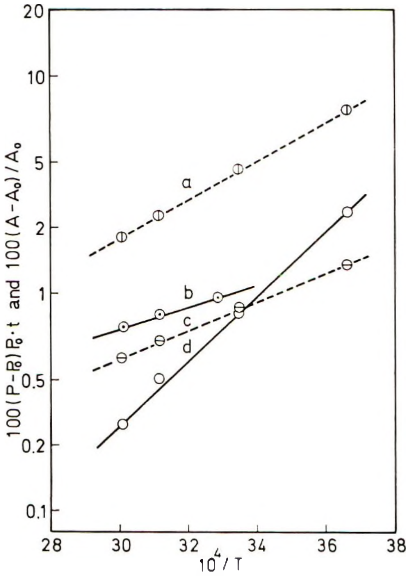

Fig. 5. Effect of irradiation temperature on (——) the rate of grafting and on (- -) equilibrium sorption on unirradiated polypropylene; (*b*, *c*) vinyl chloride at 560 mm Hg; (*a*, *d*) vinylidene chloride at 210 mm Hg. Irradiation dose rate, 3.2×10^4 rad/hr for vinyl chloride; 1.2×10^4 rad/hr for vinylidene chloride.

The overall activation energy of the grafting reaction was −2.4 kcal/mole for vinyl chloride and −6.3 kcal/mole for vinylidene chloride.

Effect of Vapor Pressure of Monomers

The grafting reactions at various vapor pressures of monomers are shown in Figures 6 and 7. In both cases the initial rate of grafting increased with the increase of vapor pressure of monomers. However, the weight increase

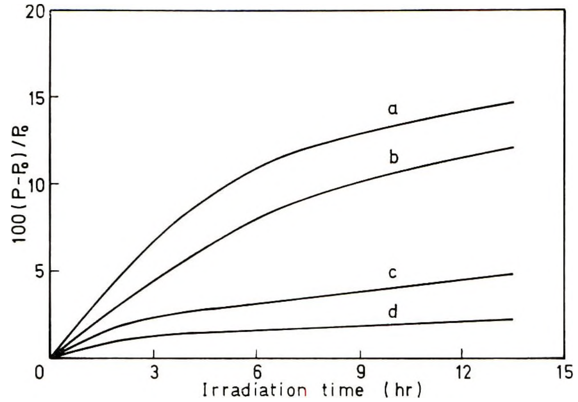

Fig. 6. Grafting of vinyl chloride at various vapor pressures: (*a*) 760 mm Hg; (*b*) 560 mm Hg; (*c*) 360 mm Hg; (*d*) 200 mm Hg. Dose rate, 3.2 × 10^4 rad/hr at 25°C.

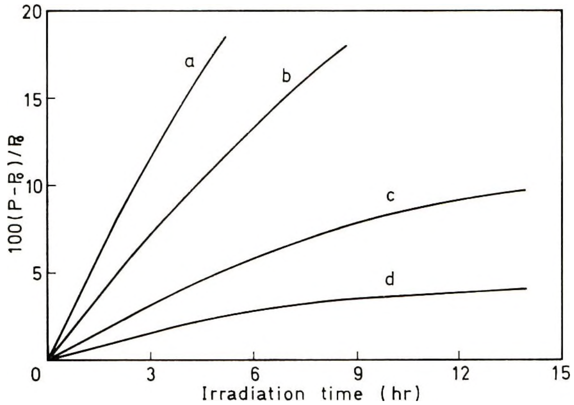

Fig. 7. Grafting of vinylidene chloride at various vapor pressures; (*a*) 340 mm Hg; (*b*) 210 mm Hg; (*c*) 100 mm Hg; (*d*) 50 mm Hg. Dose rate, 2.6 × 10^4 rad/hr at 25°C.

became less steep with increasing irradiation time, especially in vinyl chloride grafting. In each case the initial rate of grafting obeyed a strict first-order relationship with the pressure of monomer, as is seen in Figure 8. If the rate of grafting depends on the concentration of monomer in the fibers, it should be closely related to the amount of monomer sorbed at equilibrium at a given temperature. The relationship between the equilibrium sorption of vinyl chloride and vinylidene chloride and the vapor pressures of monomers represented by the broken line in Figure 8 parallels the above-mentioned dependence of grafting rate on the vapor pressure.

Effect of γ-Ray Dose Rate

The graft copolymerization reaction at various intensities is shown in Figures 9 and 10. The rate of grafting increased with increasing dose rate. The grafting rate decreased gradually above 50% grafting at the higher dose

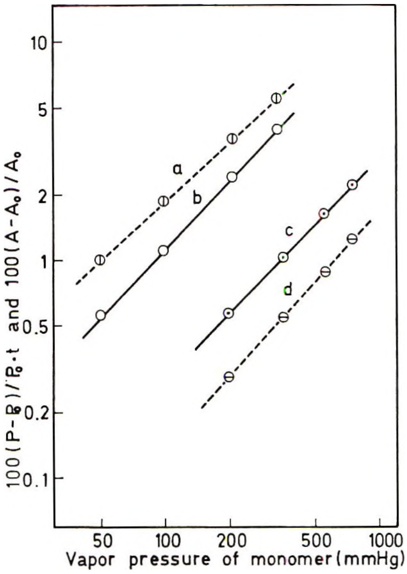

Fig. 8. Effect of monomer vapor pressure on (——) the rate of grafting and on (– –) equilibrium sorption on the unirradiated polypropylene: (*a,b*) vinylidene chloride at 25° C; (*c,d*) vinyl chloride at 25°C. Irradiation dose rate, 3.2×10^4 rad/hr for vinyl chloride; 2.6×10^4 rad/hr for vinylidene chloride.

rate, while it began to diminish below 10% grafting at the lower dose rate in vinylidene chloride. The effect of intensity on the initial rate of grafting was plotted in Figure 11. The rate of grafting is seen to correspond to a 0.9 power dependence on the γ-ray intensity with both monomers.

Post-irradiation graft copolymerization was observed, as is shown in Figure 10, when the fibers were subjected to the grafting reaction for 6 hr at 1.2×10^4 rad/hr, and allowed to stand; this indicates the presence of long-lived polymer radicals in the fibers.

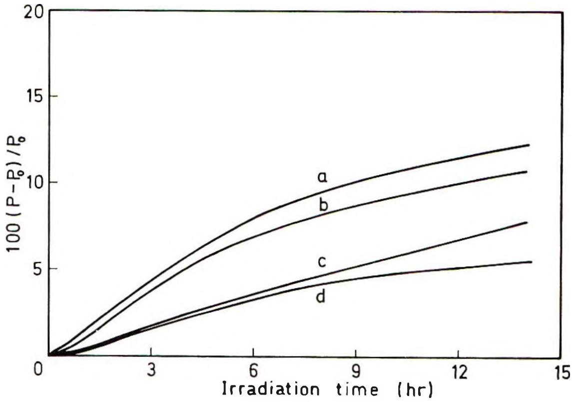

Fig. 9. Grafting of vinyl chloride at various dose rates: (*a*) 3.2×10^4 rad/hr; (*b*) 2.6×10^4 rad/hr; (*c*) 1.2×10^4 rad/hr; (*d*) 0.9×10^4 rad/hr.

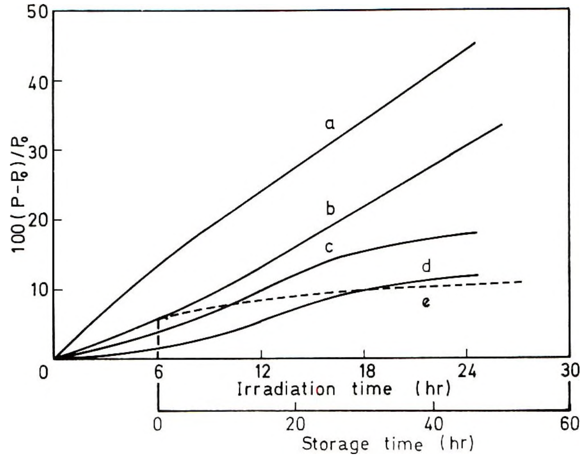

Fig. 10. Grafting of vinylidene chloride at various dose rates and the effect of storage after irradiation: (*a*) 2.6 × 10^4 rad/hr. (*b*) 1.2 × 10^4 rad/hr. (*c*) 0.66 × 10^4 rad/hr; (*d*) 0.21 × 10^4 rad/hr; (*e*) shows the increase in weight of fibers during storage after irradiation. Vinylidene chloride, 210 mm Hg; irradiation and storage temperature, 25°C.

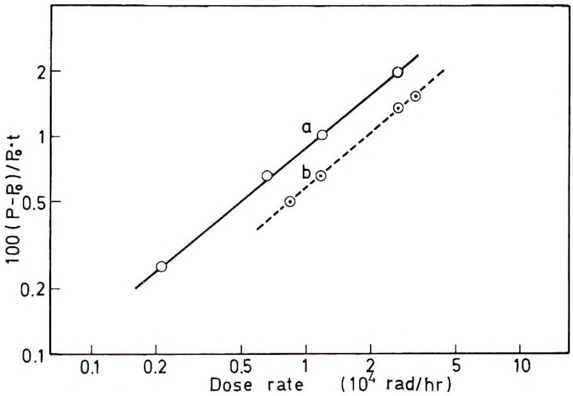

Fig. 11. Effect of dose rate on the rate of grafting: (*a*) vinylidene chloride at 210 mm Hg; (*b*) vinyl chloride at 560 mm Hg. Irradiation temperature, 25°C.

DISCUSSION

In the grafting experiment by the simultaneous technique, an increase in weight of polypropylene fibers, as observed by the spring balance method, is brought about by an increase in amount of grafting and also by possible homopolymerization. In addition, the measurement should reflect the change of amount of monomer sorbed with the accumulation of grafted polymer. In our previous experiment on the vapor-phase graft copolymerization of methyl methacrylate onto polypropylene fibers,[5] the rate of sorption as well as the amount of monomer absorbed increased markedly with the increase of the percentage of grafting, as the monomer is able to dissolve its homopolymer and the grafted branch. Unlike the case of methyl methacrylate, the equilibrium sorption amounts in the case of vinyl chloride or vinylidene chloride rather tend to decrease with the increasing amount of the grafted branch and the homopolymer. For example, the amount of monomer sorbed decreased from 0.8% to 0.3% at 11.3% grafting in vinyl chloride, and from 3% to 1.5% at 16.6% grafting in vinylidene chloride. However, because of the low solubility of both monomers in polypropylene, it is not oversimplification to ignore the change of sorption amount.

We did not observe gas-phase homopolymerization of either monomer under the conditions adopted for our experiments. However, an appreciable amount of homopolymer is likely to be occluded in the fibers, as is seen in Table I. The extraction method is not necessarily considered adequate for the estimation of the occluded homopolymer, because the vinylidene chloride-grafted fibers showed brown discoloration when extracted with hot tetrahydrofuran. It is impossible to eliminate the contribution of occluded homopolymer from our estimate of grafting in each instant, but we may assume that the occluded homopolymer occupied a fairly constant fraction in the nominal weight increase.

The surface area of the polypropylene fibers is nearly 0.15 m^2/g, and the quantity of monomer physically adsorbed on the surface will correspond to less than 0.1 wt-% of the original fibers, if the monomolecular layer formation is assumed. Therefore Figure 2 seems to reflect largely the process of monomer diffusion into the polymer. The overall diffusion constants shown in Table II roughly coincides in the order with the values presented by Kachan et al.[7] and Kurilenko et al.[8]

The monomers are considered to be rapidly diffusible, and almost all the monomer sorbed into polypropylene fibers was desorbed very easily. Accordingly, the grafting reaction in this experiment is supposed to proceed under the condition where the sorption equilibrium of monomers is always accomplished (Table II).

The amount of monomer sorbed on the polypropylene fibers at equilibrium is proportional to the vapor-pressure of the monomer, as is shown in Figure 8, which indicates the establishment of a distribution law between the vapor-phase and the fibers or which shows that the monomer exists in a dispersed state in the fibers as a result of diffusion. From thermodynamic considerations the following relationship will be applicable:

$$[M]_f/[M]_v = e^{-\Delta\mu_0/RT} = \text{const.}$$

where $[M]_f$ and $[M]_v$ denote the concentration of monomer in the fibers and in the vapor-phase, respectively, and $\Delta\mu_0$ is the difference of the standard chemical potentials.

Throughout this experiment the rate of grafting seems to keep a close relationship with the equilibrium sorption amount, because the concentration of monomer in the reaction site is defined by the absorbed amount of monomer. In general, the rate of grafting decreased gradually with increasing irradiation time, except in the high temperature experiments on vinylidene chloride. The decrease in sorption amount with the increase in the amount of the grafted branch is partly responsible for this phenomenon.

The mechanism of the grafting is far from our understanding at present, but as a crude approximation one may write eqs. (1)–(5) for various steps in the grafting reaction when bimolecular termination is assumed.

Initiation:

$$\mathrm{P\ or\ M} \overset{\gamma}{\rightsquigarrow} \mathrm{P\cdot\ or\ M\cdot} \tag{1}$$

$$\mathrm{P\cdot} + \mathrm{M} \rightarrow \mathrm{PM\cdot} \tag{2}$$

Propagation:

$$\mathrm{PM}_n\cdot \text{ or } \mathrm{M}_n\cdot + \mathrm{M} \xrightarrow{k_p} \mathrm{PM}_{n+1}\cdot \text{ or } \mathrm{M}_{n+1}\cdot \tag{3}$$

Termination:

$$\mathrm{M}_n\cdot + \mathrm{M}_m\cdot \xrightarrow{k_{t2}} \text{occluded homopolymer} \tag{4}$$

$$\mathrm{PM}_n\cdot \text{ or } \mathrm{M}_n\cdot + \mathrm{PM}_m\cdot \xrightarrow{k_{t2}} \text{graft copolymer} \tag{5}$$

Here P and $P\cdot$ represent the polypropylene polymer and its radical, M and M$\cdot$ the monomer and its radical, respectively; $\mathrm{PM}_n\cdot$, $\mathrm{PM}_{n+1}\cdot$, $\mathrm{PM}_m\cdot$ are graft copolymer radicals; $\mathrm{M}_n\cdot$, $\mathrm{M}_{n+1}\cdot$, $\mathrm{M}_m\cdot$ are the occluded homopolymer radicals, and k_p and k_{t2} are the rate constants for propagation and bimolecular termination, respectively. Introducing the conventional steady-state assumption, one obtains eq. (6) for the rate of grafting R_g which includes the rate of formation of occluded homopolymer,

$$R_g = k_p k_{t2}^{-1/2} \phi_p [\mathrm{P}]^{1/2} I^{1/2} [\mathrm{M}] \tag{6}$$

where $\phi_p[\mathrm{P}]$ is the rate of production of free radicals in the polymer, and I is the dose rate.

In another extreme case, if the polymer radical terminates solely by a monomolecular mechanism, say, by immobilization owing to the radical burial, as has often been postulated,[6] we have eqs. (7) and (8) for termination

Termination:

$$\mathrm{M}_n\cdot \xrightarrow{k_{t1}} \text{occluded homopolymer} \tag{7}$$

$$\mathrm{PM}_n\cdot \xrightarrow{k_{t1}} \text{graft copolymer} \tag{8}$$

The rate of grafting should then be given by eq. (9).

$$R_g = k_p k_t^{-1} \phi_p [\mathrm{P}] I [\mathrm{M}] \tag{9}$$

In the system where both mechanisms are operative, the rate of grafting will be proportional to [M], that is, to the vapor pressure of monomer, and also to $I^{0.5-1}$. The intensity exponents obtained are considerably higher than those in liquid-phase polymerization.[6] This presumably suggests that the one-center termination mechanism is predominant in this system.

Because [M] itself is temperature-dependent, the apparent activation energy of grafting from Figure 5 includes the contribution of the monomer concentration. The overall activation energies of grafting thus calculated by eliminating the contribution of the monomer concentration were −0.6 kcal/mole for vinyl chloride and −2.1 kcal/mole for vinylidene chloride.

Introduction of the rare gases such as helium and argon into the reaction system did not affect the rates of grafting.

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Photodecomposition of Polymethylsiloxane

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Synopsis

Infrared spectroscopy studies were undertaken to determine the effects of ultraviolet light radiation on a methylsiloxane resin. The results indicate that $SiCH_2Si$ linkages were formed as a result of irradiation at wavelengths above 281 mμ from a xenon arc lamp; on the other hand, Si—OH and $SiCH_2CH_2Si$ linkages were formed instead when the resin was exposed to the lower wavelengths emitted from a mercury vapor lamp. The different effects on the resin induced by the two ultraviolet light sources are attributed to the fact that only the energies from the mercury vapor lamp radiation are sufficient to cause the excitation of oxygen molecules in the air surrounding the irradiated polymer. The excited oxygen molecules prevented the formation of $SiCH_2Si$ structures by interacting with active $\equiv Si^{\cdot}$ units that were formed as a result of Si—C bond rupture to produce Si—OH; $SiCH_2CH_2Si$ linkages were formed as the result of a secondary reaction.

INTRODUCTION

Polysiloxanes are widely employed as protective surface coatings for a variety of specialized applications. Because they have been shown to be highly water repellent and their moisture absorption is generally very low, polysiloxanes have been designed for use as deicing coatings. For example, Baker and co-workers[1] developed a low-torque semifluid polysiloxane grease which was compatible with oil-resistant rubber and resisted the anchorage of ice. Spawn[2] found that a 0.1% polysiloxane solution in the top coat of a refrigerator gave a 30–40% improvement in runoff of water. Andrianov et al.[3] reported that the adhesion of ice to rubber, plastics, and aluminum surfaces coated with varnish was reduced by the application of a film of methyl, ethyl, or isoamyl polysiloxane. More recently, it has been shown that the durability of the ice-phobic effectiveness of polysiloxanes is limited to only short time periods because of the degradation of the coating by solar radiation.[4] To obtain a better understanding of this phenomenon, a study was undertaken to determine the effects of accelerated weathering on the molecular structure of a polysiloxane resin. Preliminary findings of this study were presented previously;[4] results are reported in more detail in this article.

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EXPERIMENTAL

Material

The methylsiloxane resin employed in this investigation was prepared by evaporating the solvent from a xylene solution containing a mixture of methyltrimethoxysilane and cyclic dimethylsiloxane polymers, $[(CH_3)_2\text{-}SiO]_{4-10}$, having an average molecular weight of approximately 370. Methyltrimethoxysilane hydrolyzed in moist air to form a methylsiloxane network that entrapped the cyclic polymer in the resin matrix.

Accelerated Weathering

Films of the resin on potassium bromide optical crystals were mounted vertically in an Atlas Electric Products Company Weather-Ometer that was modified by replacing the usual twin-carbon arcs with a 6000-W xenon lamp. The samples were exposed for preselected time intervals up to about 1500 hr. To obtain information about the effects of shorter ultraviolet wavelengths on the methylsiloxane polymer, similar resin films on sodium chloride infrared optics were exposed for time periods up to 355 hr to the radiation emitted from a General Electric Company, type G4S11, 4-W germicidal lamp placed 1 in. above the specimens.

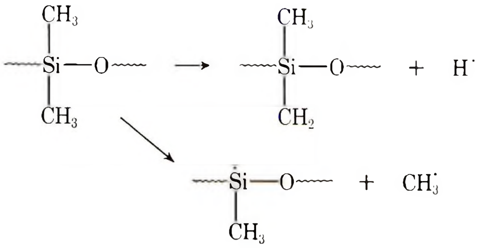
Infrared Spectroscopy

The samples coated on potassium bromide optics were measured over the 2.5–25.0 μ range with a Perkin-Elmer, Model 337, grating spectrophotometer. Infrared absorption spectra of the films cast on sodium chloride crystals were obtained over the 2.5–15.0 μ region with a Perkin-Elmer, Model 137 prism spectrophotometer.

RESULTS

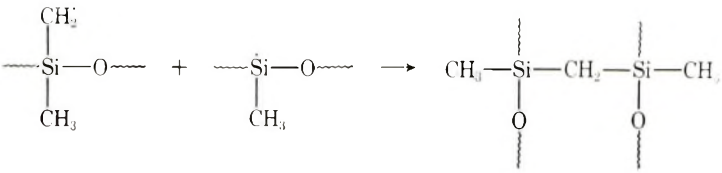
Xenon Arc Lamp Radiation

The infrared spectra of the resin before and after 1524 hr of exposure to the xenon lamp are presented in Figure 1. These data show that, except for the new absorption band appearing at 7.3 μ in the spectrum from the irradiated resin, the spectra are alike. The absorbance at 7.3 μ indicates the presence of $SiCH_2Si$ linkages in the irradiated sample,[5] which may have formed as a result of C—H and Si—C bond cleavage.



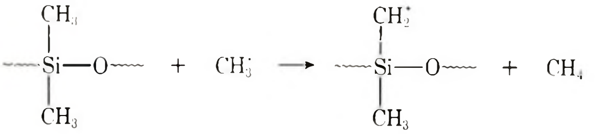
$$\sim\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}-O\sim \longrightarrow \sim\underset{CH_2}{\overset{CH_3}{\mathrm{Si}}}-O\sim + H^{\cdot} \qquad (1a)$$

$$\sim\underset{CH_3}{\dot{\mathrm{Si}}}-O\sim + CH_3^{\cdot} \qquad (1b)$$



$$\sim\!\!\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2^{\cdot}}{\mathrm{Si}}}\!-\!O\!\sim + \sim\!\!\underset{\displaystyle CH_3}{\overset{\cdot}{\mathrm{Si}}}\!-\!O\!\sim \;\longrightarrow\; CH_3\!-\!\underset{\displaystyle \overset{|}{O}}{\overset{|}{\mathrm{Si}}}\!-\!CH_2\!-\!\underset{\displaystyle \overset{|}{O}}{\overset{|}{\mathrm{Si}}}\!-\!CH_3 \qquad (1c)$$

It is also possible that the $\equiv SiCH_2^{\cdot}$ radical formed because $CH_3^{\cdot}$ abstracted a hydrogen atom from a methyl group on the same or a neighboring molecule. Bovey[6] indicates that this is the main reaction when methylsiloxane polymers are initially exposed to high-energy radiation. It is suspected from the ultraviolet radiation studies of Zhuzhgov and co-workers[7] that reactions (1) and (2) probably occur concurrently.



$$\sim\!\!\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\mathrm{Si}}}\!-\!O\!\sim + CH_3^{\cdot} \;\longrightarrow\; \sim\!\!\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2^{\cdot}}{\mathrm{Si}}}\!-\!O\!\sim + CH_4 \qquad (2)$$

Of course, it is conceivable that the reactive decomposition products could have combined to produce Si—H, $Si—CH_2CH_3$, $Si—CH_2CH_2$-Si, and Si—Si structures. The absence of new absorption bands for the first three structures at 4.4–4.8,[8] 13.5–13.6,[9] and 8.85 μ,[10] respectively, indicates that such molecular configurations were not formed when the polymer was exposed to radiation from the xenon arc lamp. Since the vibration modes of Si—Si bonds do not occur in the 2.5–25.0 μ region of the infrared spectrum, it cannot be ascertained from these data whether such linkages were produced during the irradiation process. It might be inferred from the studies by Miller,[5] however, who did not observe the formation of Si–Si crosslinks after exposing methylsiloxanes in the solid state to high-energy radiation, that such linkages were also not produced by the xenon arc lamp.

