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Two-Stage Irradiation Study on Propagation and Termination in the γ-Radiation-Induced Polymerization of Ethylene in Liquid Carbon Dioxide

MIYUKI HAGIWARA, HIROSHI MITSUI, SUEO MACHI,
and TSUTOMU KAGIYA, *Japan Atomic Energy Research Institute,*
Takasaki Radiation Chemistry Research Establishment,
Takasaki, Gunma, Japan

Synopsis

The propagation and termination reaction in the γ-radiation-induced ethylene polymerization in liquid carbon dioxide were investigated by a two-stage irradiation. After irradiation at high dose rate, the polymerization occurred at a considerable rate under the extremely low dose rate without initiation. The absolute propagation rate was determined in the second stage to be proportional to the square of ethylene fugacity and depended slightly on dose rate. The apparent activation energy for the propagation reaction is −9 kcal./mole. From these observations which are the same as those in bulk polymerization, it is concluded that carbon dioxide acts as a diluent of ethylene monomer in the propagation reaction. Also, carbon dioxide was shown to be inactive to the growing radicals without irradiation, but oxygen which is produced by the radiolysis of carbon dioxide at high dose terminates the growing radicals with formation of carbonyl in the polymer.

INTRODUCTION

In the previous papers,[1,2] liquid carbon dioxide was found to be a useful solvent for the γ-radiation-induced polymerization of ethylene. Based on the kinetics of the polymerization, the effects of carbon dioxide on the initiation and termination reaction were studied, and the transfer reaction was shown to be absent in the polymerization.

In this paper, the polymerization was studied quantitatively by the two-stage irradiation method[3] to elucidate the role of carbon dioxide in the propagation and termination reactions.

EXPERIMENTAL

The reaction vessel, ethylene monomer, carbon dioxide, irradiation facilities, and experimental procedure were as described in the previous paper.[1] The polymerization in this work was characterized by being carried out in two different stages. The first irradiation was carried out at a dose rate of 2.5×10^4 rad/hr. under a pressure of 400 kg./cm.^{2} at 20°C.; this was followed by a second irradiation at lower dose rates under various conditions. The radiation intensity was changed by varying the distance between the reactor and the ^{60}Co source.

Gas chromatographic analysis was made by using Shimadzu GC-1B with a 2-m. activated charcoal column (50°C.) for carbon monoxide and a 2-m. column with molecular sieves (50°C.) for oxygen.

RESULTS AND DISCUSSION

Propagation Reaction

In the investigation of the polymerization in liquid carbon dioxide, the polymerization rate and the molecular weight of polymer were found to increase with reaction time. From kinetic considerations based on this fact, it was concluded that a stationary-state hypothesis, that the rate of initiation is equal to that of termination, is not realized and that the lifetime of the growing radicals is long under γ-ray irradiation.

The characteristic information on the behavior of the long-lived growing radicals in the polymerization is obtained by the method of two-stage irradiation. Figure 1 shows a plot of the polymer yield against irradiation time. During period I, the reaction mixture of ethylene and carbon dioxide was irradiated at a dose rate of 2.5×10^4 rad/hr. at 20°C., and this was followed by irradiation at a dose rate of 9.0×10^2 rad/hr. at 25°C. during period II. It should be noted that the polymer increase in period II is quite large even at the low dose rate of 9.0×10^2 rad/hr. When the entire polymerization was carried out at the same low dose rate as was used in period II, the amount of polymer formed was much less than that in period II after the irradiation at high dose rate (curve *C*). Further, when the degree of polymerization is plotted against the polymer yield, a straight line was obtained in period II, as shown in Figure 2. Since the ratio of the polymer yield to the degree of polymerization is equal to the

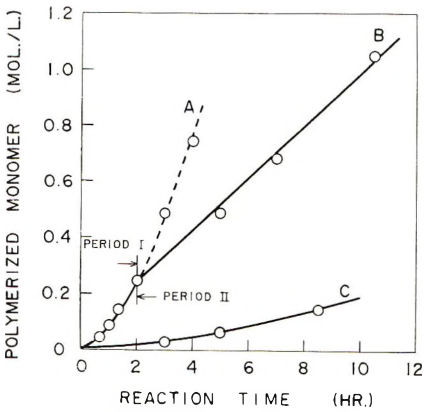

Fig. 1. Polymer yield vs. reaction time at CO_2 concentration of 23.9 mole-%: (*A*) 2.5×10^4 rad/hr., 400 kg./cm.^{2}, 20°C.; (*B*) 9.0×10^2 rad/hr., 400 kg./cm.^{2}, 25°C.; (*C*) 9.0×10^2 rad/hr., 400 kg./cm.^{2}, 25°C.

number of moles of polymer chain, it is clear that additional formation of polymer chain does not take place in period II. It can be said, therefore, that only the propagation reaction takes place, and the initiation and transfer reactions are absent in this period.

These observations are very similar to those in the bulk polymerization,[3] and indicate that the considerable number of radicals introduced in period I survive and grow under the irradiation at low dose rate in period II. Further, since the polymer yield increases linearly with the time in period II (Fig. 1), the growing radicals which survive at the end of period I are not deactivated during the irradiation with a low dose rate in period II.

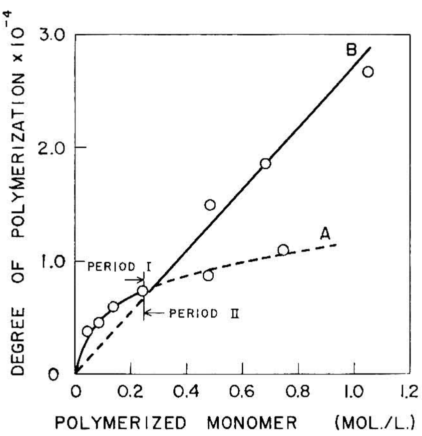

Fig. 2. Degree of polymerization vs. polymer yield at CO_2 concentration of 23.9 mole-%: (*A*) 2.5 × 10^4 rad/hr., 400 kg./cm.^{2}, 20°C.; (*B*) 9.0 × 10^2 rad/hr., 400 kg./cm.^{2}, 25°C.

On the basis of these considerations, the absolute propagation rate is calculated by the following procedure. The number of growing radicals $[R\cdot]$ which survive at the end of period I is given by eq. (1):

$$[R\cdot] = \int_0^{t_1} R_i dt - \int_0^{t_1} R_t dt \tag{1}$$

where R_i and R_t are the rates of initiation and termination, respectively, and t_1 is the irradiation time in period I. The first term of the right-hand side of eq. (1) represents the total number of growing radicals produced in period I, and the second term the number of the radicals disappearing as a result of termination. Since, as reported in the previous paper,[2] the rate of termination in the polymerization is given as:

$$R_t = k_t[Z][R\cdot] \tag{2}$$

where $k_t[Z]$ is the apparent first-order termination rate constant, eq. (1) becomes:

$$[R\cdot] = (R_i/k_t[Z])(1 - e^{-k_t[Z]t_1}) \tag{3}$$

As determined previously,[2] R_i is 1.82×10^{-5} mole/l.-hr., and $k_t[Z]$ is 1.6 hr.$^{-1}$ for the polymerization in liquid carbon dioxide of 23.9 mole-% under a pressure of 400 kg./cm.^{2} at 20°C., with a dose rate of 2.5×10^4 rad/hr. Hence,

$$[\mathrm{R}\cdot] = (1.82 \times 10^{-5}/1.6)(1 - e^{-1.6\times 2})$$
$$= 1.09 \times 10^{-5} \text{ mole/l.}$$

since t_1 is kept at 2.0 hr. in the present work.

On the other hand, the total amount of monomer consumed in period II for the growth of these radicals, ΔM_p, is given as:

$$\Delta M_p = M_p - M_p' - M_p''$$

where M_p is the total amount of monomer consumed in the polymerization of two stages, M_p' is the amount of monomer consumed in the first stage, and M_p'' is the amount of monomer consumed for the propagation of radicals produced in the second stage, M_p' is constant (0.245 mole/l.) and M_p'' is determined by carrying out the polymerization under the same conditions as were used in period II from the beginning.

The absolute propagation rate R_p is then calculated by eq. (4):

$$R_p(\text{mole } C_2H_4/\text{mole radical-hr.}) = \Delta M_p/[\mathrm{R}\cdot]t_2 \tag{4}$$

where t_2 is the irradiation time in period II.

The results are summarized in Tables I–III. Figure 3 shows the variation of the absolute propagation rate with ethylene fugacity, f_M. It is clear that the rate is proportional to the second power of the fugacity. This high exponent is also observed in the bulk polymerization. As shown in Figure 4, where R_p/f_M^2 is plotted against dose rate, the absolute propagation rate increases with increasing dose rate. The fact that all plots fall on the same straight line for both polymerization in bulk and in liquid carbon dioxide indicates that the propagation reaction proceeds in the same rate in both cases at a definite ethylene fugacity. Further, for the propagation reaction in both polymerizations, the negative apparent

TABLE I

Effect of Ethylene Fugacity on Absolute Propagation Rate[a]

Ethylene		Absolute propagation rate $\times 10^{-3}$,
Pressure, kg./cm.^{2}	Fugacity, kg./cm.^{2}	mole C_2H_4/mole radical-hr.
200	54.5	4.77
260	64.0	6.48
320	74.5	9.30
400	88.3	14.5

[a] Reaction temperature, 25°C.; dose rate, 1.0×10^4 rad/hr.; concentration of carbon dioxide, 23.9 mole-%.

TABLE II

Effect of Dose Rate on Absolute Propagation Rate[a]

Dose rate × 10^{-4}, rad/hr.	Absolute propagation rate × 10^{-3}, mole C_2H_4/mole radical-hr.
1.3	20.5
1.0	14.5
0.21	7.70
0.090	6.83[b]
0.048	6.73

[a] Reaction pressure, 400 kg./cm.^{2}; temperature, 25°C.; concentration of carbon dioxide 23.9 mole-%.

[b] Mean value of the data at different reaction times in Figure 1.

TABLE III

Effect of Temperature on Absolute Propagation Rate[a]

Temperature, °C.	Ethylene fugacity, kg./cm.^{2}	Absolute propagation rate × 10^{-3}, mole C_2H_4/mole radical-hr.
25	88.3	14.5
60	125	8.75
90	153	4.66

[a] Reaction pressure, 400 kg./cm.^{2}; dose rate, 1.0 × 10^4 rad/hr.; concentration of carbon dioxide, 23.9 mole-%.

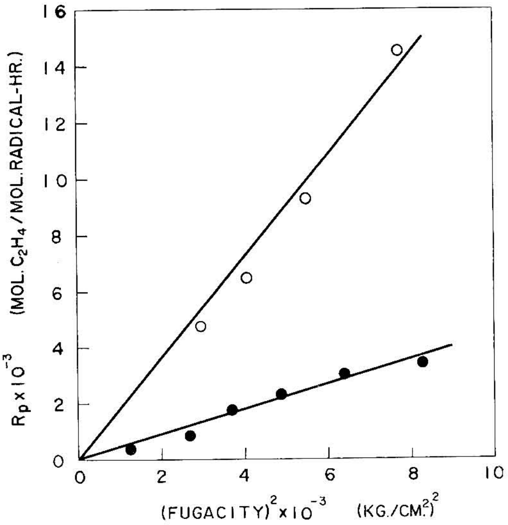

Fig. 3. Absolute propagation rate vs. square of ethylene fugacity: (○) 1.0 × 10^4 rad/hr., 25°C., CO_2 concentration, 23.9 mole-%; (●) literature values[3] for bulk polymerization at 3.0 × 10^2 rad/hr., 30°C.

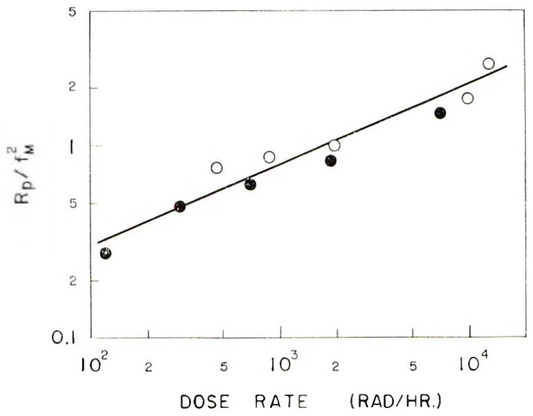

Fig. 4. Effect of dose rate on absolute propagation rate: (○) 400 kg./cm.^{2}, 25°C., CO_2 concentration, 23.9 mole-%; (●) literature values[3] normalized to the temperature of 25°C.