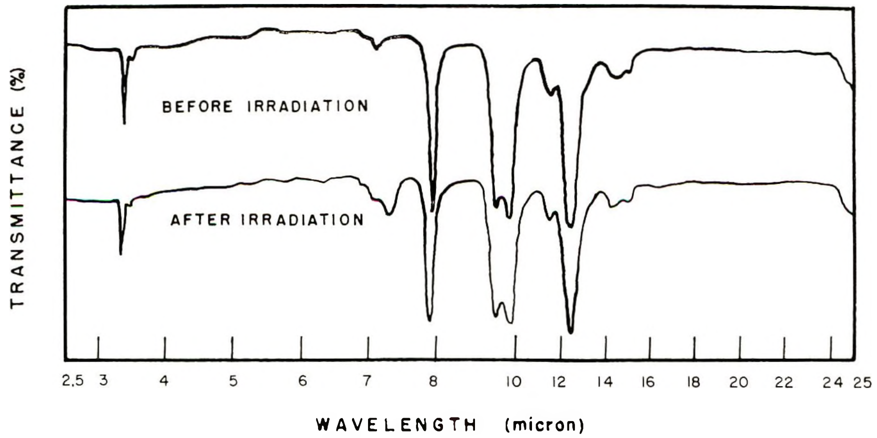


Fig. 1. Infrared spectra of untreated and xenon arc lamp-irradiated resin.

Figure 2 shows the change in intensity of the 7.3 μ absorption band as a function of time. It is evident from these data that the growth of $SiCH_2Si$ bonding is directly proportional to the amount of irradiation. Zhuzhgov and co-workers,[7] employing electron spin resonance (EPR) techniques, found that $CH_3\cdot$ and $\equiv SiCH_2\cdot$ radicals are produced in a linear relation to the radiation dose when polymethylphenylsiloxane is initially exposed to an ultraviolet light source. Although they were unable to detect the presence of $\equiv Si\cdot$ radicals in the EPR spectra of the polymer, they suggest that its absence is probably due to the occurrence of a reaction involving the recombination of radicals. It seems reasonable to assume from this study that the recombination occurred as shown in reaction (1c), wherein a $\equiv Si\cdot$ fragment interacted with a $\equiv SiCH_2\cdot$ radical that was produced as a result of ultraviolet radiation induced C—H bond rupture or through the abstraction of hydrogen from $\equiv SiCH_3$ by a $CH_3\cdot$ radical.

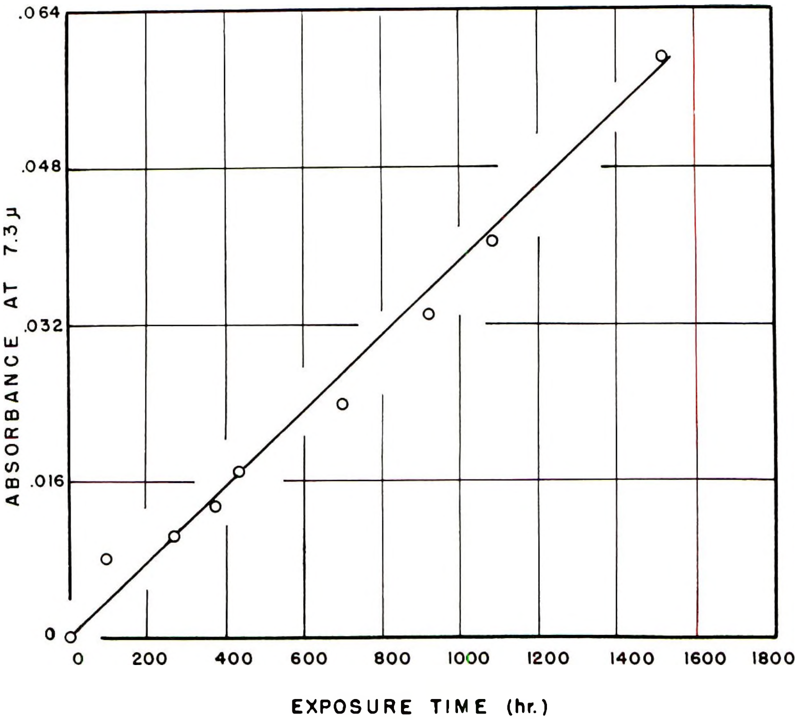


Fig. 2. Effect of irradiation on absorbance at 7.3 μ.

Mercury Vapor Lamp Radiation

The infrared spectra of the methylsiloxane resin, before and after 355 hr exposure to the ultraviolet wavelengths emitted from the mercury arc lamp, are presented in Figure 3. It is evident from a comparison of these data with the infrared spectra shown in Figure 1 that the resin underwent more structural changes due to exposure to the lower frequencies of ultraviolet radiation from the mercury vapor lamp than because of the higher wavelengths emitted by the xenon arc lamp.

The spectrum of the irradiated resin exhibits a new absorption mode at 3.0 μ that is associated with Si—OH bonding. The characteristic Si—CH_3 band at 7.94 μ appears to be less intense than in the spectrum from the original polymer. The strong Si—O frequencies in the 9–10 μ region are less sharp, particularly at 9.18 μ, and broader in the irradiated resin spectrum than in that from the untreated product. The Si—CH_3 band at 11.55 μ in the spectrum of the original polymer has been replaced by two absorption modes at about 11.15 and 11.75 μ that are attributed to the Si—OH structure.[8,11] The broad Si—CH_3 absorption band at 12.5 μ in the spectrum from the original polymer is much less intense and appears as a doublet at 12.5 and 12.78 μ in the spectrum of the irradiated resin. The band at 12.78 μ is probably associated with the Si—OH linkage.[12] The spectrum exhibited no evidence of the production of Si—H, $SiCH_2CH_3$, and $SiCH_2Si$ structures as a result of radiation from the mercury vapor lamp.

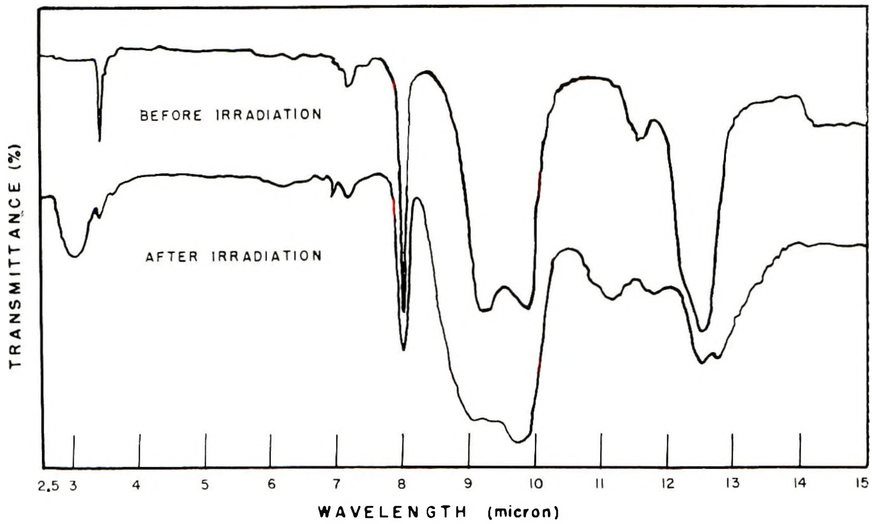


Fig. 3. Infrared spectra of untreated and mercury vapor lamp-irradiated resin.

Figure 4 shows the increase in the intensity of the 3.0 μ band as a function of irradiation time. It is evident from the results that the rate of production of Si—OH bonds was quite rapid at first and then leveled off in almost a linear manner. It is interesting to note that, as in the case of the 355-hr treated sample, the infrared spectrum of the resin after 50 hr exposure contained Si—OH vibration modes at 11.15 and 11.75 μ instead of the Si—CH_3 band at 11.55 μ in the original polymer spectrum.

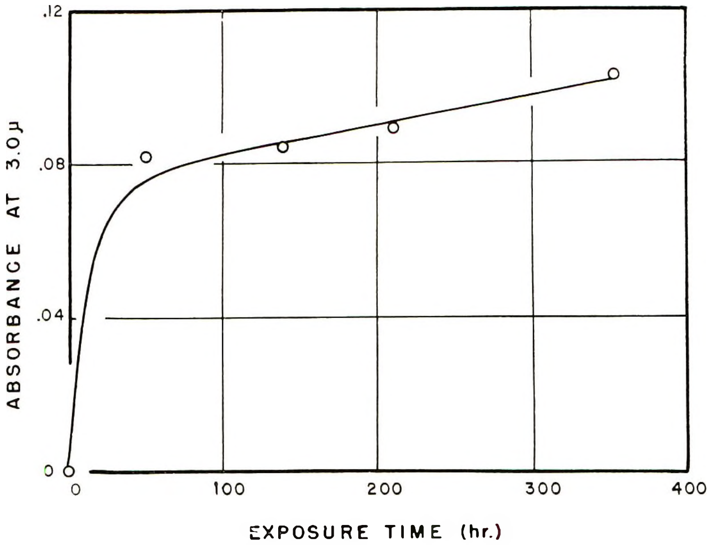
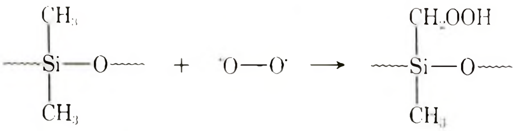


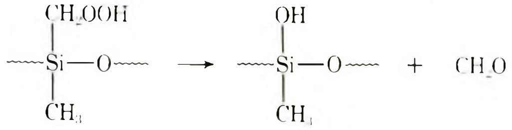
Fig. 4. Effect of irradiation time on absorbance at 3.0 μ.

The silanol structure might have formed because of the ultraviolet radiation-induced oxidation and cleavage of methyl groups [eqs. (3)].

$$O_2 \xrightarrow{h\nu} {}^{\cdot}O{-}O^{\cdot} \qquad (3a)$$



$$\sim\!\underset{CH_3}{\overset{CH_3}{Si}}{-}O\!\sim \; + \; {}^{\cdot}O{-}O^{\cdot} \longrightarrow \; \sim\!\underset{CH_3}{\overset{CH_2OOH}{Si}}{-}O\!\sim \qquad (3b)$$



$$\sim\!\underset{CH_3}{\overset{CH_2OOH}{Si}}{-}O\!\sim \; \longrightarrow \; \sim\!\underset{CH_3}{\overset{OH}{Si}}{-}O\!\sim \; + \; CH_2O \qquad (3c)$$

This series of decomposition reactions explains, at least partially, why the Si—CH_3 absorption band at 7.94 μ was less intense after irradiation of the resin. Figure 5 shows the change of intensity at 7.94 μ in relation to radiation time. The shape of the curve is the converse of that shown in Figure 4 for the intensity of the 3.0 μ absorbance of the Si—OH structure; the intensity of the Si—CH_3 band decreased rapidly during the initial 50 hr of radiation and then the rate fell off during the remainder of the exposure period.

Kuzminskii and Goldovskii[13] indicate that Si—O bonds of the main chain rupture as a result of the accumulation of reactive groups from the oxidation of methyl pendant groups. Thus, it is possible that hydrogen ions, produced probably according to eq. (1a) could have combined with $\equiv$SiO· ions formed when main chains ruptured to give Si—OH. Bovey[6] indicates, however, that there is little, if any, rupture of Si—O bonds when high mo-

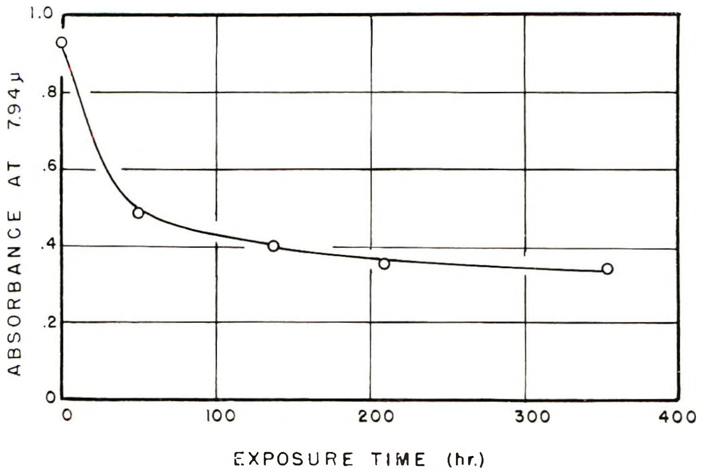
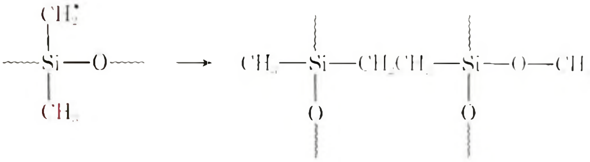


Fig. 5. Effect of irradiation time on absorbance at 7.94 μ.

lecular weight polysiloxanes are treated with high-energy radiation. It seems more reasonable, therefore, that Si—OH linkages were produced as shown in eqs. (3a)–(3c).

The decrease in sharpness and increase in width of the Si—O absorption frequency at 9.18 μ is probably due to an overlap of this band by new vibration modes that formed as a result of the decomposition of the methylsiloxane resin by radiation from the mercury vapor lamp. In this connection, Curry[10] notes that $SiCH_2CH_2Si$ groups give infrared absorptions at 8.85 and 9.5 μ that can be obscured if the structure is present in a symmetrical molecule or contains strong vibration modes from S—O bonds in the 9–10 μ region. The development of an 8.85 μ mode could account for the increase of half-width of the 9.18 μ frequency, while the 9.5 μ band might explain the decrease of sharpness.

Miller[5] as well as Dewhurst and St. Pierre[14] found that $SiCH_2CH_2Si$ crosslinks formed when polymethylsiloxanes were treated with high-energy radiation. Although several investigators[15–17] were unable to detect such crosslinks under similar conditions and they were not observed after the resin was exposed to radiation from the xenon arc lamp, infrared data suggest that they were produced as a result of the mercury vapor lamp treatment, probably as shown in eq. (4).



$$\sim\!\!\underset{CH_3}{\overset{CH_2^{\bullet}}{Si}}\!-\!O\!\sim \longrightarrow CH_3\!-\!\underset{\underset{\wr}{O}}{\overset{\wr}{Si}}\!-\!CH_2CH_2\!-\!\underset{\underset{\wr}{O}}{\overset{\wr}{Si}}\!-\!O\!-\!CH_3 \qquad (4)$$

Figure 6 shows the increase in the half-width of the 9.18 μ band with the time of radiation. Similar measurements made of the spectra from the resin sample irradiated by the xenon arc lamp showed no changes in the

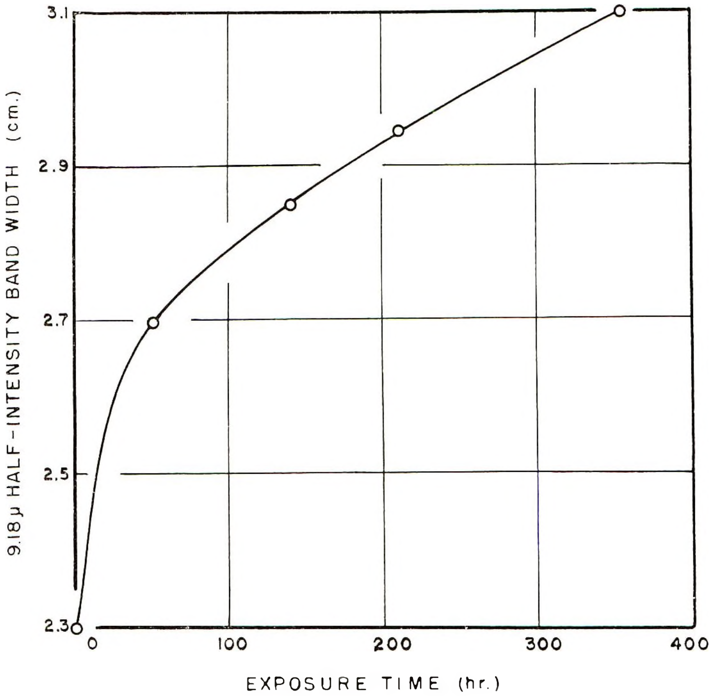
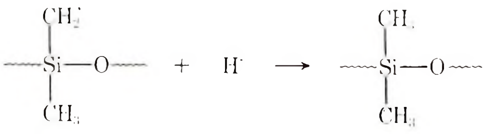


Fig. 6. Effect of irradiation time on 9.18 μ half-intensity band width.

half-width of this absorption mode. If the differences in the 9.18 μ band from the mercury vapor lamp treatment was due to the production of $SiCH_2CH_2Si$ crosslinks, then it is obvious from the results that the rate of formation of these structures decreased as the time of radiation increased. This is probably explained by the fact that the rate of $\equiv SiCH_2\cdot$ radicals that formed during ultraviolet light radiation decreased because of a reverse process [eq. (5)] that occurred concurrently.[7]



$$\sim Si(CH_2\cdot)(CH_3)-O\sim \; + \; H\cdot \longrightarrow \; \sim Si(CH_3)(CH_3)-O\sim \qquad (5)$$

DISCUSSION

It is well known that electronically excited states are created when ultraviolet light energy is absorbed by molecules. Burkhard and Winslow[18] have reported that methylsiloxanes exhibit absorption maxima at about 240–270 mμ.

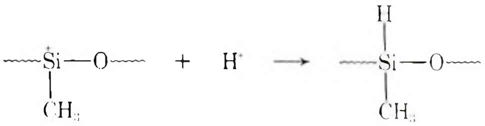
If the energy of excitation is equal to or higher than the bond dissociation energy of the weakest link in the molecule then cleavage reactions might occur. Because the absorbed energy might be transferred, however, the site at which the ultraviolet light is absorbed is not necessarily the same one where bond rupture might take place. The relation between the wavelength λ and absorbed energy is expressed by the Bohr equation:

$$E = 28.635 \times 10^3/\lambda \qquad (6)$$

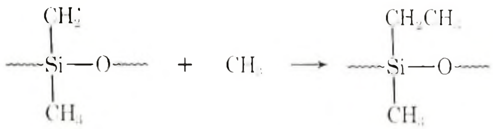
Table I lists the bond dissociation energies of linkages present in the methylsiloxane resin and the ultraviolet wavelengths, calculated from eq. (6), that are required for their rupture. Since this irradiation study was conducted in the presence of air, the list also includes oxygen.

The results of this study show that the polymethylsiloxane resin behaves differently when exposed to ultraviolet radiation emitted from a xenon arc or a mercury vapor lamp; the former light source produced SiCH_2Si linkages while the latter formed $\text{SiCH}_2\text{CH}_2\text{Si}$ and Si—OH structures. This is probably due to the fact that the xenon arc lamp employed in this study emitted light over a broad, continuous spectrum at wavelengths above 281 mμ that would furnish energies up to only about 102 kcal/mole. On the other hand, the mercury vapor lamp supplied ultraviolet radiation over the region of approximately 185–436 mμ with a very strong peak at 253.7 mμ, giving energies of about 66–155 kcal/mole from these wavelengths.

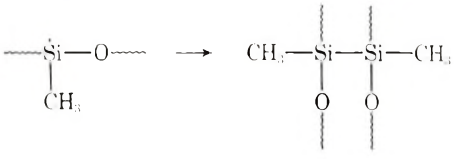
The energy of ultraviolet light from the xenon arc lamp is sufficient to rupture C—H and Si—C bonds as shown in eqs. (1a) and (1b). The reactive structures thus formed might conceivably undergo a number of different competitive reactions. For example, the $\equiv\text{Si}^{\cdot}$ and $\equiv\text{SiCH}_2^{\cdot}$ active structures may combine as shown in eq. (1c). The $\text{CH}_3^{\cdot}$ radical may abstract a hydrogen atom to form additional $\equiv\text{SiCH}_2^{\cdot}$ radicals and CH_4 as indicated in eq. (2). The $\equiv\text{SiCH}_2^{\cdot}$ radicals might interact to produce $\equiv\text{SiCH}_2\text{CH}_2\text{Si}\equiv$ linkages as shown in eq. (4). The hydrogen ions resulting from C—H rupture could undergo reaction with $\equiv\text{SiCH}_2^{\cdot}$ radicals as shown in eq. 5. Other reaction processes [eqs. (7)–(9)] should also be considered.



$$\sim\underset{\text{CH}_3}{\dot{\text{Si}}}\text{—O}\sim \;+\; \text{H}^{\cdot} \longrightarrow \sim\overset{\text{H}}{\underset{\text{CH}_3}{\text{Si}}}\text{—O}\sim \qquad (7)$$



$$\sim\overset{\text{CH}_2^{\cdot}}{\underset{\text{CH}_3}{\text{Si}}}\text{—O}\sim \;+\; \text{CH}_3^{\cdot} \longrightarrow \sim\overset{\text{CH}_2\text{CH}_3}{\underset{\text{CH}_3}{\text{Si}}}\text{—O}\sim \qquad (8)$$



$$\sim\underset{\text{CH}_3}{\dot{\text{Si}}}\text{—O}\sim \longrightarrow \text{CH}_3\text{—}\overset{|}{\underset{\underset{|}{\text{O}}}{\text{Si}}}\text{—}\overset{|}{\underset{\underset{|}{\text{O}}}{\text{Si}}}\text{—CH}_3 \qquad (9)$$

The infrared spectrum of the resin after irradiation by the xenon arc lamp only gave evidence of the production of $\equiv\text{SiCH}_2\text{Si}\equiv$ linkages. Although $\equiv\text{SiSi}\equiv$ bonds also might have formed, this is considered rather unlikely

TABLE I

Bond Dissociation Energies and Associated Ultraviolet Wavelengths

Bond	Dissociation energy E, kcal/mole	Wavelength λ, mμ
C—H (from CH_3)[18]	88	325
Si—C (from $SiCH_3$)[19]	73	392
Si—O[18]	185	155
O—O (from O_2)	118.9	243

because the methylsiloxane was exposed in the solid-state to the xenon arc lamp.[5]

To produce $\equiv SiCH_2Si \equiv$ structures it would be necessary to have both $\equiv Si^{\cdot}$ and $\equiv SiCH_2^{\cdot}$ active groups available to interact. If the radiation from the xenon arc lamp induced C—H bond rupture, and the $CH_3^{\cdot}$ radicals produced as a result of reaction (1b) abstracted hydrogen atoms from methyl groups as shown in eq. (2), then an excess of $\equiv SiCH_2^{\cdot}$ radicals would have been formed. Thus, the production of some $\equiv SiCH_2CH_2Si \equiv$ bonding should have been evident in the infrared spectrum of the irradiated resin. Of course, it is possible that any excess $\equiv SiCH_2^{\cdot}$ might have been consumed by the reversal reaction shown in equation 5. This is considered unlikely, since reactions (1a) or (2) and (5) would have to occur at the same rate to give the linear curve shown in Figure 2 for the increase of $SiCH_2Si$ units in relation to irradiation time. It seems more reasonable to postulate that the initial reaction induced by the radiation from the xenon arc lamp was Si—C bond rupture to form active $\equiv Si^{\cdot}$ and $CH_3^{\cdot}$ groups. Evidently, to accomplish this the resin investigated herein possessed absorbancies at higher frequencies than those reported by Burkhard and Winslow[18] for liquid methylsiloxanes. The $CH_3^{\cdot}$ radicals then abstracted hydrogen atoms from other methyl groups to produce active $\equiv SiCH_2^{\cdot}$ groups which in turn interacted with $\equiv Si^{\cdot}$ units to form $SiCH_2Si$ linkages.

Since the energies of the ultraviolet wavelengths supplied by the mercury vapor lamp were also adequate to produce the scission of Si—C and C—H bonds, other conditions must have existed during the radiation process which blocked the formation of $SiCH_2Si$ structures.

In this connection, it is interesting to note from Table I that the energies furnished by the mercury vapor lamp are in the range required to excite oxygen molecules in the air surrounding the irradiated resin. On the other hand, the energies released by the xenon arc lamp were insufficient for the excitation of oxygen molecules. This explains the formation of Si—OH bonds, probably by the reaction sequence shown in eqs. (3a)–(3c), during the mercury lamp radiation, and the lack of such structures resulting from the xenon arc lamp treatment.

Another possible result of the excitation of oxygen molecules by the energies from the mercury vapor lamp must also be considered. From the electronegativities of the elements involved,[20] it would be expected that the strongly electropositive silicon atom would react more readily with a strongly electronegative oxygen atom rather than with a less negative carbon atom. Hence, if the initial reaction induced by the radiation from the mercury vapor lamp was Si—C bond cleavage, as in the case of the xenon arc lamp, then the active $\equiv Si^{\cdot}$ groups thus formed would preferably seek to combine with excite odxygen molecules rather than with $\equiv SiCH_2^{\cdot}$ radicals. Thus, the active $\equiv Si^{\cdot}$ groups would be consumed, leaving the $\equiv SiCH_2^{\cdot}$ radicals to combine and form $SiCH_2CH_2Si$ linkages as in reaction (4).

$$\equiv Si + O^{\cdot}—O^{\cdot} \rightarrow \equiv Si—O—Si\equiv \tag{10}$$

Since no precautions were taken to eliminate moisture from the air surrounding the resin sample irradiated by the mercury vapor lamp, another possible explanation for the lack of formation of $SiCH_2Si$ structures might be that the active $\equiv Si^{\cdot}$ groups entered into a reaction with water vapor. Hydrogen ions thus produced might have combined to form hydrogen gas or interacted with $CH_3^{\cdot}$ or $\equiv SiCH_2^{\cdot}$ radicals to yield CH_4 and $\equiv SiCH_3$, respectively. The latter reaction may have contributed to the decrease in the rate of formation of $SiCH_2CH_2Si$ linkages as shown in Figure 6. It is interesting to note, however, that the ratio of the intensity of the Si–OH absorption mode to the half-width of the 9.18 μ band, connected with the formation of $SiCH_2CH_2Si$ linkages, in the spectra from the irradiated samples remained constant. This indicates that the number of Si–OH bonds formed during radiation was proportional to that of the $SiCH_2CH_2Si$ structure produced. It is unlikely that these reactions would have occurred in this manner if Si–OH bonds were produced as a result of the oxidation sequence shown in eqs. (3a)–(3c) as well as by the interaction of active $\equiv Si^{\cdot}$ units with water vapor. Furthermore, the reaction of $\equiv Si^{\cdot}$ structures and moisture, although possible, did not occur when the resin was irradiated by the xenon arc lamp. Thus, it is believed that reaction (11) probably contributed little, if at all, to preventing the production of $SiCH_2$-Si linkages during the irradiation of the methylsiloxane resin by the mercury vapor lamp.

$$\equiv Si + H_2O \rightarrow \equiv Si—OH + H^{\cdot} \tag{11}$$

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

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Primary Radical Termination Rate Constant at High Conversion in Radical Polymerization

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Synopsis

A primary radical termination rate constant given by: $k_{ti} = A_{1i}D_i$, where A_{1i} is a constant and D_i is the diffusion constant of the primary radical, was examined on the basis of the variation of conversion. It was proved that this rate constant is correct at high conversion. A relationship between primary radical termination rate constant and conversion was derived. The effect of variation of conversion on the gel effect is discussed.

INTRODUCTION

Ito[1] derived a chain termination rate constant and a primary radical termination rate constant, respectively, given by:

$$k_t = A_1 D_S \tag{1}$$

$$k_{ti} = A_{1i} D_i \tag{2}$$

where A_1 and A_{1i} are constants and D_S and D_i are the diffusion constants of the radical chain end and the primary radical, respectively. It was indicated that eq. (1) is correct in the range of almost complete conversion.[2,3]

The aim of this paper is to prove that the primary radical termination rate constant given by eq. (2) is correct at high conversion and to obtain a relationship between the primary radical termination rate constant and conversion. The gel effect is also discussed on the basis of the variation of conversion.

THEORY

Determination of Primary Radical Termination Rate Constant

In the past, the contribution of primary radical termination has been evaluated by an intensity exponent a in the relationship:

$$R_p = BI^a \tag{3}$$

where B is a constant, I is initiator intensity, and R_p is the polymerization rate.[4] Recently, Ito and Matsuda[5] derived a simple equation for the treatment of the radical polymerization with primary radical termination:

$$R_p/I^{1/2} = (k_p/k_t^{1/2})[\mathrm{M}] - (k_{ti}k_p/k_ik_t)I^{1/2} \tag{4}$$

where [M] is monomer concentration and k_p and k_i are the rate constants for propagation and addition to monomer of primary radical, respectively. A relationship between eqs. (3) and (4) is given by:

$$(k_{ti}/k_ik_t^{1/2})I^{1/2}/[\mathrm{M}] = \log\{(k_p/k_t^{1/2})[\mathrm{M}]/B\} + (0.5\text{-}a)\log I \tag{5}$$

under the condition:

$$(k_p/k_t^{1/2})[\mathrm{M}] \gg (k_{ti}k_p/k_tk_i)I^{1/2}$$

Relationship Between Primary Radical Termination Rate Constant and the Average Fractional Free Volume or Conversion

If it is assumed that eq. (2) is applicable for primary radical termination rate constant, the same type equations should be also applicable for the chain termination rate constant.[3]

$$k_{ti} = A_{ti}^* \exp\{-1/f_{\mathrm{i}}(T,v_1)\} \tag{6}$$

$$f_{\mathrm{i}}(T,v_1) = f_{\mathrm{i}}(T,\mathrm{O}) + \beta_{\mathrm{i}}(\mathrm{Y})v_1 \tag{7}$$

where

$$\beta_{\mathrm{i}}(T) = \gamma_{\mathrm{i}}(T) - f_{\mathrm{i}}(T,\mathrm{O})$$

A linear relationship between primary radical termination and conversion is given by:

$$\frac{1}{\log\,[(k_{ti})_{\mathrm{i}}/k_{ti}]} = -g_{\mathrm{i}}(T,x_{\mathrm{i}}) + \frac{[g_i(T,x_i)]^2}{\beta_{\mathrm{i}}(T)}\left(\frac{1}{x - x_{\mathrm{i}}}\right) \tag{8}$$

$$g_{\mathrm{i}}(T,x_{\mathrm{i}}) = f_{\mathrm{i}}(\mathrm{T},1 - x_{\mathrm{i}}).$$

In eqs. (6), (7), and (8), A_{ti}^* is a constant, $f_{\mathrm{i}}(T,v_1)$ is the average fractional free volume for primary radical termination rate constant, v_1 is the volume fraction of solvent, T is temperature, x is conversion, and $(k_{ti})_{\mathrm{i}}$ is a primary radical termination rate constant at conversion x_{i}.

Because the diffusion constant of primary radical is not equivalent to the diffusion constant of radical chain end, $f_{\mathrm{i}}(T,O)$ and $\gamma_{\mathrm{i}}(T)$ obtained for the primary radical termination rate constant should be not completely equivalent to $f(T,O)$ and $\gamma(T)$ for the chain termination rate constant.

APPLICATIONS

Calculation of Primary Radical Termination Rate Constant

Schulz and Harborth's results[6] in the bulk polymerization of methyl methacrylate (MMA) initiated by benzoyl peroxide (BPO) at 50°C are given in Table I. On the application of eq. (4) to these results, a linear relationship between $R_p/[\mathrm{C}]^{1/2}$ and $[\mathrm{C}]^{1/2}$ (where [C] denotes initiator

TABLE I

Propagation Rate R_p and Average Degree of Polymerization of Polymer formed $\bar{P}$ at Various Conversions x and at Various Initiator Concentrations [C] for the Bulk Polymerization of MMA Initiated by BPO at 50°C.[6]

x	[C], mole/l.	$R_p \times 10^5$, mole/l.-sec	$\bar{P}$
0	0.0103	9.11	6 600
	0.0207	12.24	5 000
	0.0413	16.60	3 900
	0.0826	23.24	3 050
0.2	0.0103	20.0	8 100
	0.0207	23.6	
	0.0413	29.9	4 100
	0.0826	32.5	3 100
0.3	0.0103	45.6	10 200
	0.0207	54.2	
	0.0413	66.5	5 600
	0.0826	83.5	4 050

concentration) was obtained at conversion $x = 0, 0.2$, or 0.3 (Fig. 1) and is independent of the molecular weight of polymer formed. By use of this linear relationship, $k_{ti}/k_i k_p$ values were calculated to be:

$$k_{ti}/k_i k_p = 4.5 \times 10^4 \text{ mole-sec/l at } x = 0.2$$

$$= 1.2 \times 10^4 \text{ mole-sec/l at } x = 0.3.$$

On the application of eq. (4) to Hyden and Melville's results[4] for the bulk polymerization of MMA with 2,2′-azobisisobutyronitrile (AIBN) as

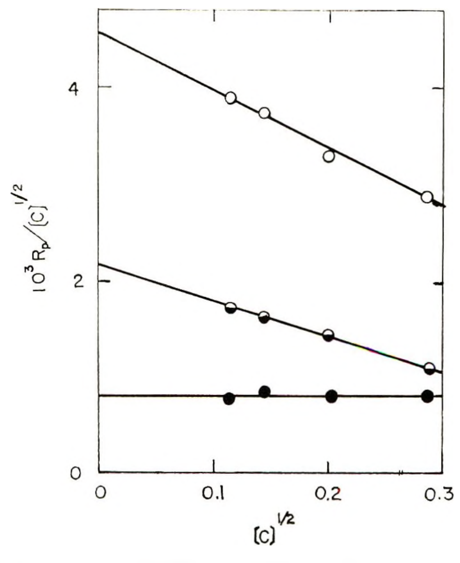

Fig. 1. Relationship between $R_p/[C]^{1/2}$ and $[C]^{1/2}$ for the bulk polymerization of MMA initiated by BPO at 50°C:[6] (●) X = 0; (◒) $x = 0.2$; (○) $x = 0.3$.

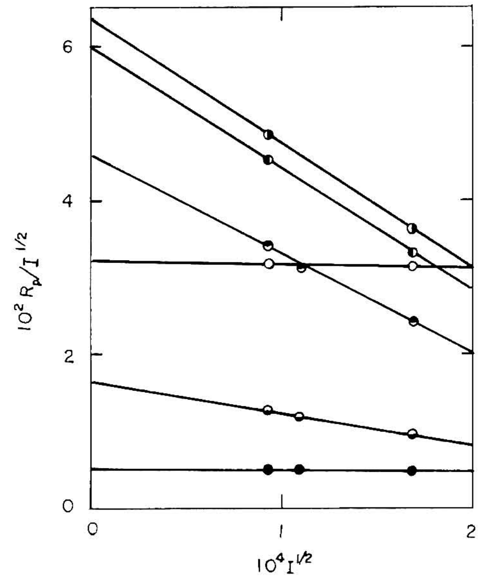

Fig. 2. Relationship between $R_p/I^{1/2}$ and $I^{1/2}$ for the bulk polymerization of MMA with AIBN as photosensitizer at 22.5°C:[4] (●) $x = 0.1$; (◒) $x = 0.2$; (◓) $x = 0.3$; (◑) $x = 0.4$; (◐) $x = 0.5$; (○) $x = 0.6$.

photosensitizer at 22.5°C, linear relationships are obtained (Fig. 2). The slope of this linear line is directly equivalent to $k_{ti}k_p/k_ik_t$. k_{ti}/k_i was calculated by using the values of $k_{ti}k_p/k_ik_t$ and k_p/k_t. These values are given in Table II. $k_{ti}k_p/k_ik_t$ or k_{ti}/k_i at conversion $x = 0.1$ and 0.6 in Table II were calculated by using eq. (5).

TABLE II

Values of $k_{ti}k_p/k_tk_i$, and k_{ti}/k_i Obtained by Using k_p/k_t at Rate of Initiation = 2.83×10^{-8} mole/l.-sec for the Bulk Polymerization of MMA with AIBN as Photosensitizer at 22.5°C.[4]

x	$k_{ti}k_p/k_tk_i$	$k_p/k_t \times 10^6$	$k_{ti}/k_i \times 10^{-5}$
0.1	1.25	9.5	1.29
0.2	37.5	46.0	0.847
0.3	125	306	0.409
0.4	158	688	0.230
0.5	158	1 275	0.124
0.6	3.2	3 710	0.0086

Linear Relationship between Primary Radical Termination Rate Constant and Conversion

On taking $x_i = 0.1$ and assuming that the rate constant for addition on to monomer of primary radical is independent of conversion and therefore constant, eq. (8) applied to the results in Table II. A linear relationship between $1/\log[(k_{ti})_i/k_{ti}]$ and $1/(x - 0.1)$ was obtained in the conversion range

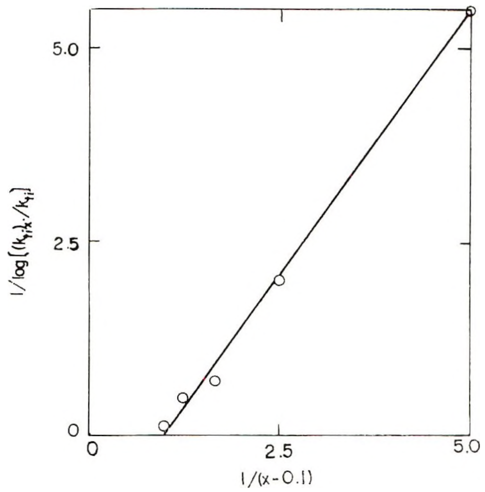

Fig. 3. Relationship between $1/\log[(k_{ti})_i/k_{ti}]$ and $1/(x - 0.1)$ for the bulk polymerization of MMA with AIBN as photosensitizer at 22.5°C.[4]

0.1–0.6 (Fig. 3). Using this linear relation, the following values were calculated: $f(22.5°\mathrm{C},0) = 0$ and $\gamma(T) = 0.61$.

This application indicates that the primary radical termination rate constant depends on conversion.

DISCUSSION

The above theories and applications indicate that the primary radical termination rate constant is independent of the molecular weight of polymer formed (Table I and Fig. 1), but depends on conversion (Fig. 3). Thus, the primary radical termination rate constant given by eq. (2) is correct for the bulk polymerization of MMA.

The treatment in this paper should be precisely correct under the condition that initiator efficiency is independent of conversion. If initiator efficiency can be treated by using Noyes' equation:[7]

$$f = 1 - 1/[\alpha_1 + (\alpha_2/\eta')] \tag{9}$$

where α_1 and α_2 are constants, and η' is a viscosity.[7,8] (Apparently, η' is not solution viscosity for the polymerization solution, but a viscosity for the mobility of primary radical.) Thus, $1/\eta'$ is given by:

$$1/\eta' = A_c^* \exp\{-1/f_c(T,v_1)\} \tag{10}$$

where A_c^* is a constant and $f_c(T,v_1)$ is the average fractional free volume for cage combination. In the bulk polymerization of vinyl acetate (VA), Bengough[9] pointed out that initiation rate is constant in the conversion range 0–0.7.

By using the notation of geminate chain recombination, the bulk polymerization of VA was treated by Allen and Patrick.[10] In this treatment, geminate chain recombination was different from chain termination between polymeric radicals. But, it is reasonable that geminate chain recombination is a process in chain termination. That is, geminate chain recombination is equivalent to recombination between radical chain ends during the collision between two spherical polymeric radicals.

Burnett and Duncan[11] derived an equation:

$$[R_p/(R_p)_0 - 1]^{1/2} = K_1^{1/2}[x - x_1] \tag{11}$$

for the explanation of the gel effect. In eq. (11), $(R_p)_0$ is the initial polymerization rate, K_1 is a constant depending on the termination rate constant and initial rate, and x_1 is the critical conversion which must be dependent on the molecular weight of the polymer produced in the early stages. By using eqs. (1) and (2) depending on conversion and eq. (4), an equation of the same type is eq. (11) could not be precisely or approximately derived. The essential theoretical basis of Burnett and Duncan's treatment[11] is different from the treatments in our papers.

Under the condition that primary radical termination is negligible, an approximate equation can be derived for conversion x':

$$R_p/(R_p)_x' = 1 + F(T,x')(x - x') \tag{12}$$

where

$$F(T,x') = \beta(T)/2[f(T,O) + \beta(T)(1 - x')]^2 - 1/(1 - x')$$

$(R_p)_x'$ denotes the polymerization rate at conversion x'. Actually, because of the effect of primary radical termination on $R_p/(R_p)_x'$ being very small in the neighborhood of conversion x', this approximate relationship should be completely correct in the conversion range in which the propagation rate constant is independent of conversion. The treatment of the gel effect by applying eq. (12) should be useful.

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Phenylated Polyquinoxalines from Bis(phenylglyoxaloyl)benzene

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Synopsis

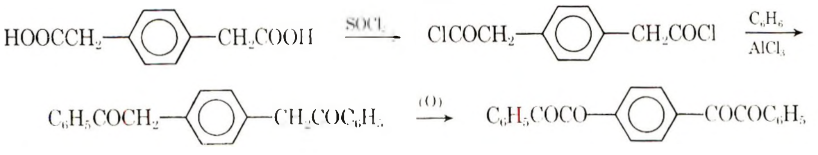
Phenyl-substituted polyquinoxalines of unusually high oxidative-thermal stability were prepared by one-step solution condensations of aromatic tetraamines with 1,4-bis-(phenylglyoxaloyl)benzene and 1,3-bis(phenylglyoxaloyl)benzene. The final polymers thus obtained show exceptionally good solubility in a variety of common organic solvents, such as chloroform, tetrachloroethane, dichlorobenzenes, and certain phenols. Polymerizations in these solvents lead to polyquinoxalines of high molecular weight at reaction rates which depend upon the solvent used. The phenylated polyquinoxalines exhibited glass transition temperatures between 253 and 317°C and polymer decomposition temperatures between 515 and 540°C, depending upon structure. Isothermal decomposition at 400°C in air showed a strong dependency of weight loss on structure. Tough, flexible films were cast from solutions.

INTRODUCTION

Polyquinoxalines[1-12] and phenylated polyquinoxalines[13,14] have recently received a considerable amount of attention. In a preceding note,[15] we reported the preparation of two phenylated polyquinoxalines prepared by the reaction of 1,4-bis(phenylglyoxaloyl)benzene with aromatic tetramines. In continuing this series, two additional phenylated polyquinoxalines containing the *m*-phenylene group have been prepared from 1,3-bis(phenylglyoxaloyl)benzene and aromatic tetramines. We now wish to report in detail on the synthesis and properties of these polymers.

EXPERIMENTAL

The bis(phenylglyoxaloyl)benzenes were obtained in good yields by the reaction route shown in eq. (1).



(1)

1,4-Bis(phenylglyoxaloyl)benzene (I). A mixture of 200 g (1 mole) of *p*-phenylenediacetic acid, 453 g (3.8 mole) of thionyl chloride, and 1 ml of dimethylformamide was refluxed for 18 hr at 75°C, resulting in a clear, red-brown solution. Excess thionyl chloride was then removed by vacuum distillation at 70°C. The residual pale-yellow crystalline solid was slurried in 300 ml of hexane and then filtered by suction. The bright yellow solid was dried at 40°C under reduced pressure and gave 205 g (90%) of product, mp 70–71°C.

A solution of 200 g (0.87 mole) of the *p*-phenylenediacetic acid chloride in 400 ml of dry benzene was added slowly to a slurry of 250 g (1.9 mole) of anhydrous aluminum chloride in 500 ml of dry benzene; addition was complete after 4 hr. The flask contents were then heated at 50–52°C for 24 hr. The resulting dark brown solution was cooled and poured into a mixture of about 3 lb of crushed ice and 400 g concentrated hydrochloric acid. A greenish precipitate formed, which was washed with water, filtered by suction, and recrystallized from 5 liters of chloroform. The yield of product was 225 g (73%), mp 203–205°C.

A mixture of 88 g (0.29 mole) of 1,4-bis(phenylacetyl)benzene, 82 g (0.74 mole) of selenium dioxide, and 600 ml of acetic anhydride was refluxed for 5 hr. The resulting reddish solution was filtered hot, and 600 ml of water were added slowly to the cooled filtrate. The product which crystallized on standing was filtered, washed with 10% sodium carbonate, and then washed with water. Recrystallization twice from ethyl alcohol gave 43.5 g (44%) of pure product, mp 122–124°C.

1,3-Bis(phenylglyoxaloyl)benzene (II). *m*-Phenylenediacetic acid (200 g, 1.0 mole) was refluxed for 24 hr in 500 g (4.5 mole) of thionyl chloride and 1 ml of dimethylformamide. The excess thionyl chloride was removed by vacuum distillation, and the black colored oil (230 g) was reacted without further purification.

To a slurry of 340 g (2.5 mole) of aluminum chloride in 600 ml of dry benzene was added dropwise a solution of the black oil dissolved in 500 ml of dry benzene. The addition was complete after 4$^1/_2$ hr. Then the flask contents were heated with stirring for 18 hr at 48–53°C. The resulting black solution was slowly poured into a mixture of about 3 lb of crushed ice containing 500 ml of concentrated hydrochloric acid. The dark-brown benzene layer was extracted in a separatory funnel, washed twice with a 10% solution of sodium carbonate, followed by three washings with water and drying over calcium sulfate. After evaporating the benzene, a dark brown oil was obtained which solidified on adding 1 liter of petroleum ether. Recrystallization once from ethyl acetate and twice from ethanol gave 98 g (30.6%) of 1,3-bis(phenylacetyl)benzene, mp 90.5–91°C.

To a solution of 62.8 (0.2 mole) of 1,3-bis(phenylacetyl)benzene in 1 liter of ethanol was added 106.8 g (0.6 mole) of *p*-nitrosodiethylaniline, and the mixture was refluxed for 5 hr. The solvent was evaporated under reduced pressure, then 600 ml 1:1 hydrochloric acid and water was added and the mixture refluxed for $^1/_2$ hr. A dark-brown oil formed which was separated and recrystallized three times with 700 ml of ethanol, giving 37.0 g (53%) of pure product, mp 98–99.5°C (see Table I for characterization).