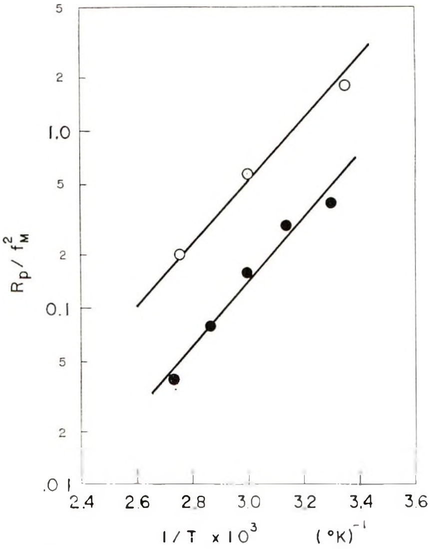

Fig. 5. Effect of temperature on absolute propagation rate: (○) 400 kg./cm.^{2}, 1.0×10^4 rad/hr., CO_2 concentration, 23.9 mole-%; (●) literature values[3] at 300 rad/hr.

activation energy of −9 kcal./mole is obtained from Figure 5. In view of the results presented above, it can be concluded that the propagation reaction in liquid carbon dioxide proceeds by the same mechanism as in the bulk polymerization, and that liquid carbon dioxide affects the propagation rate as a diluent of ethylene monomer.

Termination Reaction

The apparent termination rate constant, $k_t[Z]$, has been found to increase proportionally with the concentration of carbon dioxide.[2] Table

TABLE IV

Polymer Yield of the Two-Stage Bulk Polymerization[a]

Run	Polymer yield, mole/l.
I	0.445
II	0.456
III	0.240

[a] Period I: reaction pressure, 400 kg./cm.^{2}; temperature, 20°C.; dose rate, 2.5×10^4 rad/hr.; time, 1.0 hr.; in this period polymer yield is 0.192 mole/l. Period II: reaction pressure, 400 kg./cm.^{2}; temperature, 25°C.; dose rate, 9.0×10^2 rad/hr.; time, 2.0 hr.

IV gives the results of the polymerization carried out in bulk by the following procedure. In run II, after irradiation in period I, residual ethylene monomer was purged, and carbon dioxide was fed to 40 kg./cm.^{2} at 20°C. The system was then allowed to stand out of the radiation field for 100 hr. Fresh ethylene monomer was then charged again to 400 kg./cm.^{2} after purging carbon dioxide. The irradiation in period II was next carried out. In run III, all experimental procedures were the same as in run II except that the system containing carbon dioxide was irradiated with γ-radiation at a dose rate of 5.0×10^5 rad/hr. for 100 hr. As can be seen in

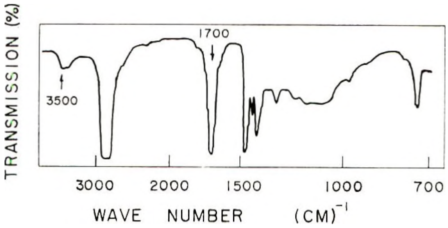

Fig. 6. Infrared spectrum of the product obtained by radiation from the mixture of ethylene and carbon dioxide: 100 kg./cm.^{2}, 20°C., 5.0×10^5 rad/hr., 125 hr., CO_2 concentration, 81.0 mole-%.

Table IV, almost the same amount of polymer is obtained in run I as in run II, while the polymer yield in run III is much lower than those in the other two runs. This indicates that the polymer radicals introduced in period I are not deactivated by carbon dioxide without irradiation, but that the deactivation of radicals takes place when the system is irradiated in the presence of carbon dioxide. It can be said, therefore, that the radiolysis products of carbon dioxide such as carbon monoxide and oxygen may play an important role in the termination reaction. As it is well known, carbon monoxide can copolymerize with ethylene on γ-ray irradiation.[4,5] Thus, the growing radicals may not be deactivated even when carbon monoxide adds to the radicals. On the other hand, oxygen is known to inhibit strongly the γ-ray ethylene polymerization.[6–8] Hence, the termination is thought to be brought about by interactions between the growing radicals and oxygen produced by the radiolysis of carbon dioxide.

The γ-ray irradiation of a mixture of ethylene and carbon dioxide (81.0 mole-% CO_2) under a pressure of 100 kg./cm.^{2} at a dose rate of 5.0×10^5 rad/hr. at 20°C. gave a yellowish grease. The elementary analysis of the product was C, 79.60%; H, 12.81%; O, 7.60%.

As shown in Figure 6, the infrared spectrum of the product displayed several strong absorption bands near 1700 cm.$^{-1}$ (assigned to C=O stretching) and 3500 cm.$^{-1}$ (assigned to OH stretching). Further, as shown in Table V, gas chromatographic analysis showed that carbon monoxide accumulated in the residual gas, but no increase in oxygen was observed. These observations suggest that the reaction of growing radicals with oxygen introduces a carbonyl, such as acid, aldehyde, and ketone into the polymer.

TABLE V
Analytical Data for Oxygen and Carbon Monoxide in Reaction Mixture

Original mixture[a]		Irradiated mixture[b]	
O_2, ppm	CO, ppm	O_2, ppm	CO, ppm
<5	0	<5	1410

[a] Concentration of carbon dioxide, 81.0 mole-%.

[b] Irradiation conditions: pressure, 100 kg./cm.^{2}; temperature, 20°C.; dose rate, 5.0×10^5 rad/hr.; time, 125 hr.

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Polytetrazoles and Polyaminotetrazoles

ELIZABETH DYER and PETER A. CHRISTIE, *Department of Chemistry, University of Delaware, Newark, Delaware 19711*

Synopsis

Polyaminotetrazoles were obtained by the action of hydrazoic acid on solutions of polycarbodiimides prepared from methylenebis(4-phenyl isocyanate), toluene 2,4-diisocyanate, 3,3′-dimethoxy-4,4′-biphenylene diisocyanate, mesitylene diisocyanate, and hexamethylene diisocyanate. The polyaminotetrazoles, which were soluble only in concentrated sulfuric acid, had inherent viscosities of 0.12–0.78. Polymerization of the disodium salts of bistetrazoles with α,ω-dihalides gave polytetrazoles without the secondary amine linkage in the chain. The bistetrazoles used were methylenebis(5-tetrazole) and 5,5′-*p*-phenylenebistetrazole, and the dihalides were α,α'-dichloro-*p*-xylene, 1,2-dibromoethane, and 1,4-dibromobutane. The polytetrazoles were soluble in concentrated sulfuric acid and had low inherent viscosities, 0.08–0.17. Thermogravimetric analyses showed that marked degradation of both classes of polymers occurred at 250–300°C.

INTRODUCTION

Many polymers have been prepared which contain heterocyclic nuclei in the chain, such as benzimidazoles,[1] quinoxalines,[2] benzoxazoles,[3] and triazoles.[4] No polytetrazoles, except those in which the tetrazole ring is a substituent on a vinyl type of polymer, have been reported. The purpose of this work was to prepare polymers having tetrazole nuclei in the polymer chain and to investigate their properties.

The accessibility of polycarbodiimides[5] and the known reactivity of monomeric carbodiimides with hydrazoic acid[6] prompted an investigation of the preparation of polyaminotetrazoles from polycarbodiimides. The preparation of polytetrazoles without the secondary amine group in the polymer chain was also undertaken to provide a comparison with the polyaminotetrazoles with respect to thermal stability.

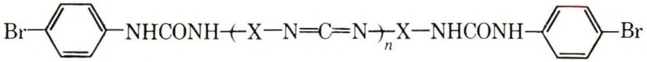
DISCUSSION

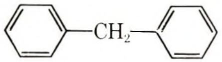
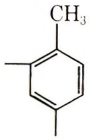
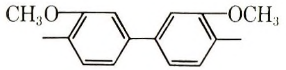
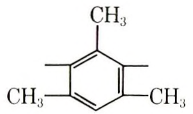
Preparation of Polycarbodiimides

The polycarbodiimides were obtained by the condensation[5,7] of diisocyanates with the useful catalyst 3-methyl-1-phenyl-3-phospholene-1-oxide. When the polymerization of mesitylene diisocyanate, methylenebis-(4-phenyl isocyanate), and toluene-2,4-diisocyanate in the presence of the phospholene oxide was carried out in xylene, the polycarbodiimides sepa-

TABLE I

Preparation and Properties of Polycarbodiimides



Polymer no.	X	Solvent[a]	Time, hr.	Yield, %	Dec. temp., °C.[b]	Analyses, (calcd.) and found C, %	H, %	N, %	Br, %[c]
1		80/20	20	87	>300	(76.60) 76.66	(4.65) 5.27	(12.83) 12.06	4.83
2		60/40	24	91	>300	(65.80) 65.67	(4.27) 5.03	(17.79) 16.14	9.30
3		50/50	60	78	240	(68.60) 67.49	(4.35) 4.88	(10.11) 9.58	10.25
4		100	24	99	250	(75.24) 75.62	(6.27) 6.54	(17.50) 16.83	0.82
5[d]	$(CH_2)_6$	40/60	145						

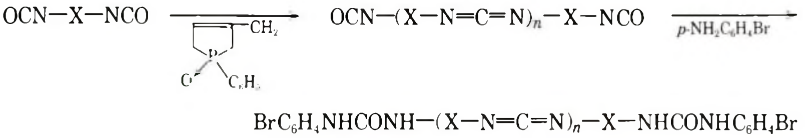
[a] Volume ratio of chloroform/chlorobenzene, polymer 4 prepared in xylene.

[b] Temperature of noticeable discoloration.

[c] Calculated for average DP determined from Br content.

[d] Polymer 5 not isolated.

rated from the polymerization medium as fine powders. With the exception of poly(mesitylenecarbodiimide), these polymers were completely insoluble in all the solvents tried. Poly(mesitylenecarbodiimide), on the other hand, was soluble in a variety of chlorinated solvents. When the polymerization of the diisocyanates was carried out in the mixed solvent (50/50 dimethyl sulfoxide–chlorobenzene) suggested by Lyman and Sadri,[8] metastable solutions of the polymers resulted if the reactions were stopped within 10–15 min. Longer times resulted in precipitation of the polymers. The metastable solutions could be maintained for a few hours.



$$\mathrm{OCN{-}X{-}NCO} \longrightarrow \mathrm{OCN{-}(X{-}N{=}C{=}N)_{\mathit{n}}{-}X{-}NCO} \xrightarrow[p\text{-}\mathrm{NH_2C_6H_4Br}]{} \mathrm{BrC_6H_4NHCONH{-}(X{-}N{=}C{=}N)_{\mathit{n}}{-}X{-}NHCONHC_6H_4Br} \qquad (1)$$

The best conditions for preparing stable solutions of polycarbodiimides other than poly(mesitylenecarbodiimide) were the use of mixtures of chloroform and chlorobenzene and end-capping with *p*-bromoaniline. Details of the conditions for the polymerizations of methylenebis(4-phenyl isocyanate), toluene-2, 4-diisocyanate, 3,3′-dimethoxy-4,4′-biphenylene diisocyanate, and hexamethylene diisocyanate in the chlorinated hydrocarbons and of mesitylene diisocyanate in xylene are shown in Table I. The ratio of chloroform to chlorobenzene was chosen to provide a reaction temperature which permitted a convenient rate of polymerization.

The progress of the polymerizations was followed by monitoring the intensities of the infrared absorption bands characteristic of the isocyanate group (at 4.4–4.5 μ) and of the carbodiimide group (at 4.7 μ). The polymerizations were arbitrarily stopped when the conversion of isocyanate to carbodiimide was approximately 85–90% complete by reaction of the isocyanate endgroups with excess *p*-bromoaniline at 25–35°C. The reaction mixture was stirred until the infrared spectrum of the solution showed no isocyanate absorption. The resulting solutions were stable, suitable for use in preparing polyaminotetrazoles.

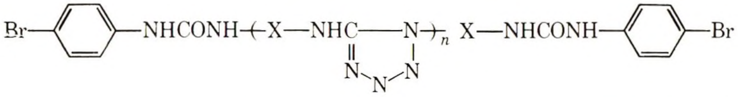
For analysis the polycarbodiimides were isolated by precipitation with acetone. White to tan powders were obtained which were generally high

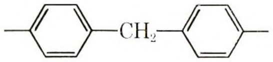
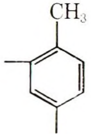
TABLE II
Molecular Weights of Polycarbodiimides

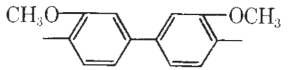
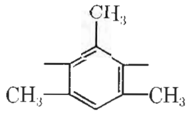
Polymer no.	$\bar{M}_n$		$\overline{\mathrm{DP}}_n$
	From % Br	From % NCN[a]	
1	3310	3070	12.6
2	1720	1640	8.9
3	1560	1500	3.5
4	19,500	16,400	110

[a] Average of two analyses.

TABLE III
Preparation and Properties of Polyaminotetrazoles



Polymer no.	X	Method[a]	Yield, %	η_{inh}[b]	Dec. temp., °C.[c]	Analyses, (calcd.)[d] and found C, %	H, %	N, %
6		A	89	0.172	>300	(65.60) 65.76	(4.32) 4.72	(25.21) 25.02
7		A	48	0.135	245	(56.20) 56.56	(3.97) 4.53	(29.30)[e] 28.84

8		A	100	0.117	270	(58.49) 59.22	(4.21) 4.08	(19.20) 19.03
9		B	91	0.780	240	(61.60) 61.57	(5.65) 6.36	(31.90)[f] 31.04
10	$(CH_2)_6$	A	72	0.263	125	(49.70) 50.03	(7.22) 7.37	(36.20)[g] 36.50

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[a] Hydrazoic acid used in method A, sodium azide in B.