TABLE I
Characterization of Monomers and Model Compounds

			Elemental analysis					
			Calculated			Found		
Compound	Mp, °C	Formula	C, %	H, %	N, %	C, %	H, %	N, %
I	123.5–124[a]	$C_{22}H_{14}O_4$	77.18	4.02	—	77.28	4.17	—
II	98.0–99.5	$C_{22}H_{14}O_4$	77.18	4.12	—	76.92	4.13	—
III	309–310	$C_{40}H_{26}N_4$	85.38	4.66	9.96	85.20	4.62	9.98
IV	224–225	$C_{34}H_{22}N_4$	83.93	4.56	11.51	83.84	4.47	11.61

[a] Lit.[16] mp, 127°C.

Model Compounds

2,2′,3,3′-Tetraphenyl-6,6′-diquinoxaline (III). A 100-ml round-bottomed flask connected to a reflux condenser was charged with 2.14 g (0.01 mole) of 3,3′-diaminobenzidine, 4.20 g (0.02 mole) of benzil, and 30 ml of chloroform. The flask content was heated to reflux for 7 hr. The brilliant yellow precipitate was suction-filtered and air-dried. The yield of crude product was 5.25 g (95%), mp 308–312°C. Recrystallization from 50:50 toluene–ethanol solution gave 3.41 g of pure material (see Table I for characterization).

1,3-Bis[2-(3-phenylquinoxalyl)]benzene (IV). This compound was obtained in 93% yield under reaction conditions analogous to those used to obtain compound III. After completion of the reaction, a clear brown chloroform solution was obtained. Evaporating the solvent gave a tan colored crude product in quantitative yield. Recrystallization from an 80:20 ethanol-chloroform solution gave the pure, light tan colored, crystalline product (see Table I for characterization).

Polymers

Poly[2,2′-(1,4-phenylene)-6,6′-bis(3-phenylquinoxaline)] (V). A 100-ml three-necked flask fitted with a nitrogen inlet tube, a mechanical stirrer, and a condenser was charged with 5.35 g (0.025 mole) of 3,3′-diaminobenzidine and 8.60 g (0.025 mole) of 1,4-bis(phenylglyoxaloyl)benzene. The flask was purged with nitrogen and 80 ml of *m*-cresol was added to give a slurry which was vigorously stirred. Initially a deep red color developed which disappeared after 5 min, giving a clear, amber, highly viscous solution (η = 1.5 dl/g, 0.5% in chloroform at 30°C; η = 2.1 dl/g, 0.5% in *m*-cresol at 30°C). Stirring was continued for an additional 15 min at room temperature with no further increase in viscosity. A portion of the polymer was precipitated from methanol using a Waring Blendor. The light yellow solid was washed three times with methanol and then redissolved in chloroform. A film was cast from the chloroform solution by evaporating the solvent at room temperature. The infrared spectra of this film showed no carbonyl band and no residual NH band, thus indicating that cyclization was complete.

A second run was made with the use of tetrachloroethane as reaction solvent. A 2.140 g (0.010 mole) quantity of 3,3′-diaminobenzidine and 3.420 g (0.010 mole) of 1,4-bis(phenylglyoxaloyl)benzene in 35 ml of tetrachloroethane was heated for 6 hr at 140°C to yield the final polymer (η = 1.47 dl/g., 0.5% chloroform at 30°C). Tough, flexible films could be cast from this solution by evaporating the solvent at room temperature.

Poly[2,2′-(1,4-phenylene)-6,6′-oxybis(3-phenylquinoxaline)] (VI). The reaction of 2.300 g (0.010 mole) of 3,3′,4,4′-tetraaminodiphenyl ether and 3.420 g (0.010 mole) of 1,4-bis(phenylglyoxaloyl)benzene in 44 ml of *m*-cresol under similar reaction conditions as described for polymer V gave 4.85 g (97%) of an almost white final polymer (η = 1.3 dl/g; 0.5% in *m*-cresol at

30°C). Heating for 6 hr at 260°C under reduced pressure produced no increase in inherent viscosity.

Poly[2,2′-(1,3-phenylene)-6,6′-bis(3-phenylquinoxaline)] (VII). To a stirred suspension of 2.140 g (0.010 mole) of 3,3′-diaminobenzene in 30 ml of *m*-cresol was added 3.420 g (0.010 mole) of 1,3-bis(phenylglyoxaloyl)-benzene in small portions over a period of 5 min. Then 14 ml of *m*-cresol was added to wash down any solid from the wall of the flask. The resulting clear, viscous solution was stirred for an additional 50 min to yield the final polymer (η = 0.84, 0.5% in *m*-cresol at 30°C).

A second run was made using chloroform as reaction solvent. The polymerization was complete after 38 hr at reflux temperature. The polymer obtained had an inherent viscosity of 0.63 dl/g (0.5% solution in chloroform at 30°C). Pale yellow films were cast from the chloroform solution.

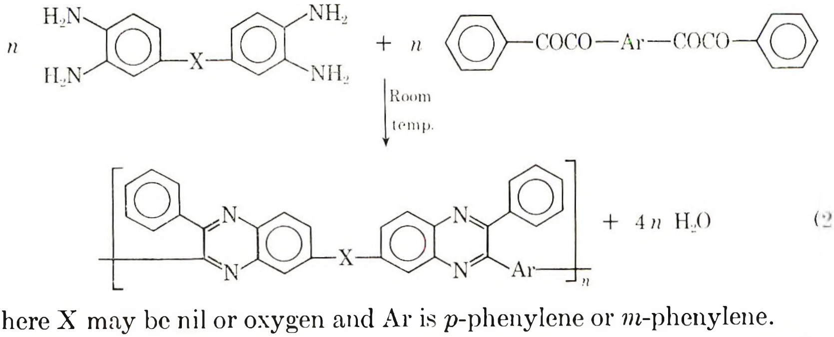
Poly[2,2′-(1,3-phenylene)-oxybis(3-phenylquinoxaline)] (VIII). The reaction of 2.300 g (0.010 mole) of 3,3′,4,4′-tetraaminodiphenyl ether with 3.420 g (0.010 mole) of 1,3-bis(phenylglyoxaloyl)benzene in 44 ml of *m*-cresol was carried out by a melted analogous to preparation of polymer V. The tan polymer had an inherent viscosity of 0.51 dl/g (0.5% solution in *m*-cresol at 30°C).

The reaction was repeated using chloroform as a solvent. Both reactants were refluxed in chloroform with stirring while a slow stream of nitrogen was passed through the solution. Small samples were removed periodically and used to follow the course of the reaction by infrared spectroscopy (disappearance of the glyoxal carbonyl band at 1685 cm^{-1}). The reaction was complete after 12 hr, resulting in a polymer with an inherent viscosity of 0.45 dl/g (0.5% solution in chloroform at 30°C).

RESULTS AND DISCUSSION

Polymer Synthesis

Four new phenylated polyquinoxalines were prepared by one-step solution condensations of aromatic bis(*o*-diamines) in combination with 1,4- or 1,3-bis(phenylglyoxaloyl)benzene at ambient temperature [eq. (2)]:



(2)

where X may be nil or oxygen and Ar is *p*-phenylene or *m*-phenylene.

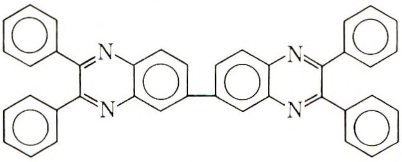
In all cases high molecular weight linear final polymers were obtained within 1 hr at room temperature with *m*-cresol as reaction solvent. In addition, the reaction of 3,3′-diaminobenzidine with 1,4-bis(phenylglyoxaloyl)benzene (I) was examined in detail under a variety of conditions (Table II). The course of the reactions was followed in the infrared by the disappearance of a carbonyl band at 1685 cm^{-1}. In all runs made, the reaction was considered complete after either no or only traces of this band was present.

Increasing the batch size from 5.56 g to 27.81 g resulted in an increase in the molecular weight (runs 1 and 3). An increase in temperature, however, resulted in no further increase in molecular weight (runs 1 and 2). It was also found that the polymerization will proceed in solvents such as tetrachloroethane or chloroform (runs 4 and 5) to yield high molecular weights.

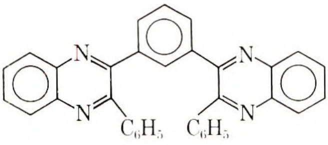
The rate of polymerization of 3,3′,4,4′-tetraaminodiphenyl ether with 1,3-bis(phenylglyoxaloyl)benzene in chloroform at 63°C was followed in the infrared. From the data in Figure 1, a plot of per cent reaction versus time was constructed (Fig. 2). During the initial stages of the reaction and up to 60% conversion it was possible to isolate a fusible prepolymer. Above 60% conversion, an infusible film-forming polymer was obtained.

Synthesis of Model Compounds

Model compound studies were undertaken to determine which segments in the polymer chain contributed to the unusual solubility characteristics. Two models (III and IV) were synthesized in chloroform under similar conditions used for the polymer synthesis.

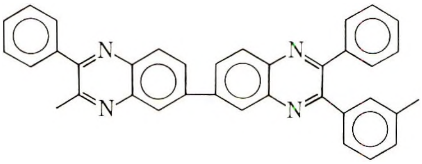


III



IV

Both models could be obtained in near quantitative yield. However, compound III was completely insoluble in chloroform, while compound IV was very soluble and had many of the other solubility characteristics of polymer VII.



VII

Thermal Properties

Glass transition temperatures T_g of the polymers shown in Table III were obtained in vacuum on polymer films by means of dielectric loss measure-

TABLE II

Synthesis of Poly[2,2′-(1,4-phenylene)-6,6′-bis(3-phenylquinoxaline)][a]

Run no.	Batch size, g	Reaction solvent	Concentration, %	Pot temperature, °C	Reaction time, hr[b]	Inherent viscosity, dl/g[c]	Remarks
1	5.56	*m*-cresol	10	Room	1	1.8	Film-forming after 20 min, no increase in inherent viscosity after heating in vacuum for 6 hr at 260°C
2	5.56	*m*-cresol	10	203	1 at room temp + 1 at 203°C	1.8	—
3	27.81	*m*-cresol	10	Room	1	2.1	Makes extremely viscous solution
4	5.56	Tetrachloroethane	15	140	1 + 6 at 140°C	1.5	Film forming after 3 hr
5	5.56	Chloroform	15	63	1 at room temp + 24 at 63°C	0.65	Film-forming after 7 hr, fusable prepolymer after 3 hr

[a] Total weight of reactants.

[b] Required for the complete consumption of 1,4-bis(phenylglyoxaloyl)benzene.

[c] Determined from 0.5% solutions at 30°C in reaction solvent.

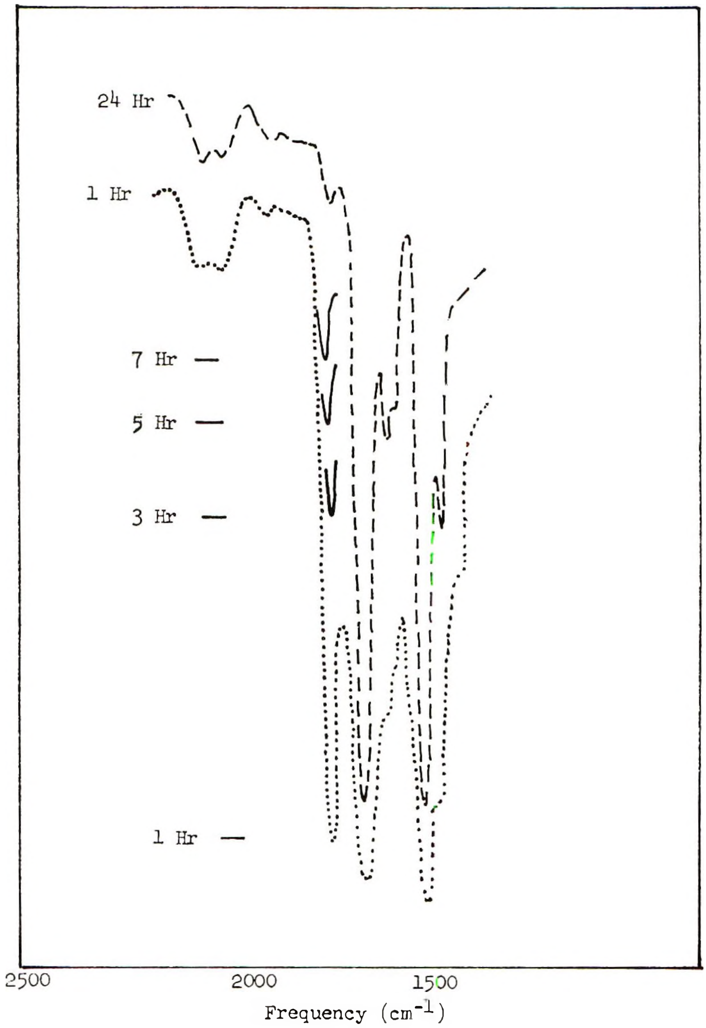


Fig. 1. Infrared spectra of products from reaction of 3,3′,4,4′-tetraaminodiphenyl ether and 1,3-bis(phenylglyoxaloyl)benzene at various times.

ments. The T_g ranged between 253 and 320°C, with lower values obtained for polymers VI and VIII, which contained the diphenyl ether linkage. Polymer V, containing the *p*-phenylene links, had very similar glass transitions even though it was anticipated that the introduction of a *m*-phenylene group would result in a lowering of this transition. All four polymers exhibited thermoplastic flow above their T_g and were fusible just below their decomposition temperatures. Thermogravimetric analysis (TGA) was performed on powdered samples of polymers synthesized at room temperature. Measurements were made in vacuum at a heating rate of 5°C/min. Under these conditions the temperatures of initial weight loss taken from the

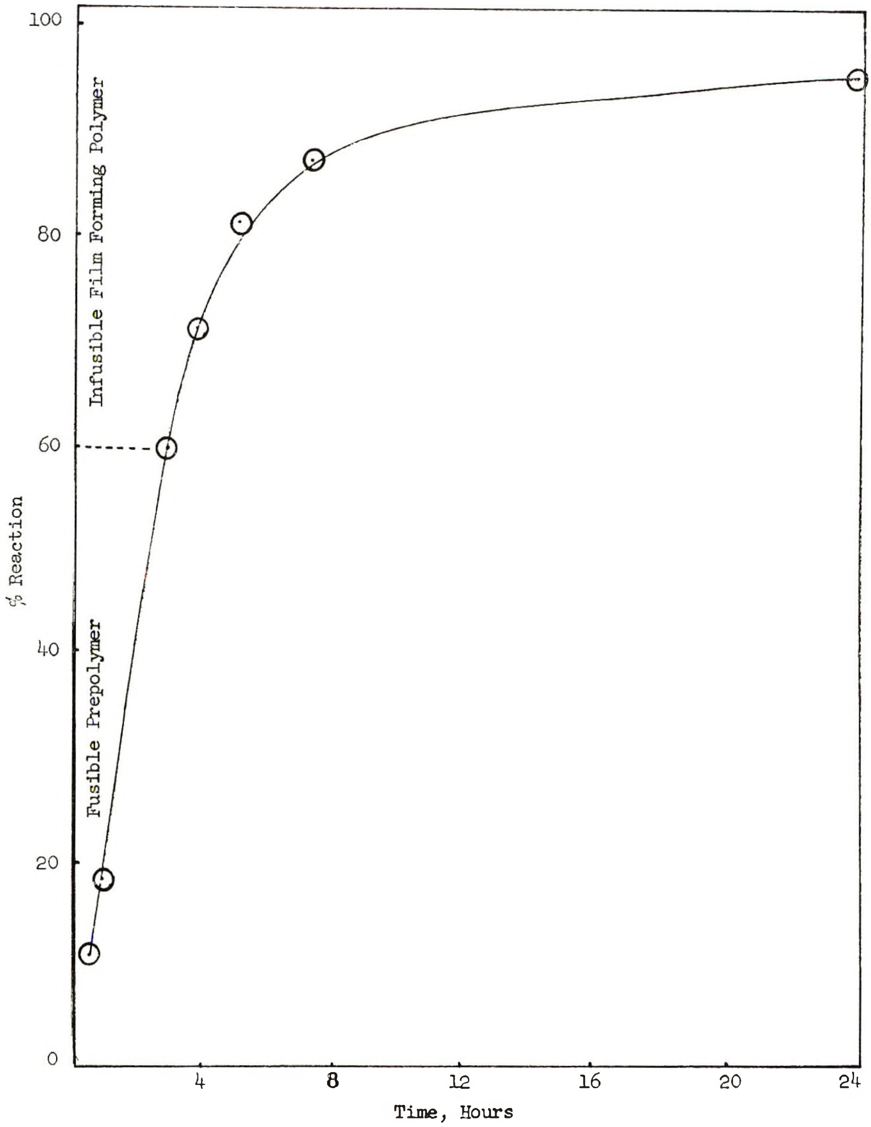
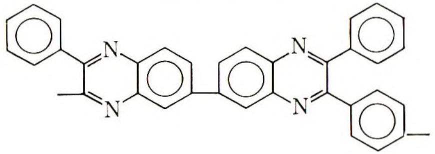
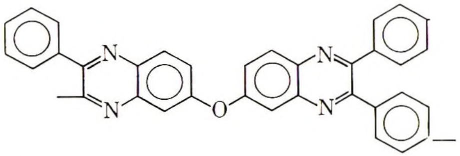
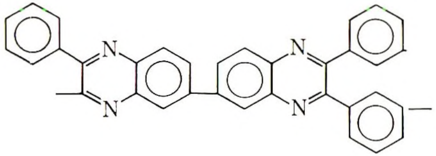
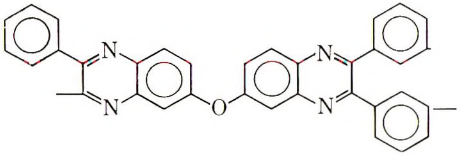


Fig. 2. Plot of per cent reaction vs. time for the polymerization of 3,3′,4,4′-tetraaminophenyl ether with 1,3-bis(phenylglyoxaloyl)benzene in $CHCl_3$ at 63°C.

intersects of the TGA curves were arbitrarily defined as polymer decomposition temperatures and varied between 515 and 540°C.

The oxidative-thermal stability of polymers was tested by means of isothermal weight loss measurements of powdered samples and films at 400°C in static air (Table III). It was found that polymers V and VII containing no oxygen linkages in the chain lost only 5 to 6% after 200 hr of aging, while polymers VI and VII containing the ether linkage lost 49 and 43% weight, respectively. Also, a film of polymer V remained creasable after 300 hr at

TABLE III
Characterization of Phenylated Polyquinoxalines

Polymer	Structure	Inherent viscosity η, dl/g[a]	Glass transition temp, °C[b]	Polymer decomposition temp, °C[c]	Isothermal aging at 400°C in static air, 200 hr wt loss, %	Elemental analysis[d] C, %	Elemental analysis[d] H, %	Elemental analysis[d] N, %
V		2.1	317	540	6	84.11 (84.28	3.88 4.16	11.62 11.56)
VI		1.3	298	515	49	81.95 (81.58	4.17 4.03	11.09 11.19)
VII		0.9	320	540	5	84.25 (84.28	4.16 4.16	11.49 11.56)
VIII		0.5	253	520	43	81.49 (81.58	4.04 4.03	11.25 11.19)

---

[a] Determined in *m*-cresol (0.5% solution at 30°C).

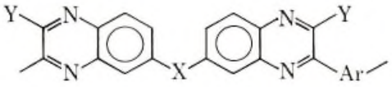
[b] Measured by dielectric loss as a function of temperature at a heating rate of 5°C/min.

[c] Obtained from TGA data in vacuum at a heating rate of 5°C/min.

[d] Calculated values shown in parentheses.

TABLE IV

Solubilities of Polyquinoxalines



Sample	Substituent			Inherent viscosity [η] in H_2SO_4	Solubility		
	X	Y	Ar		Chlorinated solvents[a]	Phenols[b]	Conc. sulfuric acid
1,2[c]	—	C_6H_5	*m*-,*p*-Phenylene	0.9–2.1	Soluble	Soluble	Soluble
3,4	O	C_6H_5	*m*-,*p*-Phenylene	0.5–1.3	Soluble	Soluble	Soluble
5	—	H	*p*-Phenylene	0.8	Insoluble	Insoluble	Soluble
6	O	H	*p*-Phenylene	0.6	Insoluble	Partially soluble	Soluble
7	O	C_6H_5	Diphenyl ether	2.1	Soluble	Partially soluble	Soluble
8	—	C_6H_5	Diphenyl ether	2.0	Soluble	Soluble	Soluble
9	—	H	Diphenyl ether	0.8	Insoluble	Soluble	Soluble
10[d]	—	H	Diphenyl ether	1.6	Insoluble	Insoluble	Soluble

[a] Solubility tested at room temperature in chloroform and tetrachloroethane (solubility is not improved in hot solvent).

[b] Solubility tested at room temperature in *m*-cresol, phenol, anisole, and *o*-methoxyphenol (solubility is slightly improved in hot solvent).

[c] Samples remained soluble after heating in air at 400°C for 24 hr.

[d] Samples obtained from Whittaker Corp., San Diego, California.

400°C in air, while polymer VI containing the ether linkage lost its film creasability after 96 hr under these conditions.

Polymer Solubility

The effect of structure on solubility of nine polyquinoxalines was investigated using twenty solvents. Table IV summarizes the results obtained from ten samples tested in two general classes of solvents.

Phenyl side groups greatly improved solubility. This effect becomes apparent by comparing samples 1–6. Samples 1–4 (polymers V–VIII) containing phenyl side groups could readily be dissolved in both chlorinated solvents and phenols in concentrations up to 30% solids, while samples 5 and 6, having hydrogen atoms in place of phenyl groups, were completely insoluble in these solvents. The x-ray analysis of phenylated and unsubstituted polyquinoxalines showed both types to be polycrystalline. It is therefore believed that the differences in solubility between the two polymer types are primarily due to differences in chemical structures (i.e., solubilizing effect from phenyl side groups) rather than caused by morphological effects. Samples 7 and 8 are the exception to this rule. However, since both polymers showed some swelling in phenols, it is believed that these polymers were at least slightly crosslinked. The solubility of samples 5 and 6 in concentrated sulfuric acid could be due to the hydrolytic breakdown of the crosslinks in this solvent.

The presence of ether groups in the polymer chains does not improve solubility in chlorinated solvents but increases solubility in phenols somewhat (compare samples 5–10).

TABLE V

Film Properties of Poly[2,2′-(1,4-phenylene)-6,6′-bis(3-phenylquinoxaline)] (V)

Property	
Color	Yellow
Crystallinity	Highly crystalline
Tensile-tear strength, dyne/cm^2[a]	6.6×10^8
Elongation at break, %	17
Retention of film creasability	
At 400°C in air	300 hr
At 250°C in air[b]	>4 months
Dielectric constant at 25°C, 1 Kc	4.6
Dielectric Loss Factor	
At 1 Kc, 25°C	0.002
At 1 Kc, 300°C	0.07
Chemical stability in boiling 50% KOH	Unaffected
Fusion temperature, °C[c]	480

[a] Determined on dog bone micro-specimens.

[b] Experiment is still in progress.

[c] Determined from DTA data and visual observation; no actual melting occurs.

Nonphenylated polyquinoxaline precursors containing the diphenylether linkage in the chain are soluble in phenols ($\eta = 0.8$ dl/g, sample 9); however, the final polymers are insoluble (sample 10).

Miscellaneous Properties

Several properties of polymer V not mentioned so far are listed in Table V.

CONCLUSIONS

Due to the highly reactive nature if 1,3- and 1,4-bis(phenylglyoxaloyl)-benzene, it is possible to obtain final high molecular weight phenylated polyquinoxalines by one-step solution condensations under mild reaction conditions. Since aromatization (cyclization) can be accomplished at ambient temperature, the probability of crosslinking side reactions is reduced. Therefore, truly linear and, consequently, soluble final polymers are obtained.

The oxidative-thermal stability was greatly improved by the introduction of phenyl side groups and by the elimination of ether linkages in the polymer chain.

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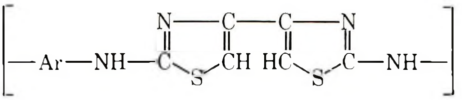
NOTES

Polythiazoles

Polythiazoles have been reported to exhibit good thermal stability.[1–5] The character of the units between thiazole units has been reported[4,5] to affect the properties of these polymers greatly, especially their solubility, molecular weight, thermal stability, film- and fiber-forming characteristics, etc. The nature of the units that have been studied are methylene and arylene in nature. The presence of arylene groups results in polymers having lower solubility, lower molecular weight, higher thermal stability, and no fiber- or film-forming characteristics. As the number of methylene groups increases, the polymers have higher molecular weight, greater solubility in various solvents, less thermal stability, and better film-forming characteristics.

In this note we wish to report the preparation of polythiazoles in which the aromatic and thiazole units are linked through a —NH— group. The introduction of the —NH— group is likely to contribute to chain stiffness, enhanced thermal stability, and a site for crosslinking, if desired.

The polythiazoles that we have prepared belong to two types: I and II, which were prepared by solution polycondensation of the corresponding bisthioureas with 1,4-dibromo-2,3-butanedione and 4,4′-(bisbromoacetyl) diphenyl ether, respectively, in dimethylformamide.



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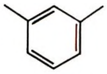

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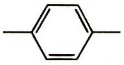

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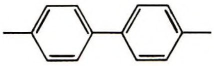

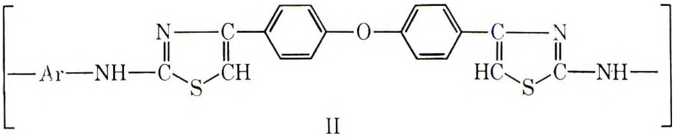

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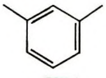

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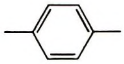

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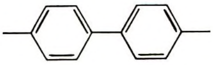

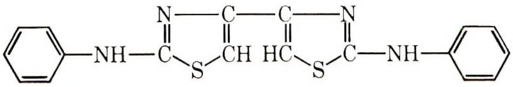

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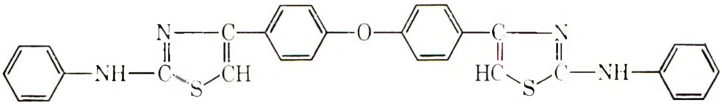

IV

EXPERIMENTAL

Materials

Solvents used were of B.D.H. and E. Merck reagent grade quality. Dimethylformamide was stored over anhydrous sodium sulfate and distilled prior to use. The reagents used for the preparation of monomers were either freshly distilled or recrystallized prior to use.

The infrared spectra were obtained with a Zeiss UR-10 spectrophotometer and the ultraviolet spectra with a Perkin-Elmer Model 137 UV-visible spectrophotometer. The TGA curves were recorded on a Stanton thermoanalytical balance.

Bisthioureas. The 1,3- and 1,4-phenylene and 4,4′-biphenylene bisthioureas were prepared[6] from the corresponding diamines and ammonium thiocyanate and recrystallized from water.

1,4-Dibromobutane-2,3-dione. This was prepared by bromination of diacetyl in carbon disulfide, mp 118°C (lit[7] mp 116–117°C). Infrared bands at 1685 (carbonyl) and 1200 cm^{-1} (CH_2Br) were observed.

4,4′-Bisacetyl Diphenyl Ether. This was prepared by Friedel-Crafts reaction of diphenyl ether with acetic anhydride in presence of anhydrous aluminum chloride. The product was isolated as pale yellow needles, mp 105°C (lit[8] mp 105–107°C).

4,4′-Bisbromoacetyl Diphenyl Ether. This was prepared by bromination of 4,4′-bisacetyl diphenyl ether in carbon disulfide. The product was collected as white needles, mp 123°C (lit.[5] mp 120–121°C). The infrared spectrum (KBr) is characterized by strong absorptions at 1685 (carbonyl), 1255 (ether), and 1200 cm^{-1} (CH_2Br).

Model Compounds

2,2′-Bisanilino-4,4′-bithiazole (III). A solution of 1.52 g (0.01 mole) of phenylthiourea and 1.22 g (0.005 mole) of 1,4-dibromo-2,3-butanedione in 190 ml of dimethylformamide was refluxed for 15 hr. The solution was concentrated to 40 ml and poured into 500 ml water. The product (1.5 g) when recrystallized from methanol, separated as pinkish needles, mp 203°C.

ANAL. Calcd for $C_{18}H_{14}N_4S_2$: C, 61.71%; H, 4.00%; S, 18.28%. Found: C, 61.59%; H, 4.11%; S, 18.03%.

Ultraviolet spectra are given in Table I.

4,4′-Bis(2-anilino-4-thiazolyl) Diphenyl Ether (IV). The procedure was same as for III; 1.52 g (0.01 mole) phenylthiourea and 2.06 g (0.005 mole) 4,4′-bisbromoacetyl diphenyl ether gave 2.1 g of crude product which when recrystallized from ethanol, separated as grey needles, mp 201°C.

ANAL. Calcd for $C_{30}H_{22}N_4S_2O$: C, 69.49%; H, 4.24%; S, 12.35%. Found: C, 69.32%; H, 4.32%; S, 12.24%.

Ultraviolet spectra are given in Table I.

General Method of Polymerization and Polymer Characterization

A solution containing equimolar amounts of the bisthiourea and bisbromoacetyl compound in dimethylformamide was refluxed under stirring for 100 hr. However, solvents like acetone, dioxane, and acetic acid could also be used. At room temperature

TABLE I
Ultraviolet Spectral Data of Model Compounds and Polymers

Substance	Medium	λ_{max}, mμ
Model III	Methanol	287
	DMF	290
IV	Methanol	287
	DMF	290
Polymer Ia	H_2SO_4	282
	DMF	285
Ib	H_2SO_4	278
IIa	DMF	287
	H_2SO_4	285
IIb	H_2SO_4	287

there was almost no reaction, but when the reaction was carried out at 50°C and above, the polycondensation proceeded smoothly and the polymers separated out in the medium. When dimethylformamide was used as the solvent, polymers Ia and IIa remained in solution, whereas the rest separated out in the medium. Polymers Ia and IIa were precipitated in methanol and were purified by dissolving in DMF and precipitating with methanol. The other polymers (Ib, Ic, IIb, and IIc) were purified by Soxhlet extraction with dimethyl-formamide. The yield was nearly quantitative irrespective of the solvent chosen. In all the experiments the reactant-to-solvent ratio was maintained at 0.1 mole/l., although the yield was not much affected by carrying out the reaction at varying ratios. The polymers were dried at 80°C under vacuum. The experimental conditions and properties of the polymers are summarized in Table II.

The polymers were characterized by their ultraviolet and infrared spectral characteristics. The ultraviolet spectra of the model and polymers were taken in DMF and H_2SO_4 and are reported in Table I. The infrared spectra were obtained on KBr disks by use of conventional sample preparation techniques.

Inherent viscosities were determined with the use of an Ostwald viscometer at 30°C at concentrations of 0.25 g/100 ml in sulfuric acid.

RESULTS AND DISCUSSION

Elemental analyses and ultraviolet spectra of the polymers and model compounds were given as evidence for the structure of polythiazoles by various authors.[1,4,5] Since these polymers are prepared by the same method, their structures as represented by repeat units is assumed. This assumption is substantiated by the presence of absorption bands characteristic of the 2-arylaminothiazole unit[9,10] and good agreement between the calculated and observed elemental analyses of polymers which are shown in Table II. Moreover, the infrared spectra of the polymers were similar in all details to those of the corresponding model compounds (Fig. 1).

The molecular weights of the polymers were determined from their bromine content by assuming the presence of one bromine at the end of the polymer chain. The molecular weight lies in the range 8000–20000. It appears that polymers containing a 1,3-phenylene unit which also remained in solution in DMF (Ia and IIa), were of higher molecular weight than those containing 1,4-phenylene or biphenylene units.

DTA measurements indicate the absence of any transition below 250°C. The thermal stability of the polymers was measured in air by the thermogravimetric method; results are shown in Figure 2. The polymers showed good thermal stability, and decomposition started at about 350°C in air. The initial thermal stability was comparable to that of the polymers in which the —NH— group is absent, whereas at higher temperatures the weight loss in these polymers is not as sharp as with the latter type.

TABLE II
Polythiazoles

Polymer	Solvent	Temp, °C	Yield, %	Color	Melting point, °C[a]	η_{inh}[b]	$\bar{M}_n$[c]	TGA, °C[d]	Analyses C, %		H, %		S, %	
									Found	Calcd	Found	Calcd	Found	Calcd
Ia	DMF	150	74	Dark brown	>460	0.23	14000	410	52.87	52.94	2.80	2.94	23.41	23.52
	Dioxane													
Ib	DMF	150	90	Brown	>460	—	8000	365	52.90	52.94	2.92	2.94	23.37	23.52
	Acetone	56	92	Brown	>460									
Ic	DMF	150	88	Red-brown	>460	—	12000	400	61.86	62.07	3.51	3.44	18.18	18.39
IIa	DMF	150	72	Brown	>460	0.38	20000	460	65.93	66.05	2.81	2.75	14.53	14.67
	Acetic acid	115	68	Brown	>460									
IIb	DMF	150	85	Black	>460	0.29	11000	420	66.01	66.05	2.69	2.75	14.50	14.67
	DMF	60	82	Black	>460									
IIc	DMF	150	88	Dark tan	>460	—	10000	425	69.62	69.76	3.80	3.87	12.23	12.40

[a] Capillary melting temperature.

[b] At 30°C and at a concentration of 0.25 g/100 ml in concentrated sulfuric acid.

[c] Based on endgroup analysis of bromine content.

[d] Temperature at which 20% loss in weight was observed (in air).

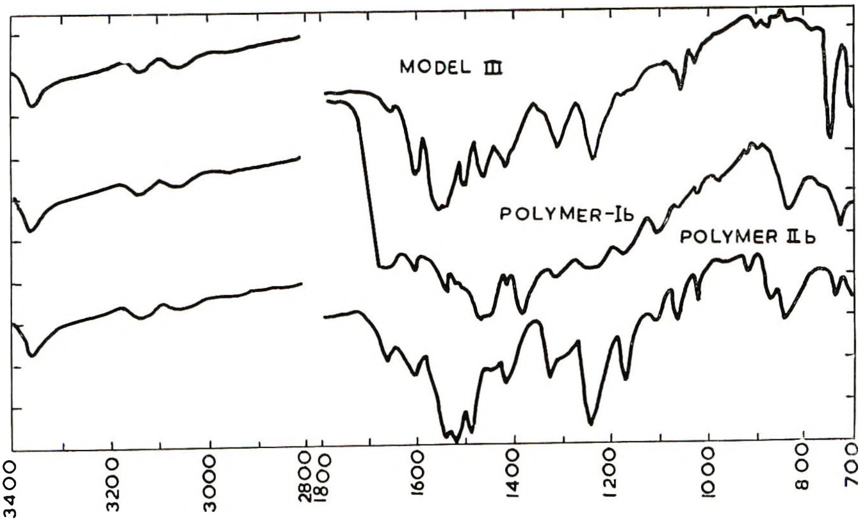

Fig. 1. Infrared spectra (KBr).

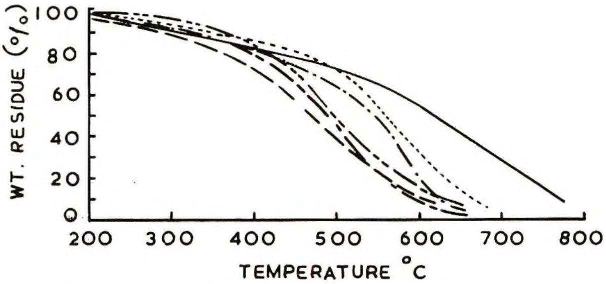

Fig. 2. Thermogravimetric analysis curves for polymers: (–·–) Ia; (– –) Ib; (– – –, Ic; (- - -) IIa; (– – – –) IIb; (——) IIc.

The polymers have varying solubility characteristics in different solvents, as shown in Table III. All of them were insoluble in common organic solvents except Ia and IIa, which were soluble in DMF, DMSO, and strong acids.

TABLE III

Solubility of the Polymers[a]

Polymer	Solvents						
	DMF	DMSO	*m*-Cresol	Concentrated H_2SO_4	Concentrated HCl	Formic acid (98%)	Concentrated HNO_3
Ia	++	++	++	++	++	++	++
Ib	–	*+	*	+	–	*	++
Ic	–	–	–	–	–	–	++
IIa	++	++	++	++	++	++	++
IIb	–	*+	*	++	–	++	++
IIc	–	–	–	+	–	–	++

[a] (++) soluble; (+) partly soluble; (*) swelling; (–) insoluble.

Polymers Ia and IIa formed brittle films from solutions in DMF, formic acid, sulfuric acid, etc.

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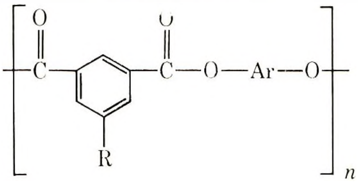
Thermal Transitions of Aromatic Polyesters with and without Side Chains

In connection with an earlier program on the preparation of fluoroaliphatic aromatic polyesters,[1,2] 5-(*n*-amyloxy)isophthaloyl chloride had been synthesized. With the availability of this monomer, it appeared desirable to prepare a number of aromatic polyesters with and without the *n*-amyloxy side chain and to determine the influence of this side chain on the reversible and irreversible thermal properties of the polymers. Accordingly, the unsubstituted and substituted polyesters (I–X) shown in Table I were prepared by the interfacial polycondensation of isophthaloyl- and 5-(*n*-amyloxy)isophthaloyl chloride with the corresponding diphenols.

TABLE I
Polyesters Prepared



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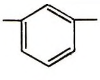
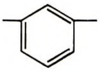
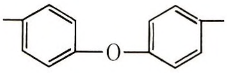
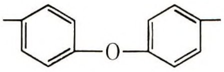
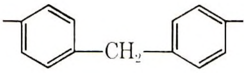
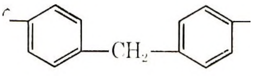
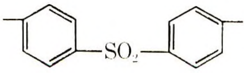
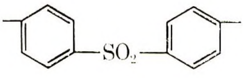
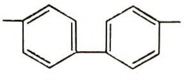
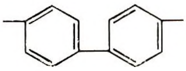
I		—H
II		—O—*n*-C_5H_{11}
III		—H
IV		—O—*n*-C_5H_{11}
V		—H
VI		—O—*n*-C_5H_{11}
VII		—H
VIII		—O—*n*-C_5H_{11}
IX		—H
X		—O—*n*-C_2H_{11}

The polymers without the *n*-amyloxy side chain have been previously characterized and described.[3,4] The polyesters were obtained in a wide range of molecular weights. This may, to some extent, limit the usefulness of comparing the thermal test data since parameters such as the glass transition temperature T_g and crystalline melting temperature T_m are normally molecular weight-dependent in the range of low molecular weights. For this reason, the conclusions drawn here are subject to qualification. It is interesting to note, however, that one of the polymers (II) was prepared in three different molecular weights in the estimated range of 3000–20000. Other than a small scattering of the results, no difference in the glass transition temperatures, crystalline melting temperatures, and decomposition temperatures (T_{dec}) of these samples could be observed.

The polymers were subjected to softening under load,[5] differential thermal analysis (DTA), and thermogravimetric analysis (TGA). The softening curves of penetration versus temperature indicated a two-step softening process. In the majority of the cases, the first step occurred in the range of T_g which was observed as a baseline shift in DTA. The second step seemed to correspond to T_m which was represented as a DTA endotherm. Softening temperatures described in the literature[3,4] for the polymers without the side chain agreed well with the second step of the softening curves.

The DTA transitions representing T_g and T_m were very reproducible. In the case of polymer IX, the melting endotherm was rather weak. The corresponding polymer with a side chain (X) did not show an observable melting point. A qualitative evaluation of the x-ray diffraction pattern indicated that the comparatively flexible polymers III and V had a much higher degree of crystallinity than the more rigid polymers VII and IX.

Table II lists T_g, T_m, and T_{dec} for the ten polyesters. T_g and T_m represent average values of the observed DTA transitions, while T_{dec} represents the highest rate of weight loss from the TGA curves.

Table II shows that, depending upon the structure of the polymer, the side chain lowers T_g by 30–80°C and T_m by 10–100°C. Rather surprising were the high T_g of the two polymers with the sulfone linkage as compared to those containing the biphenyl moiety. However, the corresponding softening curves supported the DTA data.

The T_g (°K)/T_m (°K) ratio was found to be in the range of 0.68 to 0.89. The values are somewhat higher than the ratio of approximately 0.66 which Boyer reported as the relationship between T_g and T_m for unsymmetrical polymers.[6] The present results, however, are not inconsistent with the findings of Lee and Knight, who reported no simple quantitative relationship between these parameters for all classes of polymers.[7] Their observations indicated that T_g (°K)/T_m (°K) lies between 0.5 and 0.8 in 80%

TABLE II
Thermal Transitions of Aromatic Polyesters

Polymer	η_{inh} (*m*-cresol)	T_g, °C	T_m, °C	T_g(°K)/ T_m(°K)	T_{dec}, °C
I	0.29	155	209	0.89	540
II	0.13	96	199	0.78	445
III	0.42	173	283	0.80	495
	0.62	166	282	0.80	495
	1.45	169	266	0.82	500
IV	0.30	126	278	0.72	430
V	1.18	150	348	0.68	480–530
VI	0.13	110	254	0.73	410–440
VII	0.38	249	330	0.75	435
VIII	0.11	170	246	0.85	405
IX	[a]	164	315	0.74	495
X	0.31	138	—	—	495

[a] Polymer was insoluble in *m*-cresol.

of the polymers studied. They also noted that symmetrical and unsymmetrical polymers do not have markedly different values, although polymers with ratios below 0.5 are largely symmetrical and those with ratios above 0.8 are unsymmetrical. The ratios found in the present study fall in the upper range of values as would be expected for unsymmetrical polymers.

The effect of the side chain on T_{dec} varied to a large extent. A decrease of T_{dec} between 0 and 90°C was observed with little (0–15%) difference in the weight residue at 900°C. This relatively slight influence of the side chain on the thermal stability (weight loss) in some cases can be explained on the basis of the results of a decomposition study on polymer IV and other aromatic polyesters.[8] The *n*-amyl group is removed below 350°C in the form of saturated and unsaturated hydrocarbons with cleavage occurring between the oxygen atom and the aliphatic chain. The resulting phenoxy radical provides a crosslinking site and can combine with another phenyl or phenoxy radical. The crosslinked polymer may be more resistant to breakdown than the linear polyester without a side chain. This may, in part, compensate for the loss of the *n*-amyl group.

EXPERIMENTAL

The polyesters were prepared by the interfacial polymerizations of isophthaloyl- or 5-(*n*-amyloxy)isophthaloyl chloride with the appropriate diphenols in a chloroform–water medium. The white powdery solids were purified by Soxhlet extraction with methanol and their structures verified by elemental analyses and infrared spectra. The inherent viscosities were determined with solution concentrations of 0.2–0.4 g/dl in *m*-cresol at 25°C.

TGA determinations were carried out in a nitrogen atmosphere on a modified Chevenard thermobalance at a constant heating rate of 150°C/hr. A plot of per cent weight residue versus temperature was made for each polymer.

A duPont 900 Differential Thermal Analyzer (standard cell) with a heating rate of 20°C/min in air was used for the DTA determinations. Duplicate runs were made on each polymer sample.

The softening range of the polymer samples was obtained by use of a modified Vicat apparatus.[5] Heating was performed at a constant rate of 150°C/hr. The softening range was determined from a plot of temperature versus penetration.

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Inverse Dependence of Polymerization Rate on Initiator Concentration

The polymerization of methyl methacrylate in the presence of cellulose has been investigated. Reactions were conducted in an almost saturated aqueous solution of the monomer in the presence of hydrogen peroxide as initiator and purified cotton as the cellulosic substrate. Under certain conditions the polymerization rate was found to have an inverse dependence on the peroxide concentration. The results are consistent with a diffusion-controlled temination step in which primary radicals are probably involved.

EXPERIMENTAL

Raw cotton (Davies Corp. Co. Ltd., Melbourne) was cleaned by refluxing with 1% sodium hydroxide solution for 8 hr. After washing with 0.1 *N* hydrochloric acid and conductivity water it was air-dried and kept in a closed vessel for use at a constant moisture content of 7.0%.

Polymerization conditions are given with Figure 1. Conductivity water was used throughout. Reaction mixtures were thoroughly outgassed and then gently shaken in a thermostat (±0.2°C). Poly(methyl methacrylate) was quantitatively recovered with the cellulose by filtration, washed with methanol, and dried to constant weight.

Poly(methyl methacrylate) was separated from cellulose and grafted copolymer by extraction with boiling dimethylformamide for 2 hr. The choice of extraction conditions was based on the following experiment.

Cotton containing poly(methyl methacrylate) prepared as above was boiled under reflux with toluene for 2 hr, filtered, washed with benzene, and dried. The product contained 45.0% poly(methyl methacrylate) (determined by weight and based on the original weight of cotton), but on further extraction with dimethylformamide at 80°C for 1 hr this was reduced to 43.3%. A further three successive extractions with boiling dimethylformamide for 1 hr each time, reduced the poly(methyl methacrylate) content to 40.2, 40.0, and 39.8%, respectively. A similar extraction of the original cotton for 3 hr with boiling dimethylformamide resulted in a weight loss of 0.2%. Evidently, dimethylformamide is more effective than toluene in removing homopolymer, presumably because it is able to swell the cellulose to a greater extent. Some slow degradation of cellulose in the boiling dimethylformamide occurs however, and it is necessary to limit this treatment. On this basis a compromise of 2 hr was chosen.