[b] Inherent viscosities in concentrated sulfuric acid at 25°C., at a polymer concentration of 0.5 g./100 ml.

[c] Temperature of noticeable discoloration.

[d] Calculated for average DP of parent polycarbodiimide.

[e] Based on 75% conversion to polyaminotetrazole.

[f] Based on 84% conversion to polyaminotetrazole.

[g] Based on Br content of 5.80%.

melting and insoluble in all the usual polymer solvents after being isolated. The properties and analyses of these polymers are shown in Table I.

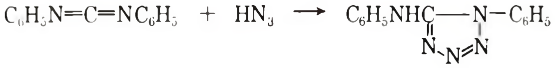
Average molecular weights were calculated from the bromine contents found by elemental analysis, assuming that all the isocyanate endgroups were completely converted to the corresponding urea by reaction with the *p*-bromoaniline. Molecular weights were also obtained by the functional group titration method developed by Smeltz[9] for polycarbodiimides. The values of molecular weights are shown in Table II. Agreement between the results obtained by the two methods is quite reasonable, in view of the analytical difficulties encountered with these polymers.

The striking differences in molecular weight of polymer 4 and the other polycarbodiimides reflect the methods of preparation of the polymers. The molecular weights of polymers 1, 2, and 3 were purposely limited by addition of the chain-stopping reagent to obviate the formation of insoluble high molecular weight polymers. Polymer 4, however, was allowed to attain higher molecular weight, since this polycarbodiimide was soluble in a variety of solvents after isolation.

Preparation of Polyaminotetrazoles

Treatment of the metastable solutions of poly[methylenebis(4-phenyl carbodiimide)] and of poly(hexamethylenecarbodiimide) with sodium azide in dimethyl sulfoxide resulted in only partial conversion of the carbodiimide linkages to aminotetrazole units as shown by the infrared spectra.

In a study of the optimum conditions for the preparation of model compounds, 1-phenyl-5-anilino-tetrazole was obtained in high yield when diphenylcarbodiimide was stirred at room temperature with an equimolar quantity of free hydrazoic acid in chloroform solution [eq. (2)].



(2)

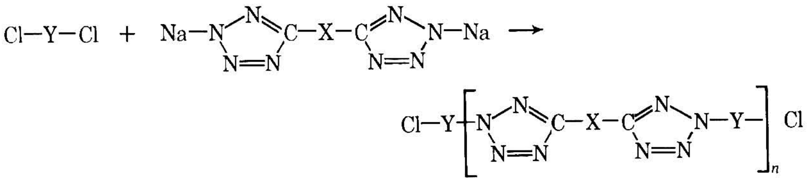
Reaction of the chloroform–chlorobenzene solutions of the polycarbodiimides with excess hydrazoic acid under similar conditions was the most successful method for the preparation of the polyaminotetrazoles. The conditions and yields of the reactions are shown in Table III. All the polyaminotetrazoles except polymer 9 were prepared by reaction of the polycarbodiimide solutions with chloroform solutions of hydrazoic acid (method A). Polymer 9 was prepared by treatment of a chloroform solution of poly(mesitylenecarbodiimide) with sodium azide in dimethyl sulfoxide (method B).

The products precipitated from solution and were obtained as fine tan or brown powders. The polyaminotetrazoles, whose properties and analyses are shown in Table III, were relatively high melting, and in contrast to the parent polycarbodiimides were soluble in concentrated sulfuric acid.

The infrared spectra of the polyaminotetrazoles showed absorption bands at 6.3, 9.1–9.2, and 10.35 μ, characteristic of the tetrazole nucleus,[14,15] and, with the exception of polymers 7 and 9, showed no residual carbodiimide absorption. The infrared spectra and elemental analyses of the products were the main evidence for the formation of polyaminotetrazoles. The theoretical values for the composition of the polymers were based on the degree of polymerization of the parent polycarbodiimides, since the derived polymers could not have higher degrees of polymerization than their precursors.

Preparation of Polytetrazoles

The method which proved to be the most successful for the polytetrazoles was the polymerization of the disodium salts of bistetrazoles with α,ω-dihalides. This method, however, was limited to the preparation of polymers containing aliphatic groups between the tetrazole nuclei, and in view of the thermal instability of alkylene groups the polytetrazoles obtained were not expected to show high resistance to thermal degradation.

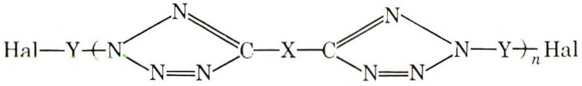

(3)

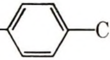
The polymerizations were conducted in refluxing 50% aqueous ethylene glycol with equimolar quantities of the reactants. A slight excess of the dihalide was added after the polymerizations had run about 48 hr. in order to obtain polymers having endgroups which both contained halogen. Details of the polymerization reactions are shown in Table IV.

The products of the reactions of the disodium salt of 5,5′-*p*-phenylenebistetrazole and dihalides were white powders which had no sharp melting points below 300°C., but became discolored at about 250°C. These polymers, (11, 12, and 13) like the polyaminotetrazoles, were soluble only in concentrated sulfuric acid. The polymer (14) obtained from the disodium salt of methylenebis(5-tetrazole) and α,α'-dichloro-*p*-xylene, however, was a yellow powder which had a true melting point at 120°C. and was soluble in dimethylformamide as well as sulfuric acid. The relatively good agreement of the analytical data for the polymers is evidence for the formation of polytetrazoles of the expected composition.

The molecular weights of the polytetrazoles, ranging from 1350 to 4840, were calculated from the halogen contents of the polymers, assuming no free tetrazole endgroups. This assumption was valid for all the polytetrazoles except 11, which was found by titration with sodium hydroxide to have 0.1009 meq. tetrazole endgroups/g. polymer. The relatively low molecular weights of the polymers obtained in these reactions were probably a consequence of the low solubilities of the products in the polymerization medium, since the polymers precipitated from solution during the reaction period.

TABLE IV
Preparation and Properties of Polytetrazoles

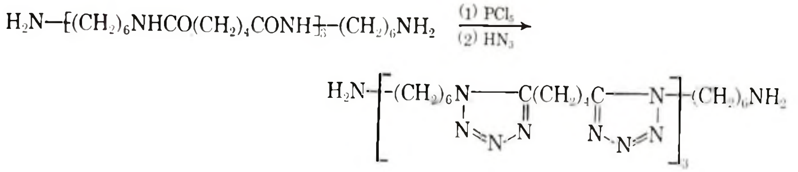


Polymer no.	X	Y	Yield, %	η_{inh}[a]	$\overline{M}_n$[b]	Dec. temp., °C.[c]	Analyses, (calcd.) and found C, %	H, %	N, %	Hal., %[d]
11		CH$_2$——CH$_2$	66	0.079	1350	240	(60.00) 58.94	(3.91) 4.13	(31.10) 31.75	5.18
12		(CH$_2$)$_2$	68	0.152	2460	240	(47.15) 47.55	(3.25) 3.74	(42.86) 42.21	6.50
13		(CH$_2$)$_4$	99	0.173	4840	270	(52.31) 51.47	(4.55) 5.02	(40.00) 40.20	3.31
14	CH$_2$	CH$_2$——CH$_2$	57	0.116	2050	120	(52.28) 52.33	(4.00) 4.21	(40.03) 40.01	3.45

[a] Inherent viscosities in conc. sulfuric acid at 25°C., using polymer conc. of 0.5 g./100 ml.
[b] Based on halogen content assuming halogen termination at both ends.
[c] Temperature of noticeable discoloration.
[d] Halogen, found by difference: Cl in polymers 11 and 14, Br in 12 and 13.

Another approach to the preparation of polytetrazoles was the conversion of polyamides to polytetrazoles by the method of von Braun and Rudolph.[12] The difficulty in carrying out reactions on high molecular weight polyamides has been cited in the literature,[13] and for this reason an oligomeric amide was chosen for the preparation of a tetrazole by this route.

The well-defined trimer of hexamethylene adipamide was prepared according to the method of Zahn and Lauer[14] by the reaction of excess hexamethylenediamine with ethyl adipate, and this was converted to the corresponding oligomeric tetrazole by treatment with phosphorus pentachloride followed by hydrazoic acid. In the preparation



$$H_2N-\left[(CH_2)_6NHCO(CH_2)_4CONH\right]_3-(CH_2)_6NH_2 \xrightarrow[(2)\ HN_3]{(1)\ PCl_5} H_2N-\left[(CH_2)_6N_4C(CH_2)_4CN_4\right]_3-(CH_2)_6NH_2 \qquad (4)$$

of the imide chloride from the trimeric amide, reaction temperatures above room temperature resulted in the formation of a dark brown gummy material. When the reaction was carried out at room temperature, however, a homogeneous solution of the imide chloride was obtained. By reaction of the imide chloride solution with hydrazoic acid the oligotetrazole was obtained. This was soluble in dimethylformamide, melted at 250–255°C. when pure, showed the typical tetrazole absorption bands, and the analytical data were in agreement with an oligomer of the expected structure.

Thermogravimetric Analyses

The thermal degradation studies of the polymers were made by measuring the weight loss in a nitrogen atmosphere at a programmed heating rate of 15°C./min. Figure 1 shows the degradation of the polyaminotetrazoles. The general shape of the curves was the same for all the polyaminotetrazoles, consisting of a region of rapid decomposition between 200 and 300°C., followed by a more or less gradual loss in weight over the remaining temperature range. The rates of decomposition of polymers 6, 7 (practically identical with 6 and not shown on the graph) 8, and 9 were very similar. Polymer 10, containing an aliphatic linkage, showed the largest deviation from this pattern. During the second step of the degradation the weight loss occurred at a rate equal to or greater than that of the first step, leaving a residue of only 20% of the original weight of this polymer at 480°C.

In the case of the polytetrazoles shown in Figure 2, two distinct types of thermograms were obtained, depending on the structure of the dihalide from which the polymer was prepared. Polymers 11 and 14, made by the reactions of the disodium salts of the bistetrazoles with α,α'-dichloro-p-xylene, exhibited stepwise degradation curves in which appreciable weight loss occurred in the temperature range of 200–300°C. and gradual weight

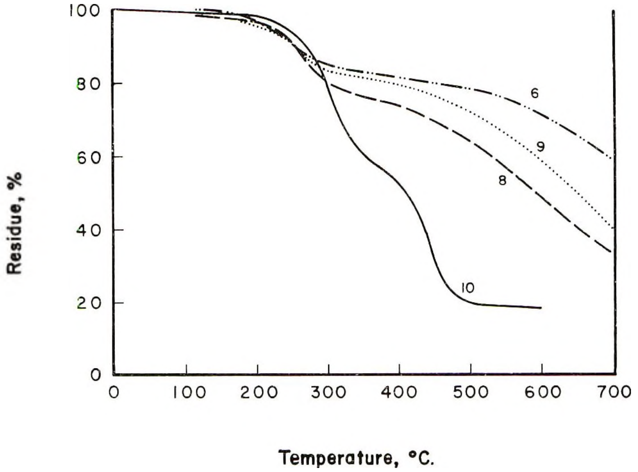
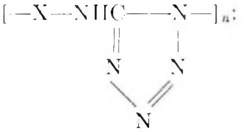


Fig. 1. Thermogravimetric analyses of poly(aminotetrazoles),



$[—X—NHC(=N—N=N)—N—]_n$:

polymer 6, X = 4,4′-methylenebis(phenylene); 8, X = 3,3′-dimethoxy-4,4′-biphenylylene; 9, X = 2,4,6-trimethyl-1,3-phenylene; 10, X = 1,6-hexamethylene.

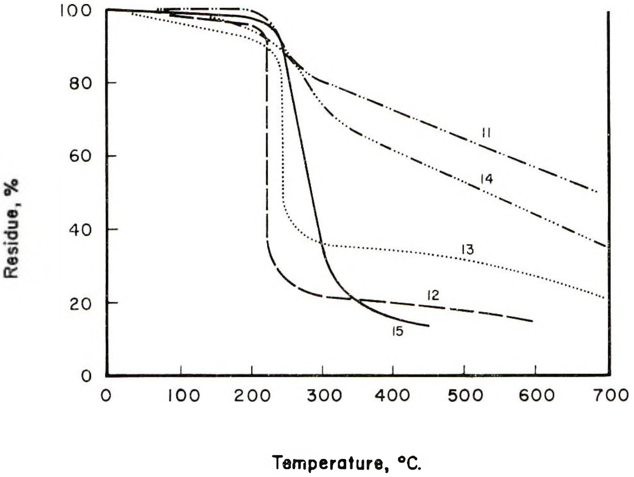
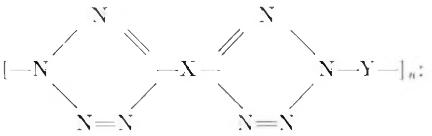


Fig. 2. Thermogravimetric analyses of poly(tetrazoles),



Polymer 11, X = 1,4-C_6H_4, Y = 1,4-$CH_2C_6H_4CH_2$; 12, X = 1,4-C_6H_4, Y = $(CH_2)_2$; 13, X = 1,4-C_6H_4, Y = $(CH_2)_4$; 14, X = CH_2, Y = 1,4-$CH_2C_6H_4CH_2$; 15, X = $(CH_2)_6$, Y = $(CH_2)_4$, n = 3.

loss occurred over the remaining temperature range. In contrast, polymers 12 and 13, made from 1,2-dibromoethane and 1,4-dibromobutane, as well as the oligomeric tetrazole 15, underwent rapid and extensive degradation at 230–250°C., and the resulting residues decomposed only slightly on further heating. A comparison of the curves for polymers 11 and 14 shows that the presence of the aromatic linkage in polymer 11 appeared to provide a slight degree of stability not found in polymer 14 which contained a methylene group in place of the *p*-phenylene group.

The low resistance to thermal degradation exhibited by the polytetrazoles and polyaminotetrazoles in comparison to other heterocyclic polymers probably reflects the lack of conjugation throughout the polymer chains. This important structural feature for thermally stable polymers is most notably absent in the largely aliphatic polytetrazoles. Due to their appreciable decomposition at relatively low temperatures, the polymers obtained in this work are of little interest as materials for high temperature applications.

EXPERIMENTAL

Catalyst and Monomers

3-Methyl-1-phenyl-3-phospholene-1-oxide was prepared by the method of McCormack[15] from isoprene and dichlorophenylphosphine followed by hydrolysis. The colorless liquid, b.p. 170–174°C./1 mm. (lit.[15] b.p. 173–174°C./0.7 mm.), was obtained in 33% yield.

Mesitylene diisocyanate was obtained by phosgenation of diaminomesitylene. Approximately 200 g. of phosgene, condensed in a coldfinger condenser, was introduced directly into a three-liter, three-necked flask equipped with stirrer, condenser, and addition funnel, and cooled in a Dry Ice–acetone bath. A solution of 100 g. (0.67 mole) of diaminomesitylene in 1.5 kg. of *o*-dichlorobenzene was added at a moderate rate with stirring. The ice bath was removed after addition of the diamine was complete and the mixture was allowed to warm to room temperature. The reaction mixture was then refluxed while gaseous phosgene was passed through the mixture. Refluxing was continued until the carbamoyl chloride had completely dissolved and no further evolution of hydrogen chloride was observed. The solvent was removed under reduced pressure and the remaining oil was distilled under reduced pressure through a Vigreux column. The fraction boiling at 110–111°C./0.5 mm. consisted of 120 g. (90%) of mesitylene diisocyanate. The product solidified at room temperature and melted at 55.5–57°C.

A 0.5 g. sample of the diisocyanate was heated for 15 min. on a steam bath with excess ethanol in the presence of a drop of triethylamine. The white crystalline product which formed on cooling was filtered and recrystallized from ethanol to give the diurethan derivative, m.p. 204–204.5°C.

Anal. Calcd. for $C_{15}H_{22}N_2O_4$: C, 61.22%; H, 7.48%; N, 9.52%. Found: C, 61.27%; H, 7.43%; N, 9.65%.

Methylenebis(5-tetrazole)[16] was prepared from 0.20 mole of malononitrile, 0.44 mole of sodium azide, 0.44 mole of ammonium chloride, and 200 ml. of dimethylformamide. It was necessary to recrystallize the product five times from ethanol and three times from acetonitrile. The pure substance (obtained in 43% yield) melted at 218–220°C. (lit.[8] m.p. 215–219°C.). Neutralization equivalent calcd. for $C_3H_4N_8$, 76.0; found, 76.5.

5,5′-*p*-Phenylenebistetrazole, dec. above 300°C., was obtained in 99% yield from terephthalonitrile.[16] Neutralization equivalent calcd. for $C_8H_6N_8$, 107.0; found, 106.2.

α,α′-Dichloro-*p*-xylene, m.p. 99–100.5°C., was prepared in 20% yield by a published method.[17]

Polymerizations

General Procedure for the Preparation of Stable Solutions of Polycarbodiimides. The preparation of poly[methylenebis(4-phenylcarbodiimide)] is typical. In a 250 ml. flask equipped with stirrer and reflux condenser was placed a solution of 5 g. (0.02 mole) of methylenebis(4-phenyl isocyanate) in 100 ml. of 80/20 chloroform–chlorobenzene. To the refluxing solution was added 0.1 g. of phospholene oxide catalyst in 5 ml. of chloroform, and the mixture was refluxed 20 hr. longer. The infrared spectrum showed approximately 90% conversion of isocyanate to carbodiimide at this point. The solution was cooled to 30–35°C. and treated with 1.0 g. (0.058 mole) of *p*-bromoaniline in 5 ml. of chloroform. The solution was stirred at this temperature for 2 hr., after which the infrared spectrum of the reaction mixture showed no isocyanate absorption at 4.4 μ. An aliquot (25 ml.) of the polymer solution was set aside for further reaction and the remaining solution was poured into vigorously stirred acetone. The precipitated polymer was filtered, washed with acetone, and dried in a vacuum oven. The yield of white polymer, m.p. >300°C., was 2.69 g. (87%).

Preparation of Polyaminotetrazoles (Method A). The reaction of a solution of poly[methylenebis(4-phenylcarbodiimide) with] hydrazoic acid is typical.

To 100 ml. of a chloroform solution of hydrazoic acid (4.6 g., 0.11 mole) was added the 25 ml. aliquot of polycarbodiimide solution in chloroform–chlorobenzene (prepared above) and the mixture was stirred at room temperature for 48 hr. The precipitate which formed was filtered, washed with chloroform, and dried. The polymer was soluble only in concentrated sulfuric acid, and was purified by reprecipitation from sulfuric acid into water. The precipitate was thoroughly washed with water, and after vacuum drying at 100°C., 1.1 g. (88.7%) of white powdery polymer, m.p. >300°C., was obtained. The infrared spectrum showed tetrazole absorption bands at 6.3, 9.2, and 10.3 μ.

Preparation of Polyaminotetrazoles (Method B). This method was applicable only to poly(mesitylene carbodiimide).

To a solution of 1.0 g. of poly(mesitylene carbodiimide) in 100 ml. of chloroform was added 5.0 g. of sodium azide in 100 ml. of hot dimethyl sulfoxide. The mixture was refluxed for 48 hr. and the precipitate which formed during the reaction period was filtered, extracted in a Soxhlet extractor with water, then acetone, and dried. The polymer was further purified by reprecipitation from sulfuric acid into water. A yield of 1.2 g. (91%) of washed and dried polymer, m.p. 240°C., was obtained.

General Procedure for the Polymerization of Disodium Salts of Bistetrazoles and Dihalides. The polymerization of the disodium salt of 5,5′-*p*-phenylenebistetrazole and 1,2-dibromoethane is typical. To a solution of 2.20 g. (0.0085 mole) of disodium salt of 5,5′-*p*-phenylenebistetrazole in 50 ml. of 50% aqueous ethylene glycol was added 1.60 g. (0.0085 mole) of 1,2-dibromoethane. The reaction mixture was refluxed for 48 hr., during which a white precipitate formed. An additional 0.18 g. (0.001 mole) of dihalide was added, and refluxing was continued for 12 hr. The reaction mixture was cooled and filtered, and the residue was washed with three 50-ml. portions of hot water, then with methanol. The polymer was soluble only in concentrated sulfuric acid, and was purified by reprecipitation from sulfuric acid into water. The precipitate was thoroughly washed with water, and after drying in a vacuum oven, 1.4 g. (68%) of white polymer, m.p. 240°C. (dec.), was obtained.

Conversion of Trimeric Hexamethyleneadipamide to an Oligotetrazole. The general procedure of Zahn and Lauer[14] was followed in the preparation of the trimer of hexamethyleneadipamide. To a 500 ml. erlenmeyer flask equipped with a magnetic stirrer were added 117 g. (1.0 mole) of hexamethylenediamine, 100 g. (0.5 mole) of ethyl adipate, and 3.5 g. of sodium ethoxide. The mixture was stirred at room temperature for 3 weeks, during which a mass of white solid formed. The solid material was broken up and stirred into two liters of boiling ethanol. The insoluble portion was filtered through a sintered glass funnel and dried. After two successive recrystallizations from dimethylformamide, 10.2 g. (7.73%) of white product, m.p. 238–240°C. (lit.[14] 241°C.), was obtained.

To a suspension of 5.0 g. (0.0063 mole) of the oligoamide in 200 ml. of dry benzene was added portionwise 7.9 g. (0.038 mole) of phosphorus pentachloride. The reaction mixture was stirred at room temperature for 12 hr., during which a yellow homogeneous solution formed. To this solution was added a benzene solution of 4.46 g. (0.104 mole) of hydrazoic acid, and the reaction mixture was stirred at room temperature for 24 hr. Solvent was removed from the brown mass at reduced pressure and the residue was treated with 1*N* sodium hydroxide to pH 8. The residue was then filtered, washed with water, and taken up in dimethylformamide. The solution was filtered to remove insoluble material, and the oligomer was precipitated by addition of the solution to rapidly stirred acetone. The yield of light brown oligotetrazole, m.p. 250–255°C., was 4.2 g. (70.5%).

ANAL. Calcd. for $C_{42}H_{76}N_{26}$: C, 53.35%; H, 8.06%; N, 38.60%. Found: C, 52.80%; H, 8.47%; N, 38.84%.

The infrared spectrum showed tetrazole absorption bands at 6.2, 9.2, and 10.4 μ, and amine absorption at 3.1 μ.

This paper is abstracted from the Ph.D. dissertation of Peter A. Christie, University of Delaware, 1967.

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Crystalline Titanium Dichloride—An Active Catalyst in Ethylene Polymerization. I. Catalyst Activation

F. X. WERBER, C. J. BENNING, W. R. WSZOLEK, and
G. E. ASHBY, *Research Division, W. R. Grace & Company,*
Clarksville, Maryland 21029

Synopsis

Crystalline titanium dichloride, in the absence of organometallic cocatalyst, is a very poor catalyst for the polymerization of ethylene. It is transformed into a very active catalyst through mechanical activation (ball-milling). This catalyst is active in the absence not only of organometallic cocatalysts, but also metals and compounds (such as aluminum and $AlCl_3$) capable of forming organometallic compounds *in situ* (i.e., with ethylene, before polymerization starts). Ball-milling causes not only the expected increase in surface area but also disproportionation of Ti^{++} to Ti^{+++} and metallic titanium, as well as a crystal phase change to a structure not previously identified with those of $TiCl_2$ or $TiCl_3$. Catalyst activity (polymerization rate) is shown to be proportional to surface area and a direct function of Ti^{++} content of the catalyst; an empirical equation relates catalyst activity to surface area and to Ti^{++} lost through disproportionation. Titanium trichloride was found to be inactive in the absence of organometallic cocatalyst, even after ball-milling. The difference in structure of the catalytically active species in the conventional Ziegler (organometallic cocatalyst) and in the titanium dichloride catalyst are discussed. The mechanism of polymerization is compared with that of the supported (CrO_3 on SiO_2/Al_2O_3 and MoO_3 on Al_2O_3) catalyst systems.

INTRODUCTION

It has been considered axiomatic that highly active Ziegler-type catalyst systems for the polymerization of olefins require a combination of a transition metal salt and organometallic cocatalyst.* Thus, the active catalyst is generally thought to be formed through the alkylation of the salt by the organometallic component; indeed, substantial evidence exists for the presence of the resulting transition metal alkyl compounds and their role as active catalysts.[1,2] A series of alkylation products can form and these, in turn, can react to yield salts of lower valence state. The sequence is illustrated with $TiCl_4$ and $AlEt_3$, the most widely studied combination:

$$TiCl_4 + AlEt_3 \rightarrow EtTiCl_3 + AlEt_2Cl \qquad (1)$$

$$EtTiCl_3 + AlEt_3 \rightarrow Et_2TiCl_2 + AlEt_2Cl \qquad (2)$$

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* We arbitrarily define "active" catalysts as those capable of forming more than 10 g. polymer/g. catalyst/hr. at an ethylene concentration not exceeding 0.15 mole fraction in the medium employed.