Considerable doubt remains as to the proportion of the poly(methyl methacrylate), which is covalently attached to cellulose, remaining after the above extraction procedures, and this leads to uncertainties in the determination of the ratios of graft to homopolymer shown in Table I. Most reliance is therefore placed on the total polymerization figures such as those shown in Figure 1.

RESULTS AND DISCUSSION

The curves in Figure 1 show the normal accelerating rate common to polymerizations in a precipitating medium. Of more significance is the effect of hydrogen peroxide on the rate. This shows a maximum rate at an intermediate peroxide concentration. Polymer samples corresponding to the two extreme curves of Figure 1 were analyzed for graft copolymer, and the results are shown in Table I. Subject to the limitations discussed above it would appear that both the homopolymerization and graft polymerization rates show an inverse dependence on initiator concentration. In addition, a higher proportion of graft copolymer is formed at the lower initiator concentration.

In a previous publication it has been shown[1] that transfer reactions between poly(methyl methacrylate) radicals and cellulose-type compounds are rare. It seems probable, therefore, that graft copolymer originates by the attack of hydroxyl radicals on the cellulose backbone within the swollen amorphous regions of the fibers. This

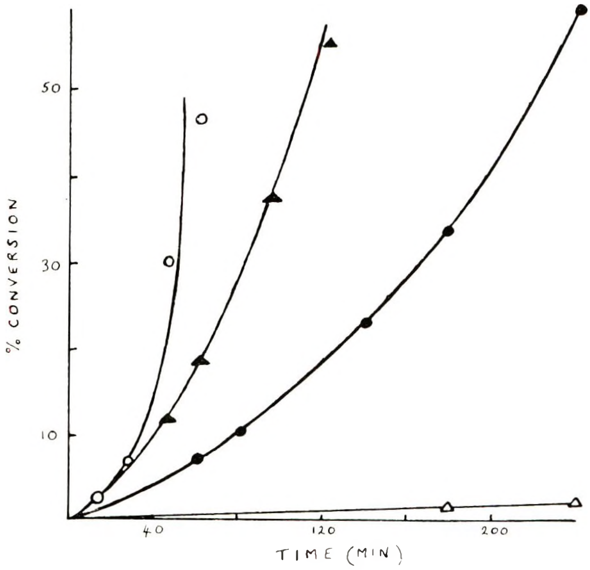

Fig. 1. Effect of reaction time on total polymer yield at various H_2O_2 concentrations (●) 6.16×10^{-2} mole/l., (○) 3.27×10^{-3} mole/l.; (▲) 3.30×10^{-4} mole/l.; (△) 0 $[M] = 0.123$ mole/l.; cellulose = 0.51 g/55 ml solution; $T = 85°C$.

TABLE I
Proportions of Graft and Homopolymer

$[H_2O_2]$, mole/l.	Time, min	Homopolymer, %	Graft copolymer, %
3.27×10^{-3}	15	31	69
	30	26	74
	45	44	56
	60	38	62
6.16×10^{-2}	60	42	58
	80	50	50
	180	78	22
	240	67	33

mechanism is supported by results obtained for the polymerization of acrylonitrile in the presence of cellulose.[2] In this case, with hydroxyl radicals as the initiating species, graft copolymer was produced, but with azobisisobutyronitrile as initiator only homopolymer was isolated. In addition hydroxyl radicals are known to abstract hydrogen atoms readily from alcohols and have been shown to attack various substrates in the presence of methyl methacrylate.[3,4] Recent ESR studies indicate that the hydroxyl radical probably abstracts a hydrogen atom from the primary hydroxyl group of the cellulose.[5] Competitive hydroxyl radical addition to monomer undoubtedly accounts for the homopolymer produced.

$$H_2O_2 \rightarrow 2OH\cdot$$

$$HO\cdot + M \rightarrow P\cdot$$

$$HO\cdot + \text{Cellulose} \rightarrow H_2O + \text{Cell}\cdot$$

$$\text{Cell}\cdot + M \rightarrow \text{Cell P}\cdot$$

Because of the heterogeneous nature of the polymerization process the termination step will be diffusion-controlled. This will apply whether radical growth occurs within the cellulose fibers or in the bulk solution. The latter case, however, by analogy with other polymerization processes in a precipitating medium, would be expected to result in a homopolymerization rate with an initiator exponent greater than 0.5.[6] Since this is not observed, it is suggested that most of the homopolymer, as well as the graft copolymer, is produced within the cellulose fibers. This is supported by visual observation for all of the reactions described. Thus the monomer competes with cellulose for hydroxyl radicals within the cellulose phase. It is also likely that growth of some polymer chains will terminate with hydroxyl radicals (i.e., primary radical termination occurs). This process will reduce the initiator exponent below 0.5,[7] although it cannot alone account for the inverse relationship observed. An explanation of the results may lie in the possibility that, because the termination step is diffusion-controlled, the rate of this process will decrease with increasing polymeric radical size. Therefore a rate equation of the following form will apply, where $\bar{k}_t$ is an average termination constant and is a function of the rate of initiation, R_i. Consequently, increasing the peroxide concentration

$$-d[\mathrm{M}]/dt = k_p[\mathrm{M}]R_i^{1/2}/(2\bar{k}_t)^{1/2}$$

can have two opposing effects on the overall polymerization rate. Thus R_i will increase, but since this also reduces the average polymer radical size, the termination rate will also increase. It is suggested that the respective importance of these effects, with the occurrence of significant primary radical termination, could account for the observed results. The increased proportion of graft copolymer formed at the higher polymerization rate would suggest that the termination reaction of polymer radicals anchored to the cellulose structure is more strongly diffusion-controlled than is the termination of the homopolymerization.

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Preparation and Properties of Polyacetylene

Watson et al.[1] studied the polymerization of acetylene with various Ziegler-type catalysts and were the first to report the preparation of a *cis*-polyacetylene. We have recently examined the preparation and properties of polyacetylene prepared by different catalyst systems and we have obtained more definitive data describing the structure and properties of *cis*- and *trans*-polyacetylene. In our work, acetylene has been polymerized via a catalyst developed by Noguchi and Kambara[2] for the polymerization of ethynylbenzene. This polyacetylene (I) has been studied using infrared spectrophotometry, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) techniques and found to have a high *cis*-polyene content in comparison to a polyacetylene (II) prepared according to the method of Luttinger,[3] which is reported to have a *trans*-polyene structure.

EXPERIMENTAL

Polymerization of Acetylene to *Cis*-Polyacetylene (I)

By the method of Noguchi and Kambara,[2] iron dimethylglyoximate·2 pyridine[4] (1.52 g) was thermally decomposed at 130–140°C in vacuum. After cooling to 25°C, triethylaluminum (16.2 ml of a 10% solution in hexane) was injected into the reaction vessel, and the catalyst was aged for 15 min. Dry benzene (100 ml) was added, and acetylene was slowly bubbled into the flask at 25°C or below, with occasional shaking until the pressure rose to 1 atm and the uptake of acetylene ceased (0.5 hr). The resulting violet gel was filtered, washed with ethanol, concentrated hydrochloric acid, water until neutral and, finally, with ethanol. The polymer (1.24 g) was dried at 25°C under vacuum for 18 hr.

Polymerization of Acetylene to *Trans*-Polyacetylene (II)

Polyacetylene II was prepared by using the cobalt nitrate–sodium borohydride–ethanol catalyst system of Luttinger.[3] The solid product was filtered off, washed with ethanol, concentrated hydrochloric acid, water until neutral, and again with ethanol. The polymer was dried at 25°C under vacuum for 18 hr.

RESULTS AND DISCUSSION

The properties of polymer I were compared with those of polymer II. Polyacetylene I was a gray-black fibrous material which could be easily pressed into pellets. As pellets, they had the feel and appearance of graphite with a greenish metallic sheen. Only after standing for several months in air did I form explosive peroxides. With evaporated gold electrodes, the electrical resistivity ρ of a pressed pellet of I was 1×10^6 ohm-cm at 298°K and the current-voltage plot was linear from 40 to 4000 V/cm. The activation energy for conduction, calculated from $\rho = \rho_0 \exp\{-E/kT\}$ was 0.305 eV under nitrogen with a linear $1/T$ versus R plot in the range of 170 to 400°K. The Seebeck voltage, measured with copper contacts under vacuum, was in the range of 0.9–1.1 mV/°K from an average pellet temperature of 298 to 388°K with temperature differentials between top and bottom thermodes ranging from 2.2 to 33°K. The sign of the Seebeck coefficient was plus at the cold junction, thereby making the *cis*-polyacetylene a *p*-type material. Jenkins[5] found the thermal conductivity of a fresh sample of I to be 1.3×10^{-3} cal/cm-sec-°K over the range 310–360°K. Previous heating to 360°K had no effect on the thermal conductivity nor on the electrical conductivity, indicating that the *cis* to *trans* rearrangement plays no part in the conduction mechanism of the polymer. Since this polymer was a soft, easily compacted material, thereby minimizing void content, the retention of thermal and electrical conduction properties could be related to the good particle-particle content. A more brittle polymer, such as II, is not as easily compacted and this, in part, could have an adverse effect on the electrical and thermal properties.

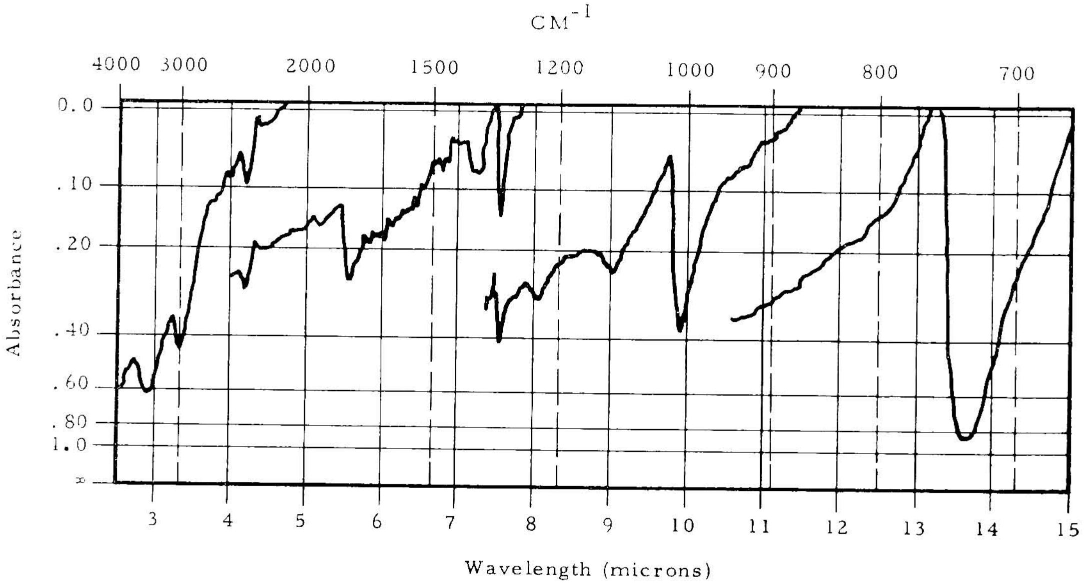

Fig. 1. Infrared spectrum of polyacetylene I.

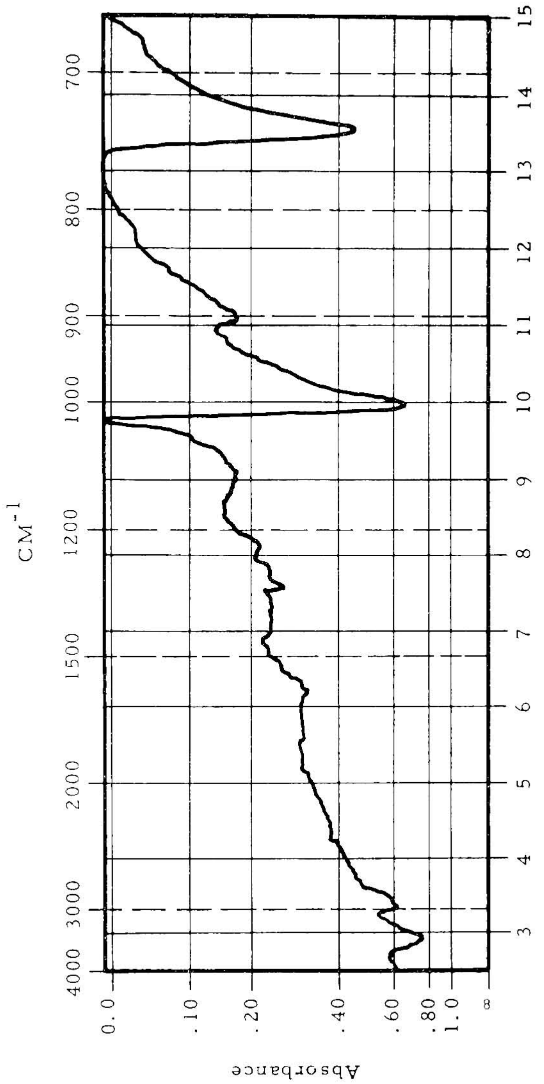

Fig. 2. Infrared spectrum of polyacetylene II.

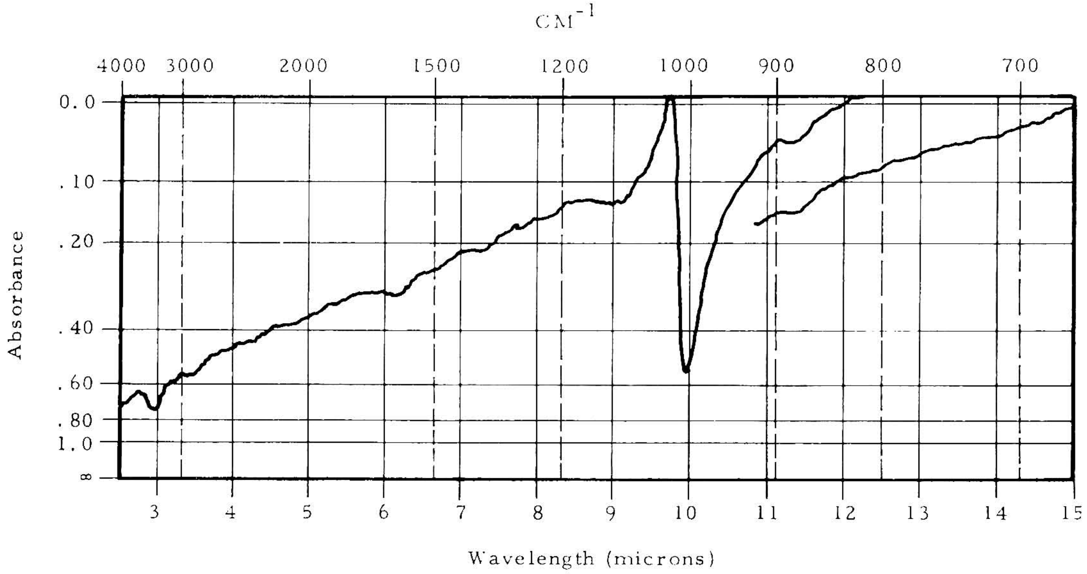

Fig. 3. Infrared spectrum of polyacetylene I (heated to 500°K in nitrogen).

Polymer II was a hard, brownish-black material which could be pressed into pellets only at high pressures. It became a lighter brown in color after a few days in air and formed explosive peroxides readily. Jenkins[5] found the thermal conductivity of a fresh sample of II, *in vacuo*, to be 5×10^{-4} cal/cm-sec-°K. We have found the electrical resistivity to be 6.0×10^{11} ohm cm *in vacuo* at 298°K with gold electrodes. The activation energy for conduction is 0.545 eV under nitrogen from 298 to 400°K, and the *I-V* plot was linear with a slope of unity over the range of 14 to 14000 V/cm.

The infrared spectra of polyacetylenes I and II (Figs. 1 and 2) show, in addition to strong black body absorption at the short wavelengths due to the long, conjugated polyene structure, strong absorptions in the vicinity of 9.95 and 13.6 μ. The 9.95 μ band is assigned to the out-of-plane deformation of the conjugated *trans* olefinic hydrogens.[6] Oroshnik and Mebane[7] have assigned the 13–15 μ region to the out-of-plane deformation of the *cis* olefinic hydrogens of simple organics, with a hypsochromic effect taking place with conjugation, e.g., 9,9′-*cis*-β-carotene at 12.84 μ. Watson et al.[1] mention an absorption for one of their polyacetylenes at 14.3–14.9 μ and assign this to the out-of-plane deformation of the *cis* olefinic hydrogens. Weaker absorptions in the spectrum of I at 7.6 μ[6] can be assigned to the in-plane hydrogen deformation modes of the *cis* and *trans* portions, respectively.

Heating polyacetylene I to 500°K under nitrogen causes the 13.6 μ band to disappear and the 9.95 μ band to increase in intensity (Fig. 3). We postulate that the 13.6 μ band is due to the *cis* olefinic out-of-plane hydrogen deformation. The absorptivities of the *trans* band at 9.9 μ and that of the *cis* band at 13.6 μ for I were found to be 20.5 l. and 25.4 l./mole-cm, respectively, and the *cis* polyene content for I and II was calculated to be 69 and 39 mole-%, respectively. Several batches of I were prepared and were consistently found to have a 60–70% *cis* content, even when prepared at 0°C. The ratio of 2-*cis* groups to 1-*trans* group indicates that a sequence of *cis-cis-trans* groups may exist, although there are no definite data to prove this.

Polyacetylene I was stored in air at room temperature, and infrared spectra were obtained at intervals of 1, 14, and 27 days after preparation. Isomerization was found to occur at room temperature with a rate of *cis* to *trans* isomerization of 5–6%/day. At −30°C, the rate of isomerization was very low.

Differential scanning calorimetry (DSC) carried out under nitrogen was used to calculate the heat of isomerization of I and II (Figs. 4 and 5). The irreversible exotherm found at 320–500°K is believed to be due to the *cis–trans* isomerization. On a mole basis

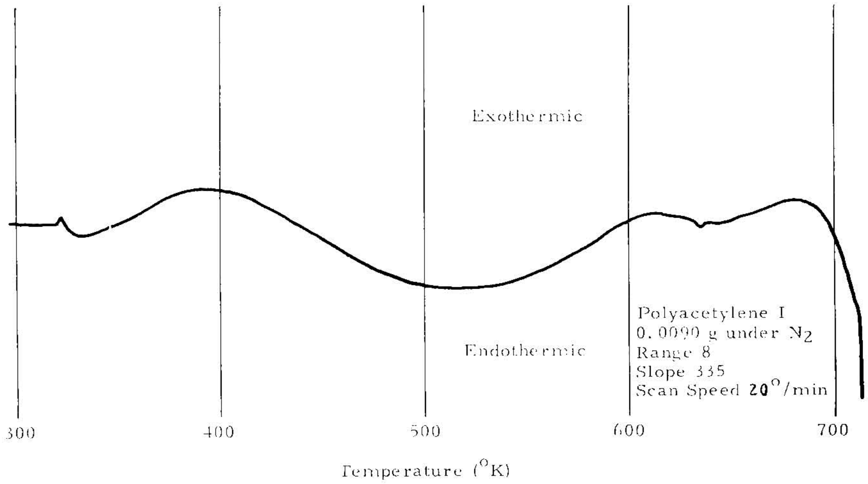

Fig. 4. DSC of polyacetylene I.

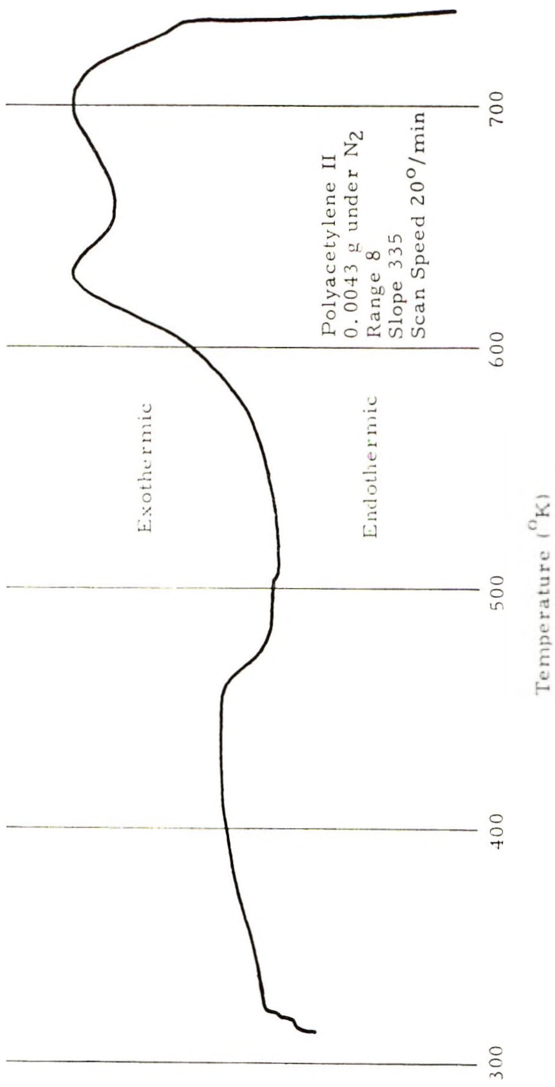

Fig. 5. DSC of polyacetylene II.

for the *cis* ethylenic double-bond content, which was calculated from infrared data, the heats of isomerization were found to be 1.6 and 1.7 kcal/mole for I and II, respectively. These values are in the range found for *cis* and *trans* isomerization of various *cis* hydrocarbons as determined from differences in heats of combustion of the *cis* and *trans* hydrocarbons.[8]

Another exotherm found in the DSC for the two acetylenes was noted in the 550–650°K region with maxima at 630°K for I and 610°K for II. The heats of transition were 24 cal/g for I and 5.3 cal/g for II. These exotherms appear to be related to a crystallization phenomenon of the polymers. Melting, with rapid decomposition, began near 740°K for a fresh preparation of I and decomposition without melting began at 685°K for polymer II.

A thermogravimetric analysis of a sample of I which had been stored for four weeks at −30°C was made in air at heating rate of 21.5°K/min. The TGA shows an onset of weight gain at 350°K and a maximum weight gain of 13.5% at 505°K. Above 505°K, an almost linear loss of weight occurs with increasing temperature until at 1000°K, 72% of the original weight has been lost. The maximum rate of weight gain was between 455 and 475°K. The maximum rate of exothermic *cis* to *trans* conversion, as determined from the DSC under nitrogen, was in the region of 420–455°K. The double bond is probably very subject to oxidative degradation during the isomerization, and this may account for the weight gain and oxidative instability of the polyacetylenes. The TGA of a sample of II which had been stored at −30°C for 4 weeks shows an explosive loss of weight at 335°K due to decomposition of the peroxides formed from air oxidation. Further work is in progress with respect to the electrical behavior of the *cis*-polyacetylene and will be reported later.