The alkylation products can react to yield ethyl radicals (which couple to form butane) and precipitated titanium halides of lower valence state:

$$2EtTiCl_3 \rightarrow 2TiCl_3 + n\text{-}C_4H_{10} \tag{3}$$

Similarly, titanium trichloride can undergo a parallel series of reactions, the final product of which is the dichloride.

$$TiCl_3 \xrightarrow{AlEt_3} EtTiCl_2 \rightarrow TiCl_2 + n\text{-}C_4H_{10} \tag{4}$$

Conflicting evidence exists regarding the optimum valence state of titanium in the catalytic intermediate. Ludlam et al.[3] reported an excellent correlation between divalent titanium content and catalyst activity in precipitated catalysts prepared from $TiCl_4$ and organoaluminum compounds. Soluble organometallic cocatalyst systems, on the other hand, are reported to be based on alkylated titanium halides in the tetravalent state.[4,5]

There exists a mountainous literature, mainly in patents, which claims polymerization catalysts made from titanium halides and free, elemental metals (Al, Mg, La, B, Zn, etc.) or metallic reducing agents other than organometallics ($LiAlH_4$, LiH, etc.). In these cases, it is quite possible that organometallic components are formed through interaction with ethylene before polymerization starts. Aluminum, aluminum chloride, and ethylene, for example, readily form the sesquihalide ($EtAlCl_2$ + Et_2AlCl).

The use of titanium dichloride alone, containing no added reducing agent or metal capable of forming an organometallic cocatalyst, has been reported in a patent.[7] This compound exhibited very poor, almost minute catalytic activity, however. We have found that titanium dichloride free from other metals or reducing agents capable of forming organometallic compounds, can be transformed through mechanical activation (ball-milling) into a highly active catalyst system for ethylene polymerization. The catalyst activity as a function of the physical and chemical properties of the catalyst will be the subject of the present paper, while the structure of the polymer, polymerization variables and scope will be treated in the following paper.[8]

EXPERIMENTAL

Preparation of Titanium Dichloride

Three different methods were used, two of which furnished titanium dichloride free from other metals:

Method A:

$$TiCl_3 + Ti \xrightarrow{450°C.} 2TiCl_2$$

Method B:

$$2TiCl_3 \xrightarrow{700°C.} TiCl_2 + TiCl_4$$

Method C:

$$TiCl_4 + 2Na \rightarrow TiCl_2 + 2NaCl$$

Reaction of Titanium Trichloride with Titanium Metal (Method A). The work of Klemm and Grimm[9] indicates that titanium trichloride and titanium interact at temperatures above 450°C. to form the dichloride. A temperature of about 700°C. was employed to make the material used in this study.

Disproportionation of Titanium Trichloride (Method B). The method of Ruff and Neumann[10] and of Schumb and Sundstrom[11] was generally followed. Titanium trichloride, formed by reduction of titanium tetrachloride with hydrogen, was heated to 700°C. in a Vycor tube under a sweep of argon. Heating was continued for 7–8 hr., until titanium tetrachloride could no longer be detected in the exit stream.

Reduction of Titanium Tetrachloride with Sodium (Method C). A procedure given in a recently issued patent[12] was generally followed. A fine dispersion of sodium (46 g., 2.0 mole) in dry toluene was prepared at 100°C. with the use of a high speed (20,000 rpm) stirring device. Titanium tetrachloride (209 g., 1.1 mole) was added over a period of 1.5 hr., at 95–107°C.; heating at 100°C. was continued for another 2 hr. The black solid which had formed was allowed to settle, and the supernatant liquid was siphoned off under argon. The residual solid was vacuum-dried. Only traces of titanium metal were formed. The product—containing a 2:1 molar excess of sodium chloride—was used directly as catalyst.

Ball-Milling of Titanium Dichloride

In a typical procedure, titanium dichloride (100 g.) was transferred in a dry box under 1–2 lb. positive argon pressure into a 1-liter stainless steel jar half full of $^1/_2$-inch stainless steel balls. The jar was closed and rolled for a predetermined time at 180 rpm. After milling, the material was removed under argon and stored in a flask under argon until used. Samples could be removed intermittently by means of a special wide-bore valve to which a storage flask could be attached. For smaller-scale experiments, a 1 pt. mill was used. After activation, the black, finely divided product was extremely pyrophoric.

Analysis of Titanium Dichloride

Determination of Total Di-, Tri-, and Tetravalent Titanium. A catalyst sample is dissolved in dilute (10%) sulfuric acid. All titanium salts are oxidized to the tetravalent state with nitric acid. Ammonium hydroxide is added, the precipitate is filtered off, ignited, and weighed as titanium dioxide. The oxide was analyzed by emission spectroscopy and shown to be 99+% pure titanium dioxide.

Acid-Insoluble Material in Titanium Dichloride Catalyst. A sample of catalyst is treated with (10%) H_2SO_4; the insoluble material is filtered off, dried, and weighed.

Divalent Titanium in Titanium Dichloride by Hydrogen Evolution. This method is applicable to the determination of milligram quantities of titanium dichloride in the presence of titanium trichloride, titanium tetrachloride, and other metal compounds which do not evolve hydrogen from a dilute aqueous acid solution.

Titanium dichloride will react with water to evolve one molecule of hydrogen for each two molecules of dichloride:

$$2Ti^{++} + 2H_2O \rightarrow 2Ti^{+++} + 2OH^- + H_2 \qquad (5)$$

Evolved hydrogen is swept from a reaction flask by a stream of pure carbon dioxide. The combined gases enter a gas buret, where the carbon dioxide is dissolved in 50% potassium hydroxide solution. The volume of undissolved hydrogen is measured and related to weight per cent titanium dichloride.

To prevent hydrolysis of the Ti^{+++}, 10 vol.-% sulfuric acid is used as solvent instead of water.

Trivalent Titanium by Permanganate Oxidation. This method is applicable to the determination of total Ti^{+++} in the presence of Ti^{++++}. Ti^{++} and any other materials which are oxidized by potassium permanganate will be titrated if present.

$Titanium^{+++}$ is titrated with standard potassium permanganate in an atmosphere of argon and in the presence of Zimmerman-Reinhardt reagent.

The redox equation is:

$$5Ti^{+3} + Mn^{+7} + 8H^+ \rightarrow 5Ti^{+4} + Mn^{+2} + 4H_2O \qquad (6)$$

The complete equation is:

$$20TiCl_3 + 4KMnO_4 + 16H_2SO_4 \rightarrow 15TiCl_4 + 4MnSO_4 + 5Ti(SO_4)_2 + 2K_2SO_4 + 16H_2O \qquad (7)$$

The transition of color is from purple to water-clear to pink and the endpoint is sharp.

X-Ray Analysis of Titanium Dichloride Samples

Diffraction patterns were recorded on film. Powdered samples were transferred and sealed into glass capillary tubes under dry nitrogen. The tubes were mounted in a 114-mm. Debye-Scherrer camera (North American Philips Corp.). Exposures of 4–6 hr. were employed, using copper radiation filtered with nickel. The position of the diffraction lines was read from the film to the nearest 0.1° 2θ.

Surface Area Measurement

The surface area is measured by a procedure based on one devised by Nelon and Eggertsen.[13] This method is applicable to all solids that do not react with nitrogen. Surface areas obtained on standard samples of bone char, silica, and titanium dioxide varied by ±15% from the reported values determined with the conventional BET[14] pressure–volume apparatus.

Polymerization of Ethylene

A 1-liter jacketed, stirred autoclave of special design was used. Heating was controlled by using a boiling liquid (usually water) as heat transfer medium in the jacket; temperature could be adjusted by varying the boiling point of the liquid, through adjustment of carbon dioxide pressure (from a tank) in the jacket. Three hundred grams of solvent were fed from a reservoir to the reactor directly through alumina–Molecular Sieve (4-A) drying towers. The solvent reservoir was kept on a scale; individual charges were pressured into the reactor with nitrogen and metered by weighing the reservoir before and after charging the reactor. Ethylene was fed through similar drying towers; its concentration in the reactor was maintained constant throughout each run by feeding on demand. Flow of ethylene was observed through a calibrated flowmeter (Fisher & Porter Co.). A wide-bore ball valve on the reactor served to introduce catalyst at atmospheric or at elevated pressures. Great care was exercised to remove absorbed oxygen and moisture from the reactor before each run.

The products of each run were recovered as follows: The reactor contents (solvent–suspension of polymer) were poured into about three times the volume of a 5% solution of hydrochloric acid in isopropanol in a Waring Blendor. The slurry was then filtered and added to more wash solution and refluxed for 4–12 hr., filtered, washed with isopropanol, and dried overnight at 60°C./100 mm. pressure.

Ethylene was polymerization grade, obtained from Phillips Chemical Co. It was used directly, being dried only through the towers mentioned above.

Acid-washed cyclohexane (85%) was obtained from Phillips Chemical Co. Moisture and oxygen were removed by tapping 3–5% of the material by distillation under nitrogen; further drying was effected in the drying columns.

Nitrogen (General Electric Co. lamp-grade) was the inert gas used throughout this study.

RESULTS

Catalyst Changes during Activation

In agreement with the results reported in a patent to Farbenfabriken Bayer,[7] we found that (unmilled) titanium dichloride prepared by any of the methods listed had very low to unmeasurable catalyst activity. After initial experiments indicated that ball-milling increased the polymerization rate substantially, measurements of surface area were undertaken. These early results showed that although, as expected, surface area increased with milling, the increase was not nearly as marked as that in catalyst activity. This led to a more thorough investigation and correlation of catalyst activity with chemical, crystallographic, and particle-size changes in the catalyst as well as with surface area.

TABLE I

Physical and Chemical Changes on Ball-Milling of Titanium Dichloride

Sample no.	$TiCl_2$, %		$TiCl_3$, %		Ti°, %		Surface area, m.²/g.	Polymerization rate, g./g. cat./hr.[a]	Specific viscosity[b]
	Weight	Mole	Weight	Mole	Weight	Mole			
Original	87.5	91.3	6.8	5.1	1.4	3.6	2–3	1.7	8.0
Milled 1 day	76.7	81.2	16.7	13.6	2.4	6.3	10.7–9.8	121	6.3
Milled 4 days	46.5	49.4	41.5	34.2	6.3	16.4	16.2–21.4	92	5.6
Milled 5 days	45	45.7	44.4	35.0	7.7	19.4	27.0	94	5.3
Milled 6 days	39	40.2	50.3	40.0	7.8	20.0	19.8–16.5	72	6.6
Milled 9 days	25.3	25.9	61.2	48.4	10.1	25.7	15.5–17.2	16	8.9

[a] Polymerization of 450 psi ethylene, 145°C., cyclohexane as solvent.
Catalyst concentration: 0.8–1.2 g.; polymerization time 1–1.5 hr.
No induction periods were observed except with the unmilled catalyst

[b] At 0.1% concentration in Decalin at 130°C.

TABLE II
Powder Diffraction Patterns of Titanium Chlorides

Dichloride[a]		Dichloride (phase A)		Phase B		Dichloride[c]		Trichloride[d]	
d, A.	*I*	*d*, A.	*I*[b]	*d*, A.	*I*	*d*, A.	*I*	*d*, A.	*I*
6.09	80	6.06	S	5.75	S	5.88	25	[e]	
5.20	20	5.15	W	3.02	W	2.94	6	2.93	40
2.68	100	2.67	S	2.87	F	2.73	100	2.73	100
2.51	20	2.49	F	2.49	S				
2.38	20	2.37	F						
2.27	20	2.26	F	2.27	F				
2.14	60	2.13	M			2.13	42	2.12	100
2.03	10								
1.95	40	1.96	F	1.92	F				
1.86	40	1.85	F	1.76	M	1.78	29	1.77	60
1.72	50	1.72	W			1.70	6	1.69	10
1.68	40	1.68	F						
1.66	20					1.65	19	1.64	100
1.53	40	1.52	W			1.49	9	1.51	10
						1.47	4	1.48	80
				1.41	W	1.37	8	1.36	50

[a] Data of Farber et al.[16]

[b] S = strong, M = medium, W = weak, F = faint.

[c] Data of Benziger and Rundle.[17]

[d] Data of Klemm and Kroze.[18]

[e] Line may be present, but cut off by beam-trap.

Table I presents data on the chemical analysis, surface area, catalyst activity in ethylene polymerization and properties of the polymer formed as a function of ball-milling. The sample of titanium dichloride chosen was prepared by method A and obtained from the New Jersey Zinc Company. The data are graphically shown in Figure 1. The chemical analysis shown represents direct determination of each titanium valence; none was determined by difference. The experimental series shown here has been reproduced two other times, with results in good agreement. Similar maxima in catalyst activity were found, though rate of "activation" of the catalyst depends on energy input in each milling experiment, i.e., the ratio of steel balls to titanium salt. Catalyst activities far higher than those reported here have been obtained routinely.

The data clearly show that milling at room temperature induces disproportionation of the titanium dichloride according to eq. (8):

$$3TiCl_2 \rightarrow 2TiCl_3 + Ti \qquad (8)$$

This reaction has not been previously reported.* At temperatures above

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* Prof. Bruno Zwolinski (Texas A&M University) has called to our attention the fact that the change in free energy of formation (ΔF_f) for the disproportionation reaction at room temperature (298°K.), based on published values[15] for $TiCl_2$ and $TiCl_3$, is as follows: in the crystalline phase, $\Delta F_{fc} = +25.2$, in the gas phase, $\Delta F_{fg} = -27.8$. Thus, either the published values for ΔF_f in the crystalline phase are erroneous, or the reaction in the ball-mill, at the surface of the crystals is equivalent to reaction in the gas phase.

600°C., titanium dichloride disproportionates to the metal and $TiCl_4$;[11] since the trichloride is thermally less stable than the dichloride ($TiCl_3$ begins to disproportionate at 450°C. to $TiCl_2$ and $TiCl_4$), one would expect $TiCl_2$ to react as it does at the higher temperatures.

Surface area reached a peak in 4–5 days of milling and then declined. Most surprising was the sharp decline in polymerization rate with time of milling following a peak in rate, ultimately down to one-tenth that at the peak.

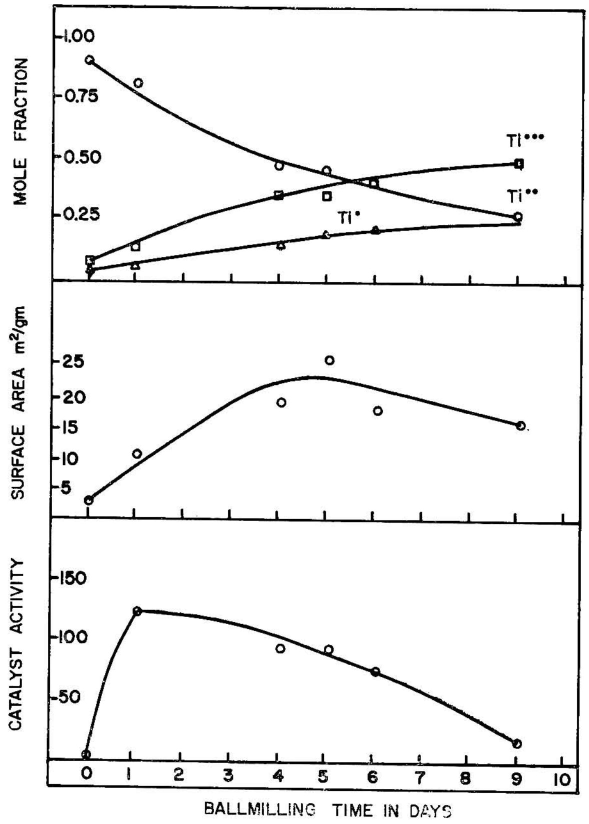


Fig. 1. Catalyst composition, surface area, and activity vs. ball-milling time.

The x-ray powder diffraction pattern of the original titanium dichloride (prepared by method A) shows a diffraction spectrum almost identical to that recently described for $TiCl_2$.[16] We shall call the structure represented by this pattern phase A. Upon milling, a new crystalline phase (phase B) appears, whose diffraction pattern does not closely resemble any of the published patterns for either the di- or trichloride. After 5 days' milling, phase A is completely gone and phase B is the only one visible.

The x-ray powder patterns of Phase A, Phase B, and the data for the dichloride of Farber, et al.[16] are shown in Table II. For comparison, the patterns for titanium dichloride described by Benziger and Rundle[17] and for the trichloride by Klemm and Krose[18] are given.

The similarity in crystal structure between titanium dichloride and trichloride have been amply demonstrated. The structures of the two halides have been characterized as layerlike, with a trigonal unit cell. In the case of $TiCl_2$, with Ti at 0,0,0, chlorine atoms are located at $^1/_3$, $^2/_3$, u and $-^1/_3$, $-^2/_3$, $-u$, where $u = 1.47$ A.[17] $TiCl_3$ has two-thirds (on an average) of a titanium atom at 0,0,0 and chlorines at $^1/_3$, $^2/_3$ and z, and $-^1/_3$, $-^2/_3$, and $-z$, where $z = 1.38$ A. Thus, the Ti–Cl spacings are rather similar, and the significant difference between the two structures is the absence in the trichloride of one out of three titanium atoms of the dichloride. The interlayer titanium distance is approximately the same.

The metallic titanium residue from the milled samples—after dissolution of the halides—was shown to be amorphous by separate x-ray examination. Based on the above facts, we can conclude that the milling process brings about migration of titanium ions within the $TiCl_2$ lattice. These ions aggregate to form amorphous titanium, leaving behind holes. We cannot conclude whether these holes exist at random in the lattice or whether they also aggregate, giving long-range $TiCl_3$ order.

Titanium Trichloride

The catalytic activity of titanium trichloride (obtained by hydrogen reduction of $TiCl_4$) was checked in independent experiments. Neither milled nor unmilled titanium trichloride polymerized ethylene to measurable amounts of polymer. These experiments provide independent proof that $TiCl_2$ is required in an active catalyst.

Alternate Titanium Dichloride Preparations

Titanium dichloride prepared by methods B and C were similarly evaluated for catalyst activity before and after ball-milling. The results which were obtained are shown in Table III.

TABLE III

	Catalyst activity, g. polymer/g. catalyst/hr.	
	Before milling	After 2 days' milling
$TiCl_2$ (Method B)	1	90
$TiCl_2$ (Method C)	2	2

Method C, involving reduction of titanium tetrachloride by metallic sodium, yields a 2:1 molar ratio of sodium chloride to titanium dichloride. The possibility therefore existed that the presence of NaCl, rather than the preparative method, is responsible for the low catalytic activity, i.e., that NaCl acts as a catalyst poison. This was found to be the case. Titanium dichloride (prepared by method A) was milled with dry sodium chloride in several molar ratios, from Na:Ti of 2:1 to 10:1. These preparations were inactive in the polymerization of ethylene. Method B gave an active catalyst, similar in behavior to that made by method A.

One can therefore conclude that titanium dichloride, prepared by any method yielding products free from salts of other metals, can be converted into a highly active ethylene polymerization catalyst by mechanical activation.

DISCUSSION

If one neglects the practically inactive original (unmilled) catalyst, the results indicate qualitatively that catalyst activity is a direct function of $TiCl_2$ concentration. In other studies carried out in our laboratories, we have found that the rate of polymerization of propylene with ball-milled $TiCl_3$ catalyst/$AlEt_2Cl$ cocatalyst is directly proportional to surface area of the catalyst.[9] It therefore seemed of interest to see whether surface area could be similarly correlated with catalyst activity in the data reported here.

To arrive at an expression incorporating these thoughts, we made the following specific assumptions:

(*1*) Polymerization rate is proportional to surface area.

(*2*) Removal of each Ti^{++} from the crystal lattice leads to a constant, finite drop in the number of sites active in polymerization (not necessarily one active site per Ti^{++} lost). We can then set up the equation:

$$R_t = R_{P0} - B(C_{\mathrm{Ti}^\circ}) \tag{9}$$

where R_{Pt} is the specific polymerization rate at ball-milling time t (in g. polymer/g. catalyst-m.^{2} surface area-hr.). This is simply the observed catalyst activity (polymerization rate) divided by surface area of the catalyst. R_{P0} is the specific polymerization rate (g. polymer/g. catalyst-m.^{2} surface area-hr.) for a (hypothetical) catalyst consisting of $TiCl_2$ alone; C_{Ti° is the mole per cent Ti° formed in ball-milling, and B is a constant (i.e., loss in specific polymerization rate, given in the same units as above, per mole per cent Ti° formed).

By using the data from Table I, the constants R_{P0} and B were calculated by fitting the data to eq. (9) by the method of least squares. Data from the original, non-ball-milled $TiCl_2$ were ignored, since the influence of absorbed surface poisons remaining from the preparation of the catalyst (e.g., $TiCl_4$) may outweigh other effects. Following are the values thus determined:

$$R_{P0} = 14.8 \text{ g./m.}^2\text{-hr.}$$
$$B = 0.556 \text{ g./m.}^2\text{-hr.-mole Ti}^\circ$$

Fitting these constants back into the data, we obtain the comparison between experimentally determined and calculated values of R_{Pt} shown in Table IV.

TABLE IV

Ball-milling time, days	R_{P0} (exptl.)	R_{P_t} (calcd.)
1	11.8	11.3
4	5.0	5.7
5	3.5	4.0
6	4.0	3.7
9	1.0	0.4

Considering the error involved in the chemical analysis, in surface area determination, and in polymerization rate, this is fair agreement. (Note that the largest error occurs in the bottom set of values, at the lowest and thus least accurate polymerization rate.)

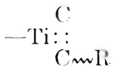
Study of the constants R_{P0} and B lead to some interesting conclusions. If we divide R_{P0} by 100, it assumes the same dimensions as B, or a specific polymerization rate per mole per cent. The ratio

$$(B/R_{P0}) \times 100 = (0.556/14.8) \times 100 = 3.8$$

then gives us the number of catalytically active $TiCl_2$ molecules lost for each atom of metallic titanium formed. This is 0.8 molecules more than predicted on the basis of the stoichiometry of eq. (1), if we assumed that molecules of $TiCl_2$ lost and active sites lost are directly proportional.

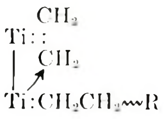
We believe that the evidence we have presented is quite conclusive that $TiCl_2$, free from absorbed poisons, is an active catalyst for ethylene polymerization. The quantitative picture is somewhat obscured by the disproportionation of $TiCl_2$ to $TiCl_3$ and Ti, found to take place in mechanical activation; however, the data show that catalyst activity is proportional to surface area, as well as dependent on $TiCl_2$ content.

We cannot distinguish between the following alternative postulates for the structure of the active catalyst complex: (I),



$$-\mathrm{Ti}{:}{:}\begin{matrix}\mathrm{C}\\ \mathrm{C}\!\sim\!\mathrm{R}\end{matrix}$$

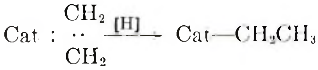
where initiation and propagation take place at a single titanium atom, versus II,



$$\begin{array}{l}\mathrm{Ti}{:}{:}\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{matrix}\\ \ \ |\ \ \nearrow\\ \mathrm{Ti{:}CH_2CH_2}\!\sim\!\mathrm{R}\end{array}$$

where each catalytically active site contains a complex of two or more adjacent Ti^{++} ions, and the growing polymer chain is adsorbed to both (or, alternately, to one and the other) titanium atom.

Also left open is the relationship, if any, between the structure of active Ziegler catalysts made with organometallic cocatalysts and the present catalyst. Superficially, this system presents the same problem posed by the supported oxide catalyst.[20] Where does the hydrogen atom come from to generate the original initiated species?



$$\mathrm{Cat}:\overset{\mathrm{CH_2}}{\underset{\mathrm{CH_2}}{\cdot\cdot}}\xrightarrow{[\mathrm{H}]}\mathrm{Cat{-}CH_2CH_3}$$

Propagation, chain-transfer, and termination can take place exactly as postulated for the CrO_3 on SiO_2/Al_2O_3 (Phillips) and MoO_3 on Al_2O_3 (Std. of Indiana) catalyst systems.[20]

A more complete crystallographic characterization of the active catalyst may cast more light on the detailed mechanism of the catalytic process.

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Crystalline Titanium Dichloride—An Active Catalyst in Ethylene Polymerization. II. Polymer Structure, Polymerization Variables, and Scope

C. J. BENNING, W. R. WSZOLEK, and F. X. WERBER,
Research Division, W. R. Grace & Company, Clarksville, Maryland 21029

Synopsis

Polymerization of ethylene with ball-milled titanium dichloride leads to a completely linear polymer with terminal unsaturation corresponding to approximately one carbon-carbon double bond per molecule. Polymerization rate is first-order in both monomer and catalyst concentration at 140°C. Due to a thermal deactivation of the catalyst, the polymerization rate falls sharply with temperature above 180°C. Propylene and butene-1 will copolymerize with ethylene in this system, propylene more efficiently than butene-1. Evidence for copolymerization of *trans*-2-butene, but not of the *cis*-isomer or of isobutene, in trace concentrations is presented. Propylene is homopolymerized to a product low in isotactic content. The significance of the structural and (limited) kinetic data in terms of the mechanism of polymerization are discussed.

INTRODUCTION

The previous paper[1] dealt with the chemical and physical properties of titanium dichloride catalysts active in ethylene polymerization. This report will deal with kinetic variables in ethylene polymerization, with the structure of the polymer, and with the scope of application of this catalyst to other olefins and in copolymerization.

EXPERIMENTAL

Catalyst Preparation

Titanium dichloride prepared by method A in the previous paper[1] was used. Titanium dichloride content before milling varied between 94 and 97 wt.-%, the rest being metallic titanium and the trichloride. The salt was dry-milled by the previously described procedure[1] to optimum catalyst activity.

Polymerization

The equipment and procedure for homopolymerization of ethylene has been described previously.[1] Argon (Matheson C.P.) was used in place of nitrogen for all experiments at temperatures above 160°C., since nitrogen was found to have a poisoning effect at these temperatures.