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Synthesis and Properties of Cyclic Di(ethylene Terephthalate)

Cyclic oligoesters of terephthalic acid and ethylene glycol can be synthesized by reacting the dichlorides of the oligoester dicarboxylic acids with oligoester diols in dilute solutions:

$$\mathrm{Cl[{-}CO(C_6H_4)CO{-}O(CH_2)_2O{-}]_m{-}COC_6H_4COCl} +$$

$$\mathrm{H[{-}O(CH_2)_2O{-}CO(C_6H_4)CO{-}]_n{-}O(CH_2)_2OH} \xrightarrow[-2\mathrm{HCl}]{\text{Base}}$$

$$\downarrow$$

$$\boxed{\mathrm{{-}[O(CH_2)_2O{-}COC_6H_4CO]_{m+n+1}{-}}}$$

The first successful synthesis of a cyclic ethylene glycol terephthalate was carried out by Meraskentis and Zahn[1] with the preparation of the trimer. Recently Zahn and Repin[2] succeeded in synthesizing the whole series of these oligomers from trimer to heptamer.

The isolation of the cyclic dimer from a mixture of oligomers obtained by reacting the terephthalyl chloride with terephthalic acid–diethylene glycol is reported here.

The reaction was carried out in benzene, and pyridine was used as base. The mixture of reaction products obtained consisted of linear and cyclic oligomers in which the proportion of dimer was 24%. Other isolated cyclic oligomers were the trimer (10%), tetramer (49%), pentamer (1.4%) and hexamer (0.6%). The reaction products were separated by means of thin-layer chromatography. The solvent system which gave the best separation results was a mixture of tetrachloroethane and tetrahydrofurane (95:5).

Weissenberg and precession x-ray photographs showed the crystals to be monoclinic with the monoclinic angle very near to 90°. The calculated unit cell dimensions are: $a = 8.58 \pm 0.05$; $b = 12.75 \pm 0.1$; $c = 8.01 \pm 0.04$; $\beta = 90.7 \pm 02$. The reflection conditions in the class $(0k0)$ reflexes is $k = 2n$ and in the class $(h0l)$, $l = 2n$. This indicates that the unit cell has a space group symmetry $P2_1/c$. Assuming that the unit cell contains two molecules, the density 1.455 can be calculated (experimental at 20°C, 1.456).

The fact that there are only two molecules in the cell indicates that the molecules are located in special positions,[3] and they are centrosymmetric. This leads to the stereochemical conclusion that the mean planes of both benzene rings are parallel and that both ethylene glycol residues in the molecule have the same configuration.

Measurements of refractive indices have shown that the crystals are strongly birefringent. The indicatrix axes have the values $n_Z = 1.80$, $n_Y = 1.64$, and $n_X = 1.45$.

The infrared spectrum of this compound, shown in Figure 1, includes absorption bands

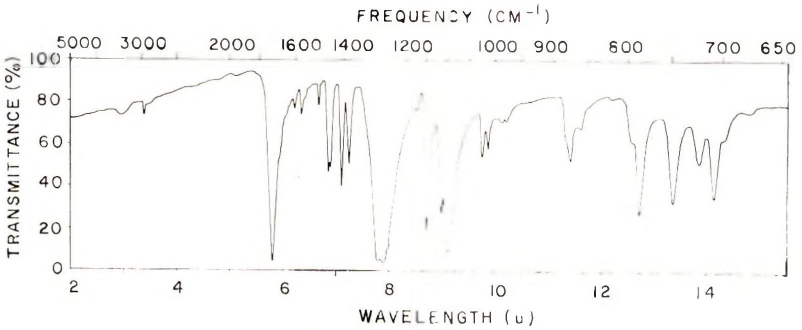

Fig. 1. Infrared absorption spectrum of compound.

which are also present in other oligomers of this series and in PET. Such bands are at 1720 cm^{-1} (C=O stretching), 1263 cm^{-1} (=C—O stretching), 875 cm^{-1} (terephthaloyl out-of-plane bending mode ν_{17B}),[4] 1409 cm^{-1} (C—C terephthaloyl in-plane stretching, ν_{13}' mode[4]), 793 cm^{-1} (combination band of C=O rocking and CCO bending modes[4]), 1095 cm^{-1} (probably C—O symmetric stretching vibration of a glycol residue with *gauche* configuration[5]).

Since many of the absorption bands which are characteristic for the rotational isomerism are absent in the infrared spectrum of the dimer it is not possible to conclude whether the configuration of the ethylene glycol residue is *gauche* or *trans*. Nevertheless the bands at 1384 cm^{-1} (linear dimer 1389 cm^{-1}),[6] 1442 cm^{-1} (PET 1445 cm^{-1}),[6] and 881 cm^{-1} (ethylene glycol 881 cm^{-1})[5] give some evidence for the existence of the *gauche* form.

Absorption bands assigned to a hydroxyl group are very weak.

EXPERIMENTAL

Three liters benzene, 0.004 mole (0.802 g) of terephthalyl chloride ($Cl—CO—C_6H_4—CO—Cl$), 0.004 mole (1.016 g) of terephthalic acid diethylene glycol ($HO—CH_2CH_2—OCO—C_6H_4CO—OCH_2CH_2OH$), 0.01 mole (0.79 g) pyridine, and magnesium powder (2 g) were placed in a three-necked flask. The mixture was heated at 80°C with vigorous stirring in a nitrogen atmosphere for 3 days. The solvent was evaporated until about 100 ml were left. The solid material was filtered and the solution was poured into an excess of petroleum ether. The precipitate was filtered, washed with H_2O, dried, and extracted with tetrachloroethane. The solution was transferred onto silica gel layers (thickness 1 mm) for chromatographic separation. A mixture of tetrachloroethane: tetrahydrofuran (95:5) was used as solvent system. The bands corresponding to dimer (fastest bands) were scratched off and extracted with dioxane. The substance was recrystallized in acetone (0.261 g, yield 17%) into colorless hexagonal prisms, which melt at 229°C. Analysis showed C, 62.40%, H, 4.35% (calculated: C, 62.5%; H, 4.2%). Vapor pressure osmometry yielded values of 382, 383, 385, 385 (average 384) for the molecular weight (mass spectroscopy gave 384, calculated 384).

We are greatly indebted to Professor H. Zahn for his interest in this work. We thank Mrs. K. Hoener for technical assistance. We wish also to thank the Landesamt für Forschung of Land Nordrhein-Westfalen, Düsseldorf, and the Arbeitsgemeinschaft Industrieller Forschungsvereinigungen (AIF), Köln, (Research Project 1033) for supporting this work.

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Comment on "Polycondensation Equilibrium and the Kinetics of the Catalyzed Transesterification in the Formation of Polyethylene Terephthalate"

In a recent study of the catalyzed transesterification reaction in the formation of poly(ethylene terephthalate), Fontana suggested[1] that experimental data obtained by Griehl and Förster[2] point to the occurrence of a reversible dissociation reaction in the polymer. Unfortunately, in this reinterpretation of the data of Griehl and Förster an error was introduced by using the concept "mole fraction of glycol" in two different meanings.

In the polymeric system the "mole fraction of glycol" may be defined in two ways:

$$g_1 \equiv G/N$$

$$g_2 \equiv G/N_0$$

where G = concentration of glycol (in moles/kg), N = concentration of macromolecules (in moles/kg), N_0 = concentration of repeating units (in moles/kg) and concentrations of glycol in the denominators are neglected. Since $N_0 = \overline{\mathrm{DP}}(N)$, $g_1 = \overline{\mathrm{DP}}(g_2)$. By using his equation (20):

$$K = g(\overline{\mathrm{DP}} - 1)$$

Fontana evidently chose the first definition: $g = g_1$ [This may be seen if this equation is compared with eq. (8) in the paper of Griehl and Förster]. Values of the degree of dissociation α of the polyester were then calculated with the aid of "mole fractions of glycol" as given by Griehl and Förster (second column of Table IV of Fontana, sixth column of Table I of Griehl and Förster).

However, the latter authors calculated their "mole fraction" x_g from the measurements of the vapor pressure of glycol in equilibrium with the molten polymer [eq. (17) of Griehl and Förster]

$$x_g = P_g/P_g^0$$

As has been pointed out by Challa,[3,4] application of this equation is not correct for the polymeric system. The statistic-thermodynamical theory of Flory and Huggins[5] should be applied here, which gives:

$$P_g/P_g^0 = v_g e^{(1+\mu)}$$

As the volume fraction of glycol is certainly proportional to the concentration of glycol (moles/kg), and the values of N_0 and μ are constant, the last two equations may be replaced by

$$x_g = P_g/P_g^0 = (G/N_0)\beta = g_2\beta$$

in which β is a proportionality factor. This means, that "mole fractions" as calculated by Griehl and Förster differ by a constant factor β from our second definition of mole fraction of glycol.

As the factor β was assumed to be 1 by Griehl and Förster, their value of equilibrium constant K is wrong by a constant factor β. It is quite clear, however, that if their values of x_g are substituted for g_1, as was done by Fontana, an additional error of $g_2/g_1 = 1/\overline{\mathrm{DP}}$ is introduced in the calculation of K. This error completely accounts for the rapid increase of the calculated value of K in the paper of Fontana (Table IV, third column).

The substitution of the values of $g_2\beta$ in his formula (21), where values of g_1 should have been substituted, accounts for the rather unrealistic high values of α (fourth column). The occurrence of a reversible dissociation reaction of the polymer was suggested by the linear relationship between $[(1/\alpha) - 1]$ and $g^{1/2}$ (Fig. 4, Fontana).

As the values of α are not correct, it may be concluded that no evidence is present to assume a reversible dissociation reaction in polyester.

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Mechanism of Vinyl Monomer Polymerization in the Presence of Trialkylboranes and Inhibitors

In a previous paper the mechanism of polymerization of methyl methacrylate (MMA) in the presence of triethylborane (TEB) with azobisisobutyronitrile (AIBN) as initiator and *p*-benzoquinone (BQ) as inhibitor was discussed. The present communication is concerned with several sets of experiments that were carried out in order to obtain further support of the mechanism there proposed.

EXPERIMENTAL

The polymerization technique and molecular weight determinations were the same as previously described.[1] The low molecular weight polymer formed in the different runs of the present work was isolated in the following way. The polymerization reaction was stopped by immersing the polymerization tubes in an ice-water bath, and their contents were poured into ammonia–methanol mixtures. Then, the solutions were completely vacuum evaporated. The resulting white solid was washed with water and dried to constant weight. All runs were carried out at 70°C.

RESULTS AND DISCUSSION

Figure 1 shows experimental results of several runs carried out with the use of AIBN, MMA, and BQ in order to check our experimental technique. As can be seen from Figure 1, the expected inverse dependence on BQ concentrations is obtained. It was found that z, defined as the ratio of k_2 to k_1, was 4.1, in good agreement with previous results.[2] k_2 and k_1 are the specific rate constants related to the following reactions:

$$\mathrm{M}^{\cdot}_{x} + \mathrm{M} \xrightarrow{k_1} \mathrm{M}^{\cdot}_{x+1}$$

$$\mathrm{M}^{\cdot}_{x} + \mathrm{BQ} \xrightarrow{k_2} \mathrm{M}_x\mathrm{BQ}^{\cdot}$$

According to the accepted mechanism of the inhibited polymerization[3] and assuming that $M_x\mathrm{BQ}^{\cdot}$ is not able to reinitiate any chain

$$R_p = (k_1/k_2)2fk_i[\mathrm{AIBN}][\mathrm{M}]/[\mathrm{BQ}] \tag{1}$$

$$= \nu R_i$$

where:

ν is the average chain length, R_p is the polymerization rate, f is the efficiency of the initiator, k_i is the specific rate constant of the initiation step, and R_i is the initiation rate.

On inserting our experimental data, a value of 12 is obtained for ν, which is in reasonably good agreement with molecular weights of approximately 3000 found, by means of viscosity measurements, for polymeric materials obtained under these conditions. It is assumed that the polymerization terminates by combination.

In another set of experiments, the overall polymerization rate of a system containing constant concentrations of AIBN, MMA, TEB, and BQ was measured. The behavior of this system is shown in curve B of Figure 2. For the sake of comparison the inhibited (curve A) and uninhibited (curve C) overall polymerization rates were included in Figure 2. It can be seen that the initial rate is almost identical to that of the normal polymerization, and that it is followed by a process having a similar rate to that of the inhibited polymerization. This behavior is in agreement with that expected in terms of the mechanism previously proposed:[1]

$$\mathrm{M}^{\cdot}_{x} + \mathrm{BQ} \rightarrow \mathrm{M}_x\mathrm{BQ}^{\cdot} \tag{2}$$

$$\mathrm{M}_x\mathrm{BQ}^{\cdot} + \mathrm{TEB} \rightarrow \mathrm{M}_x\mathrm{BQBEt}_2 + \mathrm{Et}^{\cdot} \tag{3}$$

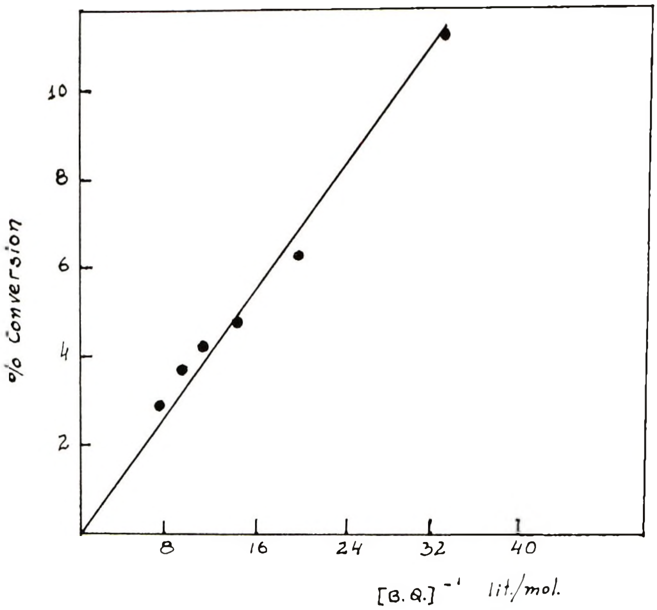

Fig. 1. Polymerization conversion dependence on inverse BQ concentration. Temperature, 70°C; polymerization time, 2 hr; [AIBN], 0.08 mole/l.

$$\mathrm{Et}^{\cdot} + \mathrm{M} \rightarrow \mathrm{EtM}^{\cdot} \tag{4}$$

$$\mathrm{M}_x\mathrm{BQBEt}_2 + \mathrm{M}_x\mathrm{BQ}^{\cdot} \rightarrow (\mathrm{M}_x\mathrm{BQ})_2\mathrm{BEt} + \mathrm{Et}^{\cdot} \tag{5}$$

In this mechanism the resonance-stabilized radicals $M_x\mathrm{BQ}^{\cdot}$, which are usually unable to continue chain growth, give a fast transfer reaction with TEB, thereby producing highly reactive ethyl radicals, which in turn initiate new chains. [Reaction (5) would account for two ethyl radicals for each TEB molecule.] These processes would lead to an overall polymerization rate closely similar to that of the normal polymerization. This parallel will be maintained until all the TEB has been consumed. The main difference between both processes lies in the molecular weight of the polymer, which is considerably lower when TEB is present,[1] as a result of the chain transfer represented by eqs. (2) and (3). The solid product obtained under these conditions showed a molecular weight of approximately 4500; this value is remarkably similar to that obtained in the inhibited polymerization, thus indicating that ν is not essentially affected by the presence of TEB. Hence, it can be concluded that when TEB is present the system gives a similar rate to that obtained in the uninhibited polymerization, but yields polymer of molecular weight comparable to that obtained in the inhibited polymerization. This evidence is in agreement with the proposed mechanism.

The second part of curve B can be clearly understood if it is noted that BQ concentration is considerably higher than twice the TEB concentration. This allows that, even if it is assumed that two ethyl radicals are produced by each TEB molecule, the remaining BQ concentration is nearly the same as that of curve A. Consequently, very similar polymerization rates must be obtained.

In a third set of experiments, the overall polymerization rate dependence on the TEB concentration, at constant time of polymerization, was studied. The experimental results are shown in Figure 3. According to the proposed mechanism and neglecting the small contribution to the overall yield of the strongly inhibited reaction, eq. (6)

$$\text{Yield} = \nu[\mathrm{TEB}]/[\mathrm{MMA}] \tag{6}$$

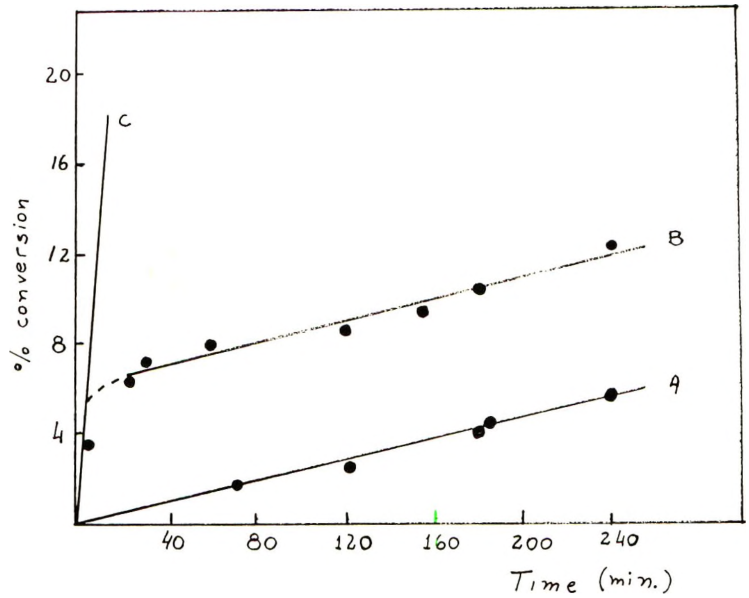

Fig. 2. Polymerization conversion as a function of time at 70°C: (*A*) [AIBN] = 0.08 mole/l.; [BQ] = 0.15 mole/l.; (*B*) [AIBN] = 0.08 mole/l.; [BQ] = 0.15 mole/l.; [TEB] = 0.026 mole/l. (*C*) [AIBN] = 0.08 mole/l.

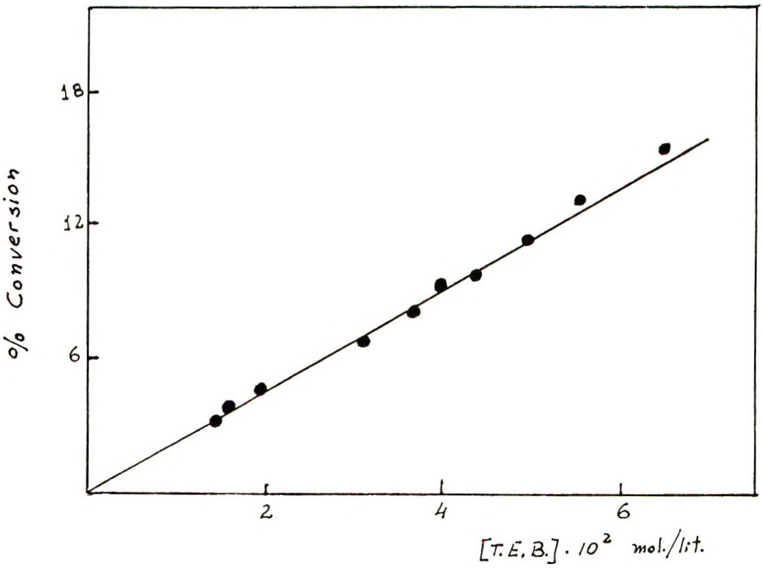

Fig. 3. Polymerization conversion dependence on [TEB] at 70°C. Polymerization time, 20 min; [BQ] = 0.15 mole/l.; [AIBN = 0.08 mole/l.].

will hold, if the time is long enough so as to assure complete using up of the TEB. In eq. (6), ν is the average chain length corresponding to the inhibited reaction. If it is assumed that ν is nearly independent of BQ consumption (an oversimplification that does not introduce a great error when [TEB]/[BQ] is low), the agreement between eq.

(6) and the experimental data of Figure 3 is quite satisfactory. The value of the average chain length ν obtained from the data of Figure 3 is approximately 21 if one considers that one ethyl radical is produced by each TEB molecule, while a value of approximately 11 is obtained for ν if it is assumed that two transfer reactions on each TEB molecule can occur. Remembering that a value of $\nu = 12$ was obtained without TEB, a good proof of consistency for the proposed mechanism is obtained. Furthermore, although our experiments cannot be conclusive about how many transfer reactions occur on each TEB molecule, they seem to favor the conclusion that two ethyl radicals are produced by each TEB molecule. In addition, some evidence supporting that two alkyl radicals are produced in the reaction of one molecule of trialkylborane with oxygenated radicals has been recently advanced.[4]

Another way of proving the consistency of the proposed mechanism comes from the comparison of the inhibited polymerization rate (Fig. 1), with the slope of Figure 3. Dividing eq. (1) in the form $R_p = \nu R_i$ by eq. (6) and assuming that the efficiency of the AIBN in this process is approximately 0.5,[5] the following expression is obtained:

$$k_i = 2R_p[\text{TEB}]/\text{yield }[\text{MMA}][\text{AIBN}] \qquad (7)$$

where the factor two accounts for the occurrence of reaction (5).

On inserting the experimental data of both sets of experiments, a value of $k_i = 4.4 \times 10^{-5}$ sec^{-1} is obtained, which is in good agreement with accepted values.[6,7]

All these experimental data strongly support the previously advanced mechanism of vinyl polymerization in the presence of trialkylboron compounds,[1] and additionally confirm the fact that free-radical displacement reactions on trialkylboranes occur rapidly if the attacking radical has an oxygen atom or resonance contribution.[8-10] Furthermore, they suggest that the reaction between alkyl boranes and vinyl ketones may occur through a free radical mechanism.[11]

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Controlling the Nature of Terephthalonitrile Oxide Polymerization

Iwakura et al.[1] first reported the synthesis of terephthalonitrile oxide and proposed its use as a monomer in polymerization. Overberger and Fujimoto[2] mentioned that homopolymerization might yield either 1,2,5- or 1,2,4-oxadiazolediyl radicals between the *p*-phenylene radicals. They suggested that solid-state polymerization formed both types of oxadiazoleidyl radicals, whereas solution polymerization yielded the 1,2,5-structure only, in their opinion. Fujimoto[3] used crystallographic data to support the idea that the 1,2,4-structure was preferred in solid state polymerization.

We have considered the mechanisms and conditions for homopolymerizing terephthalonitrile oxide and investigated the possibility of directing this polymerization exclusively toward the *N*-oxide of poly(1,2,4-oxadiazolediyl-*p*-phenylene) or toward the 1,2,5-isomer. Anionic, cationic, and free-radical initiators have been employed in solution polymerization experiments, as well as radiation and thermal treatment of the solid terephthalonitrile oxide.

The following polymerization conditions were successful: P1, cationic, 2 hr at $-85°C$ in $CHCl_3$, $SnCl_4$ initiator; P2, Cationic, 2 hr at $-60°C$ in CCl_4–CH_2Cl mixture, PCl_3 initiator; P3, free-radical, refluxing CCl_4 for 22 hr, azobisisobutyronitrile initiator; P4, free-radical, refluxing C_6H_6 for 22 hr, azobisisobutyronitrile initiator; P5, uncatalyzed, stirred in dimethylformamide for 20 hr at 25°C; P6, uncatalyzed, standing in CH_3CN for 100 hr at 25°C; P7, uncatalyzed, stirred in acetone for 20 hrs. at 25°C; P8, uncatalyzed, refluxing tetrahydrofuran for 24 hr; P9, uncatalyzed, refluxing toluene for 24 hr; P10, uncatalyzed, standing in hexamethylphosphoramide for 24 hr; P11, uncatalyzed, heating solid monomer for 24 hr at 100°C.