Most ethylene–propylene copolymerization experiments were carried out with (known) monomer mixtures charged from a reservoir kept at high enough temperature to maintain both monomers in the gaseous state. The monomers were fed on demand, maintaining the charge reservoir at slightly higher than reactor pressure. The reservoir contents were analyzed by vapor-phase chromatography before and after each run to determine if there was any change in composition.

Higher boiling comonomers and, in some cases, propylene were charged as liquids to the reactor prior to the introduction of ethylene.

Propylene, butene-1, *cis*- and *trans*-butene-2, and isobutylene were Matheson C.P. grade and purified in the same way as ethylene.[1]

Cyclohexane or toluene was used as solvent. To keep the partial pressure of the solvent low, toluene was always used at temperatures above 200°C. It was distilled from sodium and then processed in the same way as cyclohexane.[1]

Analytical

Infrared spectral determinations of terminal methyl, branched methyl and ethyl, terminal vinyl, vinylidene, internal and total unsaturation were based on methods developed in the laboratories of the Research Division of W. R. Grace & Co. and the Phillips Petroleum Co.

Determinations of specific viscosity were done in 0.1% concentration in decalin at 130°C.

RESULTS AND DISCUSSION

Reaction Parameters in Ethylene Polymerization

Figure 1 shows dependence of rate and molecular weight on polymerization temperature. The data are too widely scattered to indicate more than trends, by means of the straight lines drawn. Above 180–200°C., the catalyst undergoes severe thermal deactivation, which accounts for the sharp drop in rates. Thus, a catalyst heated in toluene at 240°C. for 1 hr. was nearly inactive in subsequent polymerization at 150°C.

Very high catalyst activity was observed at temperatures down to 20°C. The products were insoluble in decalin, and thus molecular weights were too high to be measured.

Dependence of rate on ethylene concentration (Fig. 2) is clearly first-order within the limits measured. A slight dependence of molecular weight on ethylene concentration was also noted, but again difficulty in measuring the very high molecular weights involved resulted in some scatter in the data.

Polymerization rate was found to be first-order in catalyst concentration, down to a low "threshold" level, dictated by the presence of catalyst poisons. Catalyst concentration had no effect on molecular weight, however.

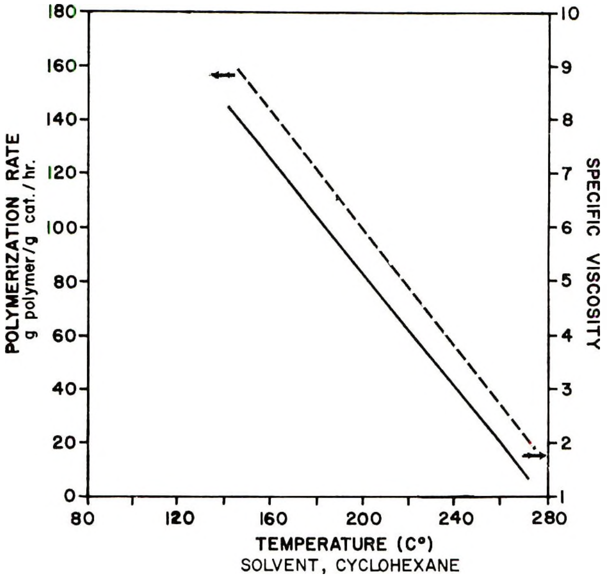

Fig. 1. Effect of temperature on rate and molecular weight.

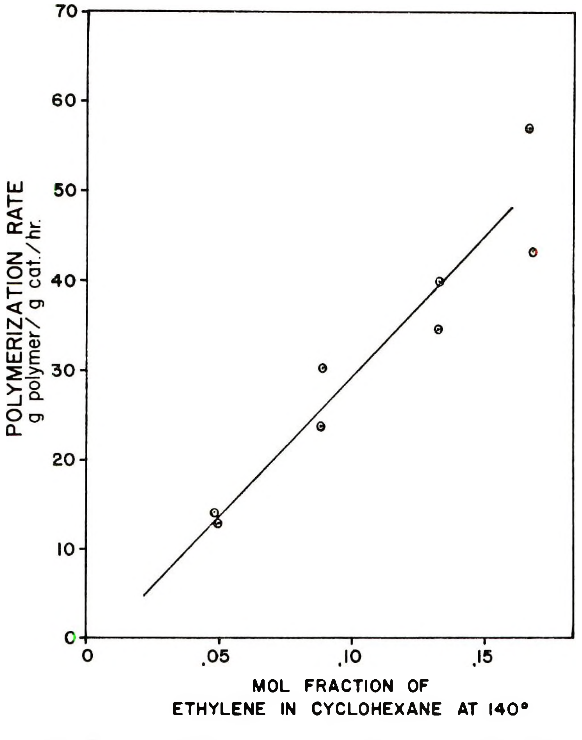

Fig. 2. Effect of ethylene concentration on reaction rate.

Structure of Polyethylene

Table I shows the analytical data on a typical polymer prepared with ball-milled titanium dichloride at 145°C. The content of methyl groups, density, and crystalline melting point show quite clearly that the polymer is completely linear and identical in structure to that produced with the so-called Phillips (CrO_3 on SiO_2/Al_2O_3) catalyst system.[2] The titanium dichloride catalyst thus differs from the heterogeneous Ziegler catalyst systems based on aluminum alkyls and $TiCl_4$, which produce moderate branching in polyethylene (3 to 7 branch-methyls per 1000 carbon atoms).

TABLE I
Properties of Polyethylene Prepared with Titanium Dichloride Catalyst

	$TiCl_2$ Catalyst[a]	CrO_3 on SiO_2/Al_2O_3[b]
Specific viscosity	2.55	2.7
Density	0.958	0.957
Melting point, °C.	135–139	136–138
C=C (1645 cm.$^{-1}$), %	0.26	0.25
trans HC=CH (965 cm.$^{-1}$), %	trace	trace
CH_3/1000 C (1378 cm.$^{-1}$)	1.6 ± 0.5	1.7 ± 0.5
—$CH=CH_2$/1000 C (909 cm.$^{-1}$)	1.6 ± 0.5	1.7 ± 0.5

[a] Polymerization conditions: 450 psi ethylene, cyclohexane as solvent, 180°C.
[b] Grex 60-007 (Allied Chemical).

At polymerization temperatures below 200°C., unsaturation in the polymer produced is nearly all terminal; concentration is equivalent to the presence of one carbon–carbon double bond per molecule. At polymerization temperatures above 200°C., a fraction of total unsaturation, increasing with polymerization temperature, is present as internal *trans* CH=CH. Presumably, this is formed through catalyzed isomerization of the initially terminal double bonds. The polymer remains linear, however, over the whole range of polymerization temperatures studied.

Polymer formed at several molecular weights was fractionated by a modified Desreux technique (i.e., elution from a support coated with polymer). The distribution was found to be extremely broad, resembling closely that obtained with Phillips and other heterogeneous catalyst systems.

From the above-cited evidence a polymerization mechanism typical also of the well-known supported heterogeneous catalysts can be deduced:[3] (1) adsorption of monomer, followed by an initiation step of an as yet not understood nature; (2) propagation; (3) termination (desorption of polymer) followed by reinitiation; and/or (4) chain-transfer with monomer leading to desorbed polymer and initiated catalyst complex, ready for propagation.

$$[\text{Cat.}] + CH_2 = CH_2 \rightarrow [\text{Cat.}] \curvearrowleft \underset{\text{I}}{\begin{matrix} CH_2 \\ :: \\ CH_2 \end{matrix}} \xrightarrow{[H]} \text{Cat.}-CH_2CH_3 \tag{1}$$

$$[\text{Cat.}]\ CH_2CH_3 + CH_2{=}CH_2 \rightarrow \underset{\text{II}}{[\text{Cat.}]\ (CH_2-CH_2)-CH_2CH_3} \tag{2}$$

$$\text{II} \rightarrow [\text{Cat.}]\ \text{H} + \underset{\text{III}}{CH_2{=}CH-(CH_2-CH_2)_{n-1}CH_2CH_3} \tag{3}$$

$$\text{II} + CH_2{=}CH_2 \rightarrow \text{I} + \text{III} \tag{4}$$

The broad molecular weight distribution of the polymer indicates that the rate constants of one or more of the above kinetic steps vary with the molecular weight of the chain.

It was desirable to find a way to limit and control molecular weight independent of polymerization temperature. The use of hydrogen provided such a control; however, even low concentrations of hydrogen (5–10% mole-% in the monomer feed) led to substantial drop in catalyst activity. Polymerization temperature thus remained the only practically feasible variable for control of molecular weight.

Polypropylene

Propylene was polymerized to a polymer about 30% insoluble in heptane. The polymerization temperature was about 120°C., cyclohexane was used as solvent, propylene concentration was 200 psi. The maximum polymerization rate was about 30 g. polymer/g. catalyst/hr. 1-Butene would not homopolymerize with titanium dichloride.

Ethylene Copolymers

Propylene. Table II shows the effect of varying propylene feed concentrations on polymerization rate, propylene incorporation and molecular

TABLE II

Ethylene–Propylene Copolymerization

Weight of catalyst, g.	Polymerization rate, g. polymer/g. cat.-hr.[a]	C_3H_6, mole-%		Specific viscosity[c]	Vinyl/1000 C (909 cm.$^{-1}$)	Vinylidene/1000 C (888 cm.$^{-1}$)
		In feed	In polymer[b]			
0.9	160	5.2	1.9	4.5	0.9	0.08
1.2	112	8.7	5.4	3.2	0.6	0.03
1.1	90	16.5	8.8	5.6	0.7	0.17
1.57	68	20.3	14.0	2.0	0.86	0.17
0.9	121	(control)		8.1	0.91	0.05

[a] Polymerization temperature, 150 ± 4°C.; 1/2 hr. reaction time; 300 g. toluene as solvent.

[b] Determined by $-CH_3$ content (1378 cm.$^{-1}$).

[c] Concentration in decalin, 0.1%; 130°C.

TABLE III

Ethylene-1-Butene Copolymerization

Wt. of catalyst, g.	Butene-1 charged, g.	Reaction temp., °C.	Ethylene pressure, psig	Reaction time, hr.	Polymerization rate, g. polymer/g. cat.-hr.	Butene in polymer, mole-%[a]	Specific viscosity[b]	Vinyl/1000 C (909 cm.$^{-1}$)	Vinylidene/1000 C (808 cm.$^{-1}$)	Vinylidene × 100/vinyl
1.08	4.7	153–72	425–75	0.5	101	0.5	10.5	0.54	0.02	4
1.06	13	151–78	425–50	0.5	112	2.1	6.1	0.61	0.03	5.5
1.10	13	147–61	505–20	0.3	59	1.8	9.2	0.41	0.02	5.1
0.92	19	151–64	400–05	0.5	109	2.5	7.6	0.54	0.03	6
1.06	27	151–76	425–75	0.5	91	5.6	3.7	0.47	0.06	13
1.08	33	150–72	425–72	0.5	78	6.4	4.0	0.44	0.08	18
0.90	40	150–71	425–75	0.5	85	6.9	3.7	0.51	0.11	22

[a] Determined by —C_2H_5 content (1378 cm.$^{-1}$).

[b] Concentration in decalin, 0.1%; 130°C.

weight. It is interesting to note the increase in rate, in the presence of low propylene concentrations, compared to homopolymerization of ethylene. The rate increase was also observed when the catalyst was first contacted with propylene and then ethylene, but not if the monomers were charged in the reverse order.

1-Butene. Table III lists selected data on the butene copolymerization experiments. The charging technique differed from that used with propylene, butene being charged first. Because of the lack of constancy of the reaction temperature, the data are not good enough for calculating reliable reactivity ratios; since ethylene concentration remained constant and conversion of butene remained low, such a calculation would otherwise be possible. It is quite clear, however, that the incorporation of butene in the copolymer is far less favorable than that of propylene in the corresponding case.

In the case of both the propylene–ethylene and butene-1–ethylene copolymers, molecular weight decreases with increasing comonomer concentration. At the higher incorporation of the comonomer, the ratio

$$\frac{\text{Vinylidene/1000 C atoms}}{\text{Vinyl/1000 C atoms}}$$

exceeds the mole fraction of comonomer in the polymer, indicating that desorption of polymer and reinitiation, or chain transfer by monomer, takes place more readily at a growing chain ending in a propylene or butene-derived unit than at one derived from ethylene. Thus, reactions (3) and/or (4) shown above proceed faster when there is branching at the β-carbon. This is entirely analogous to the behavior of aluminum alkyls in elimination and olefin exchange reactions.[4]

Butene-2. Natta and co-workers have reported the preparation of ethylene–2-butene copolymers.[5] They were able to incorporate *cis*-2-butene more efficiently than the *trans* isomer, under their conditions. In contrast, we have been unable to obtain evidence of incorporation of *cis*-2-butene with titanium dichloride as catalyst (at 150°C.). On the other hand, *trans*-2-butene does copolymerize to a very slight degree under these conditions. The data are presented in Table IV.