Irradiation of solid terephthalonitrile oxide with up to 200000 rad as 6 Mev electrons did not result in polymerization. Sodium naphthalene addition to a terephthalonitrile oxide solution in glycol diethyl ether under anhydrous conditions also failed to initiate polymerization. We conclude that chain polymerization of terephthalonitrile oxide can occur with either radical or cationic initiation but not with anionic initiation.

The infrared spectroscopy of the samples indicated that structural differences could be deduced from the presence or absence of absorption at 825, 925, and 960 cm^{-1}. Most of the polymers had absorption in all these regions; however, one cationic polymer (P2) had absorption at 925 and 850 cm^{-1} but not in the other diagnostic regions (Fig. 1). One radical polymer (P4) had absorption at 960 but not at 925 cm^{-1}, and a pro-

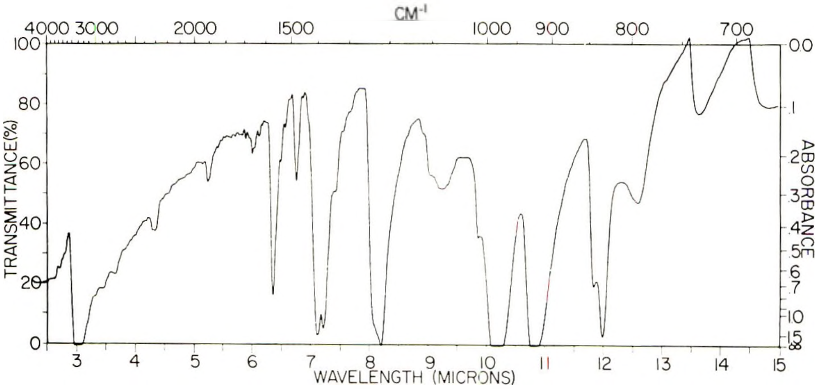

Fig. 1. Infrared spectrum of cationic polymer from terephthalonitrile oxide (KBr disk).

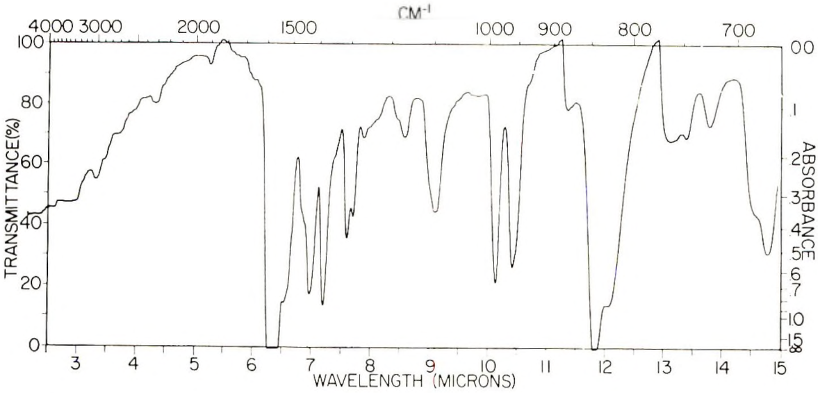

Fig. 2. Infrared spectrum of radical polymer from terephthalonitrile oxide (KBr disk).

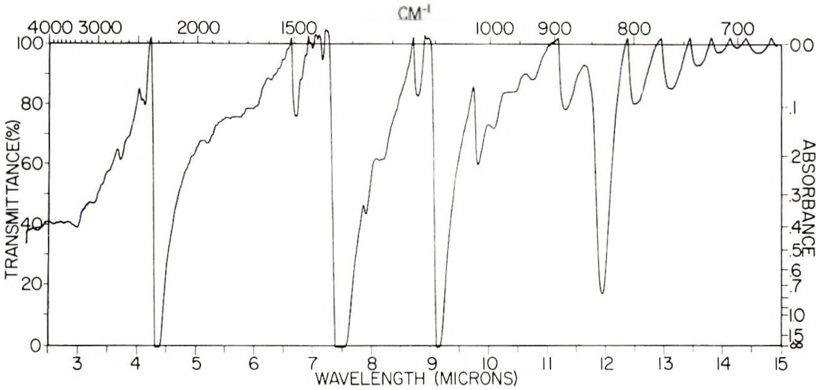

Fig. 3. Infrared spectrum of terephthalonitrile monomer (KBr disk).

nounced shoulder at 825 cm^{-1} (Fig. 2). The monomer has strong absorptions at 840, 1100, and 1330 cm^{-1} (Fig. 3). If the latter two peaks are absent, the presence of a peak at 850 cm^{-1} is considered significant in a polymer sample.

These results can be used to determine the chemical structure of the repeat units making up any specific polymer. The work of Boyer et al.[4] with model compounds of the 1,2,5-structure shows that the substituted dibenzoyl derivatives of furoxan, which are the closest model compounds to the poly(1,2,5-oxadiazolediyl-*p*-phenylene) *N*-oxide structure postulated by Overberger and Fujimoto, have absorption maxima at 850 and 930 cm^{-1}. On this basis, we assign to the cationic polymer (P2) the structure *N*-oxide of poly(1,2,5-oxadiazolediyl-*p*-phenylene) and consider the radical polymer (P4) to be the 1,2,4-isomer.

The proportions of the two isomers in the various polymers we have made have been estimated by comparing absorption intensities at 960 and 925 cm^{-1}, (see Table I). By selection of conditions, it is possible to control the polymerization to form polymer in which no 1,2,5 isomer can be detected (azo initiator, benzene solvent) or no 1,2,4 isomer can be detected (PCl_3 initiator, mixed chlorocarbon solvent).

In a recent publication, Rafikov and co-workers polymerized terephthalonitrile oxide in benzene or toluene without initiator.[5] The infrared spectrum of the resultant polymer was very similar to that we obtained in benzene with azo initiator (Fig. 2). Rafikov and

TABLE I
Structural Repeating Units in Polymers Made from Terephthalonitrile Oxide

Code	Polymerization mechanism	Initiator	Solvent	Oxadiazolediyl unit 1,2,4-, %	1,2,5-, %
P1	Cationic	$SnCl_4$	$CHCl_3$	40	60
P2	Cationic	PCl_3	$CCl_4 + CH_2Cl_2$	0	100
P3	Radical	Azo	CCl_4	70	30
P4	Radical	Azo	C_6H_6	100	0
P5	[a]	None added	Me_2NCHO	70	30
P7	[a]	None added	Me_2CO	60	40
P8	[a]	None added	Tetrahydrofuran	90	10
P9	[a]	None added	PhMe	100	0
P10	[a]	None added	$(Me_2N)_3PO$	70	30
P11	[a]	None added	None	70	30

[a] Not known.

co-workers do not recognize the possibility of isomeric repeating units, first pointed out by Overberger and Fujimoto,[2] and their publication does not contribute to the elucidation of this problem.

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Infrared Study of Conformation of Chain Termination Obtained with $Zn(C_2H_5)_2$ in Stereospecific Polymerization

The role of diethylzinc as a chain transfer agent when added to Ziegler-Natta catalyst system has been very well established by Natta et al.[1,2] The chain termination of the polymerization takes place through chain transfer with diethylzinc. It is explained that diethylzinc exchanges an ethyl group with the alkyl group of the aluminum alkyl and an equilibrium is reached. Thus, the ethyl group is introduced at the end of a growing polymeric chain:

$$\text{Cat—P} + \text{Zn}(\text{C}_2\text{H}_5)_2 \rightarrow \text{Cat—C}_2\text{H}_5 + \text{ZnC}_2\text{H}_5\text{—P}$$

where P is a growing polymeric chain. Further, during the discussion of the reaction mechanism of polymerization with Ziegler-Natta catalyst system, Pasquon[3] as well as Boor[4] have supported the effect of diethylzinc as a chain transfer agent.

It has been stated in an earlier publication[5] by the present authors that during the polymerization of styrene with chromium acetyl acetonate and triethyl aluminum catalyst system in benzene at 30°C, diethylzinc added to the reaction system acts as a chain transfer agent (Table I). It is evident that the chromium acetyl acetonate–triethylaluminum catalyst system polymerizes styrene by a Ziegler-Natta type reaction mechanism.

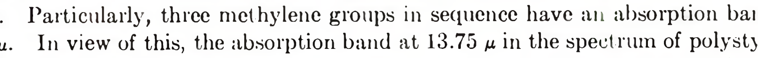
TABLE I[a]

$[\text{ZnEt}_2]$, M	$1/P_n$	MW
0.1	0.74	13 570
0.05	0.66	15 190
0.025	0.5	18 310
0.0125	0.5	18 500
0.0	0.29	36 180

[a] Conditions: $[\text{Cr(acac)}_3] = 1.0 \times 10^{-2}M$; $[\text{AlEt}_3] = 6.0 \times 10^{-2}M$; [monomer] $= 4.32M$; reaction time = 2 hrs; Al/Cr = 6:1.

Since the ethyl group is introduced at the end of the polymeric chain, it is of interest to determine the endgroup of the polymeric chain by infrared examination. Infrared spectra of a 5% solution of polymer in carbon disulfide were recorded on an Infracord instrument, and a sodium chloride cell of 0.1 mm thickness was used to increase the thickness of the medium to obtain absorption band due to the traces of the alkyl group in the polymer.

As seen in Figure 1, a peculiar absorption band is observed at 13.75 μ, and the intensity of the band increases with increasing concentration the ethylzinc group in the polystyrene chain. This kind of absorption is always absent in the spectrum of polystyrene. According to the literature,[6,7] methylene groups of paraffins absorb in the range of 13.0–14.0 μ. Particularly, three methylene groups in sequence have an absorption band at 13.74 μ. In view of this, the absorption band at 13.75 μ in the spectrum of polystyrene can be attributed to the presence of three methylene groups in the polymer. This seems to be the effect of the *n*-propyl chain ending formed due to addition of one ethyl group from diethylzinc to the end of the polymeric chain:



$$\text{Cat—}(\text{CH}_2\text{—}\underset{\text{C}_6\text{H}_5}{\text{CH}})_n + \text{Zn}(\text{C}_2\text{H}_5)_2 \rightarrow \text{Cat—C}_2\text{H}_5 + \text{ZnC}_2\text{H}_5\text{—}(\text{CH}_2\text{=}\underset{\text{C}_6\text{H}_5}{\text{CH}})_n$$

Similarly, typical absorption bands are noted at 13.7 and 13.9 μ due to three and five methylene groups present in the ethylene-propylene copolymer obtained with the VOCl_3–

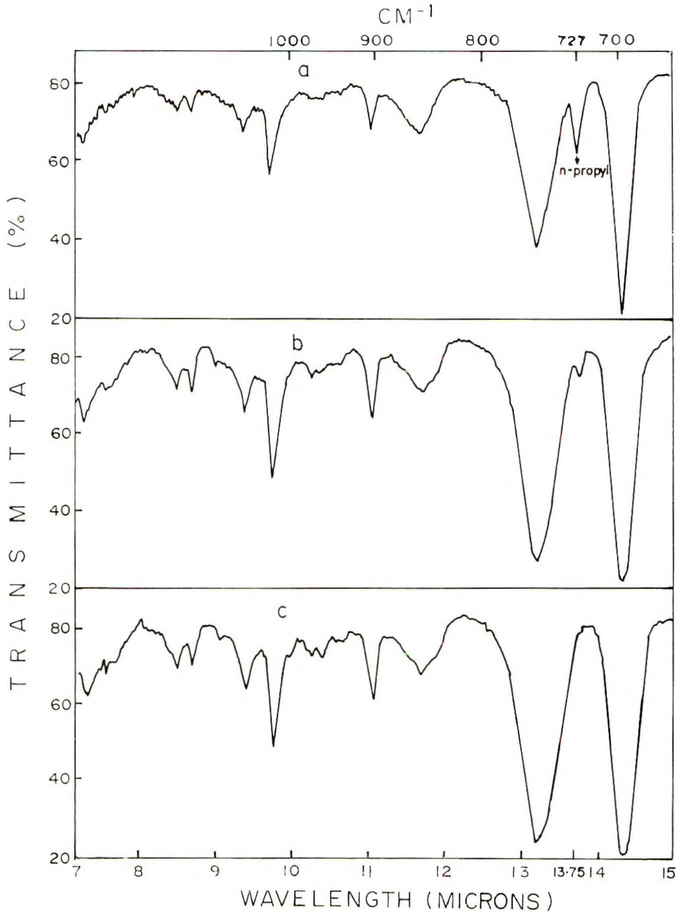


Fig. 1. Infrared spectra of polystyrene obtained with $Cr(acac)_3$–$AlEt_3$ in presence of $Zn(C_2H_5)_2$: (*a*) 0.1*M*; (*b*) 0.05*M*; (*c*) 0.025*M*.

$Al(C_2H_5)_3$ catalyst system[8] as well as in the copolymer of styrene and 5-methylhexane-1 produced with $TiCl_3$–$Al(C_2H_5)_3$ catalyst system.[9]

It is hence very clear that the absorption band at 13.75 μ in spectra of polystyrene obtained with the chromium acetyl acetonate–triethyl aluminum catalyst system in presence of diethylzinc is a result of the sequence of methylene groups of *n*-propyl chain ends of the polymer chain. Incidentally, the chain termination with diethyl zinc or with triethyl aluminum can thus easily be understood on the basis of the infrared findings.

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α-Trifluoroacetoxystyrene

In this note we will describe some of our work concerned with the synthesis and polymerization of α-trifluoroacetoxystyrene with the ultimate purpose in mind of preparing an α-substituted poly(vinyl alcohol), i.e., the α-phenyl derivative. The slow rate of chain growth during the polymerization of isopropenyl acetate severely limits the molecular weight, so that the α-methyl poly(vinyl alcohols) obtained by alcoholysis are also of low DP. The same is true of α-trifluoromethyl-vinyl acetate,[1,2] but some partially α-trifluoromethyl-substituted poly(vinyl alcohols) of reasonably high $\overline{\text{DP}}$ were obtained by alcoholysis of vinyl acetate–α-trifluoromethylvinyl acetate copolymers.

Some years ago we prepared poly-α-acetoxystyrene by radical-initiated polymerization of the monomer,[3] but attempts at base-catalyzed alcoholysis of this polymer to phenylated PVA were unsuccessful. Attempts at acid-catalyzed hydrolysis were not made because of the possibility of dehydration to phenylated polyvinylene. We have shown in the past that when benzoyl peroxide is decomposed in solid polystyrene[4] both aliphatic and aromatic benzoate esters of polystyrene are formed. These polymeric esters are completely and readily alcoholyzed to the corresponding polyols. We concluded that attack on the polystyrene backbone by benzoyloxy radicals occurred primarily on the secondary rather than on the tertiary carbon atoms in spite of the resonance stabilization of the tertiary radical. To further verify these results we have recently prepared styrene co-polymers with α-acetoxystyrene and β-acetoxystyrene[5] and subjected them to alcoholysis by using the method previously described.[4] Whereas alcoholysis of the β-acetoxystyrene copolymer to the polyol was rapid and complete, the α-acetoxystyrene copolymer remained essentially unchanged. The difficulty must be due to steric hindrance. Going to poly-α-trifluoroacetoxystyrene should not improve the steric situation but because of the much faster rates of hydrolysis of trifluoroacetates than acetates, the activation energy must be considerably lower; for this reason we decided to look at α-trifluoroacetoxystyrene.

Several methods for preparing α-trifluoroacetoxystyrene were tried; by far the best one is as follows.

Trifluoroacetic acid, 28.5 g (0.25 mole) was added dropwise to 51 g (0.5 mole) of freshly distilled phenyl acetylene containing 2.5 g of red mercuric oxide and 2.5 g of mercuric sulfate. As the temperature rose rapidly, addition was slowed down to maintain the temperature below 50°C. The reaction mixture was held at 45°C overnight. As much of the salts as possible were filtered off and the filtrate was fractionally distilled. After a forerun of phenyl acetylene, product was collected at 78–81°C/14 mm. The product was then redistilled through a 24-plate spinning band column. The overall yield was 50% for the monomer, bp 75°C/13.5 mm, $n_{\text{D}}^{24.8} = 1.4595$. Elemental analysis of α-trifluoroacetoxystyrene gave C, 55.69%; H, 3.37%; F, 26.42% (calcd: C, 55.57%; H, 3.26%; F, 26.39%). The infrared spectrum of the monomer is given in Figure 1. If the phenyl acetylene is added to the trifluoroacetic acid or a sufficient excess of phenyl acetylene is not employed, the main products of the reaction are trifluoroacetic anhydride and acetophenone, implying that the intermediate is 1,1 ditrifluoroacetoxy-ethylbenzene,[6] which in the presence of acid decomposes on heating to the products obtained.

α-Trifluoroacetoxystyrene was also prepared (but in much poorer yield) in the following manner. 1-Hydroxy-2-bromoethylbenzene, bp 120–123/5 mm., was prepared by the reaction of styrene with *N*-bromosuccinimide.[7] The styrene bromohydrin (205 g) was mixed with 300 g of trifluoroacetic anhydride at room temperature. After an initial exothermic reaction and 18 hr at room temperature, 246 g of α-trifluoroacetoxy-β-bromoethylbenzene was isolated by distillation, bp 72°C/1.5 mm. α-Trifluoroacetoxy-β-bromoethylbenzene was dissolved in excess dry triethylamine and the solution was heated at 65°C overnight. The theoretical amount of triethylamine hydrobromide was filtered off and the filtrate fractionally distilled. A large, flat boiling fraction was collected at 76°C/11 mm. Infrared analyses and vapor-phase chromatography indicated

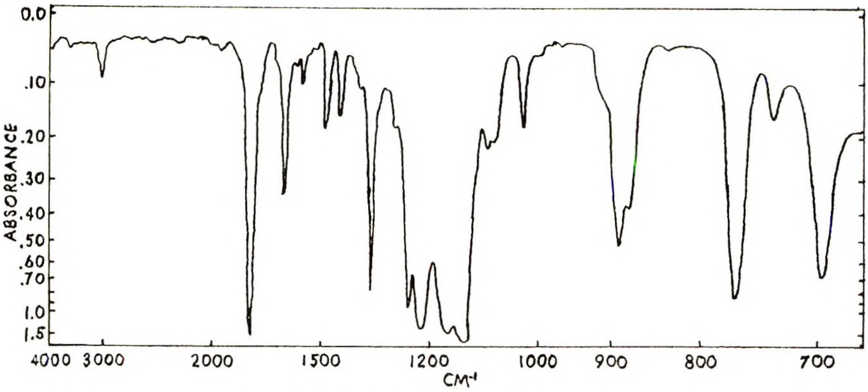

Fig. 1. Infrared spectrum of monomer.

that the material was only 78.7% α-trifluoroacetoxystyrene. Repeated distillations through a multi-plate spinning band column as well as attempts to acylate the acetophenone impurity with isopropenyl trifluoroacetate failed to produce pure monomer. Preparative vapor-phase chromatography finally produced monomer having the properties identical to those of the monomer produced from phenylacetylene.

Several other methods for preparing the monomer were also attempted. Direct acylation of acetophenone with trifluoroacetic anhydride at 100°C in a bomb with the use of a potassium acetate catalyst yielded a flat boiling fraction, 86–88°C/16 mm, which appeared to be an azeotrope of acetophenone and trifluoroacetic acid. The infrared spectrum gave no evidence of the presence of the desired α-trifluoroacetoxystyrene.

1,2-Ditrifluoroacetoxystyrene, bp 83°C/2 mm., $n_D^{25} = 1.4084$, $d_{25} = 1.3831$, was prepared in good yield by refluxing overnight 1,2-dihydroxyethylbenzene with excess trifluoroacetic anhydride followed by fractional distillation. However attempts to split out trifluoroacetic acid with powdered potassium hydroxide at 180°C or trihexylamine at 120°C were unsuccessful.

So far our attempts at polymerization have not been too successful. Monomer (2 g) in an evacuated sealed glass tube was exposed for 60 hr to a General Electric AH-4 ultraviolet source from which the glass jacket was removed. The monomer became brown in color, and there was a slight increase in viscosity. Attempts to isolate polymer by precipitation into hexane, ether, or methanol were unsuccessful, but allowing the hexane solution to evaporate yielded a very small amount of a brown, glassy polymer. An infrared spectrum of this material (Fig. 2) was obtained by casting a film from acetone

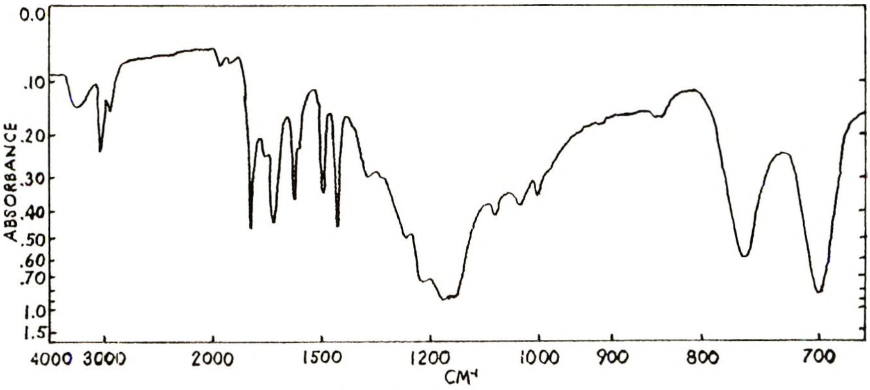

Fig. 2. Infrared spectrum of polymer.

on a silver chloride disk. Comparison of Figures 1 and 2 indicates that bands at 1 640, 1 330, 895 and 888 cm^{-1} associated with —C=C—stretching in the monomer have disappeared. We have not been able to explain a band at 1 680 cm^{-1}. Similar results were obtained when 2 g of monomer containing 2 mg of azobisisobutyronitrile were sealed off in an evacuated glass tube and heated for 5 days at 65°C.

As expected, no polymer was obtained when 2 g of monomer in 6 ml of methylene chloride was cooled to −60°C and catalyzed with 0.02 ml of commercial BF_3 etherate diluted 10:1 with methylene chloride. Similarly, when 2 g of monomer in 20 ml of tetrahydrofuran was treated at −60°C with 0.1 ml of 0.79*M* butyllithium, no polymer could be isolated.

Surprisingly, when 2.16 g (0.01 mole) of monomer and 1.04 g (0.01 mole) of styrene were heated with 0.1% of azobisisobutyronitrile at 65°C for 75 hr, the polymer that was isolated was essentially pure polystyrene. We would have expected that the presence of the α-trifluoroacetoxy group would have tended to make the monomer alternate with styrene more than α-acetoxystyrene which forms a copolymer with styrene with no difficulty.

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