TABLE IV
Copolymerization of Ethylene and *trans*-Butene-2

Wt. of catalyst, g.	*trans*-Butene-2, ml.	Polymerization rate, g./g.-hr.[a]	Butene in polymer, mole-%[b]	Specific viscosity	Vinyl/1000 C
0.91	45	138	0.1	6.0	0.9
0.92	67	75	0.3	4.1	0.8
0.92	143	54	0.4	4.2	0.7
0.99	193	56	0.5	4.2	0.7

[a] Reaction temperature, 150 ± 5°C.; ethylene pressure, 450–475 psi.

[b] Based on methyl branching (1378 cm.$^{-1}$).

Isobutylene did not copolymerize to a demonstrable degree under the conditions.

CONCLUSIONS

We have demonstrated that mechanical activation of titanium dichloride furnishes an active heterogeneous catalyst for the polymerization of ethylene. The polymer is completely linear and is formed with one terminal double bond per polymer chain. At ambient temperatures polymer of very high molecular weight—too high to be measured, far in excess of one million—is formed. Propylene and butene-1 can be copolymerized with ethylene. The copolymers are random in composition; in the case of propylene, rubbery copolymers with crystallinity below 20% have been made.

It is quite clear that (divalent) titanium dichloride can function as an active catalyst for the polymerization of ethylene. Organometallic cocatalysts or combinations of compounds which can form organometallic compounds *in situ* are not essential for high polymerization rate.

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Photoinduced Microstructural Changes in 1,4-Polyisoprene*

MORTON A. GOLUB† and C. L. STEPHENS, *Stanford Research Institute, Menlo Park, California 94025*

Synopsis

An infrared and NMR study was made of the microstructural changes produced in thin films of purified *cis*- and *trans*-1,4-polyisoprene when irradiated with ultraviolet light *in vacuo* at room temperature. The major photochemical processes observed were *cis–trans* isomerization and loss of 1,4 double bonds, the latter process being accompanied by the formation of vinylidene and vinyl double bonds as well as some endlinking. Very surprisingly, the loss of original double bonds contributed also to a novel photocyclization which gave rise to cyclopropyl groups in the polyisoprene chain. The isomerization and the formation of cyclopropyl groups are presumed to proceed through triplet and biradical states of the 1,4 double bonds, while the vinylidene and vinyl double bonds must result from chain rupture at the carbon–carbon bond joining successive isoprene units. Hydrogen abstraction and double-bond migration are of negligible importance in the overall photochemistry of polyisoprene.

INTRODUCTION

Considerable interest has been shown for many years in the light aging or weathering of rubber products, but mainly from a technological standpoint. Very little fundamental work has been done on the photooxidation of 1,4-polyisoprene and even less on its photolysis in the absence of oxygen. The lack of attention to the latter topic is surprising in view of the many recent papers dealing with the radiolysis of 1,4-polyisoprene *in vacuo*.[1] A survey of prior work on the photodegradation of rubber has appeared recently,[2] and it is evident that there is a need for a detailed study (using modern tools like infrared and NMR spectroscopy) of the microstructural changes produced in thin films of purified 1,4-polyisoprene when exposed to ultraviolet radiation *in vacuo*. Such a study has never been carried out, although infrared spectroscopy has been used to examine the photooxidation of 1,4-polyisoprene[3] and also the photolysis of high-1,2-polybutadiene[4] and 1,4-polybutadiene.[5]

The only fundamental work reported on the photolysis of 1,4-polyisoprene dates back over twenty years; Bateman[6,7] showed that irradiation of

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† Present address: Ames Research Center, National Aeronautics and Space Administration, Moffett Field, California 94035.

thoroughly degassed, purified hevea rubber films with ultraviolet light in the wavelength range 2300–3650 A. resulted in gas evolution, mostly hydrogen, with a quantum yield of the order of 4×10^{-4}. The largest relative yield, observed for the range 2350–2850 A., was about 2.5 times this value, so that an upper limit of 10^{-3} could be set for the efficiency of noncondensable gas formation. The hydrogen was assumed to arise from photoinduced rupture of α-methylenic carbon–hydrogen bonds, followed by the exothermic reaction,

$$H + RH \rightarrow H_2 + \dot{R}$$

where $\dot{R}$ is an allylic radical, while the resulting polymeric radicals R then combine to produce crosslinks. The attendant insolubilization of the ultraviolet-irradiated polyisoprene restricted its chemical examination, but there was tentative indication of a decrease in the unsaturation with a quantum yield that could be as high as 0.1.[6,8] Since quantum yields approaching this order of magnitude were obtained recently for the photochemical *cis–trans* isomerization and loss of 1,4 double bonds in polybutadiene,[5] it was of interest to see if these and other processes could be observed also in polyisoprene by use of appropriate spectroscopic techniques. The present paper, which describes the first infrared and NMR study of the photoinduced microstructural changes in 1,4-polyisoprene, can be regarded as both an extension of Bateman's original work[6,7] and as a followup to our prior work on the ultraviolet irradiation of 1,4-polybutadiene films.[5] At the same time, this paper provides useful data for a comparison of the photolysis and radiolysis of solid 1,4-polyisoprene.

EXPERIMENTAL

Materials

Four different polymers were used in this work: naturally occurring all-*cis* (hevea) and all-*trans* (balata) 1,4-polyisoprenes, and a synthetic polyisoprene of very high *cis* content (>97%; Ameripol SN), all obtained from the B. F. Goodrich Research Center, Brecksville, Ohio, and a 1,4-polyisoprene-3-*d* of high *cis* content, prepared by the late Dr. David Craig and Mr. Harold Tucker of the Goodrich Center. Most of the work, however, was carried out on hevea, the other polymers being used to obtain supporting data for mechanism purposes. The three *cis*-polyisoprenes were purified by successive precipitations from benzene solution using methanol as precipitant, while the *trans*-polyisoprene was purified by dissolving it in hot hexane and allowing it to crystallize out of solution at −20°C. Stock solutions of the purified polymers in benzene were then prepared and stored under nitrogen.

Irradiations

Thin films were cast from stock solutions onto rock salt plates, sealed in evacuated tubes ($<10^{-5}$ mm.) having quartz (and in a few instances Pyrex) windows, and irradiated at room temperature with the ultraviolet light from a Hanovia 450-w. quartz medium-pressure lamp. Since negligible change was observed in the polymer films irradiated in the Pyrex tubes, while considerable change occurred in the films irradiated in quartz tubes, it was concluded that the maximum effective wavelength for photochemical reaction in polyisoprene was below 3000 A., with the major reaction probably occurring at 2537 A., just as was noted for polybutadiene.[5] Several irradiations were also carried out with a Pen-Ray low-pressure mercury lamp (as described previously[5]), which was effectively a monochromatic source of 2537 A. radiation of known intensity. The Pen-Ray lamp was used to estimate quantum yields for *cis–trans* isomerization and loss of 1,4 double bonds in polyisoprene.

Microstructural Analysis

The polymer films were analyzed before and after irradiation by infrared spectroscopy with a Perkin-Elmer Model 221 spectrophotometer. The irradiated polymers were further characterized by means of NMR spectra (obtained with a Varian HA-100 spectrometer) of carbon tetrachloride solutions of the soluble fractions, the gel fractions having been discarded. Since the infrared spectrum of the sol was generally very similar to that of the irradiated film prior to fractionation, it was assumed that the microstructures of the sol and gel fractions were substantially the same except for crosslinks in the gel fraction. The NMR solutions contained a small amount of benzene as an internal reference; this was used in place of the customary tetramethylsilane so that an important signal around 10 τ in

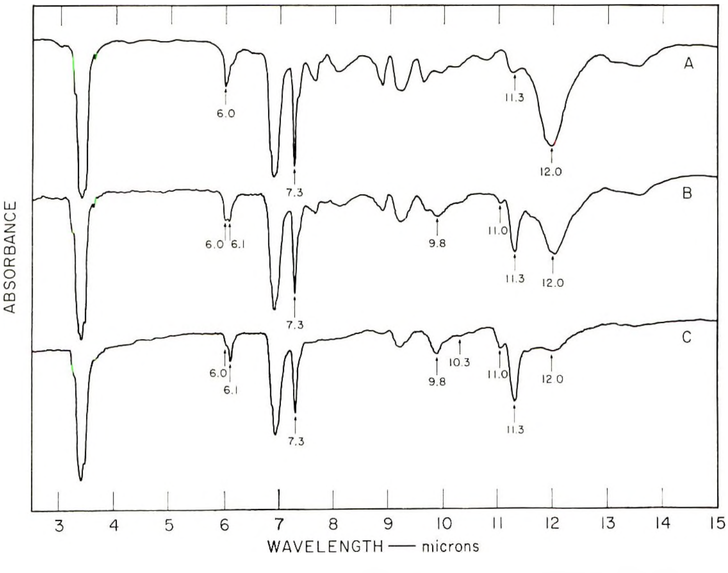


Fig. 1. Typical infrared spectra of a hevea film (*A*) before and after (*B*,*C*) successive exposures to ultraviolet radiation *in vacuo*.

the irradiated polyisoprene could be observed without interference from the TMS signal.

Typical infrared spectra of a *cis*-polyisoprene (hevea) film before and after extensive ultraviolet irradiation *in vacuo* are shown in Figure 1, while Figure 2 shows the corresponding NMR spectrum of the highly irradiated polymer.

The sharp decrease in the 12.0 μ [$—C(CH_3)═CH—$ units, *cis* or *trans*] band, the development of a strong band at 11.3 μ $\left(\rangle C═CH_2 \text{ units}\right)$, and another band at 11.0 μ ($—CH═CH_2$ units), and the accompanying decrease in the 6.0 μ band and growth of the 6.1 μ band (C═C stretching vibrations of internal and external double bonds, respectively), indicate that many, but not all, of the 1,4 double bonds in hevea which disappear during irradiation are replaced, in part, by vinylidene and vinyl double bonds. Since the absorption coefficient of the *trans* $—C(CH_3)═CH—$ unit is only 0.625 times that of the corresponding *cis* unit,[1] some of the decrease in the 12 μ band in irradiated hevea is probably associated with *cis–trans* isomerization, for which there is ample NMR confirmation. It should be noted, parenthetically, that the spectrum of the unirradiated hevea shows a peak at 11.3 μ which has nothing at all to do with exomethylene structures.[9,10]

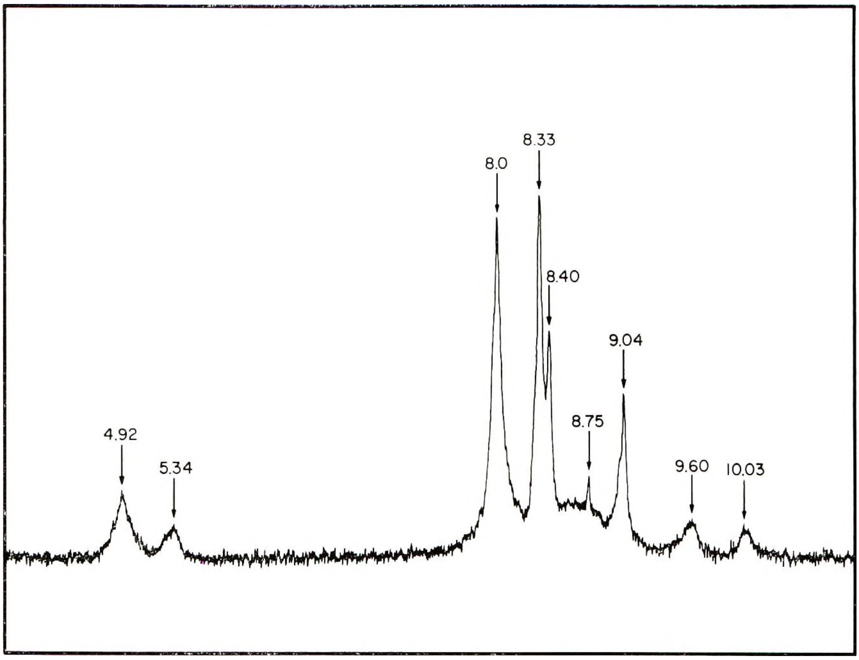


Fig 2. NMR spectrum of extensively ultraviolet-irradiated hevea (corresponding to infrared spectrum *C* in Figure 1). The significant peaks are identified by their τ values.

In addition to the NMR peaks at 4.92 ($-CH=$), 8.0 ($-CH_2-\overset{|}{C}=$), and 8.33 τ (*cis* $CH_3-\overset{|}{C}=$), found in the spectrum of th[illegible] all-*cis* polyisoprene,[9] important new peaks appear at 5.34 $\left(>C=CH_2\right)$, 8.40 (*trans* $CH_3-\overset{|}{C}=$), 8.75 ($-CH_2-\overset{|}{\underset{|}{C}}-$), and 9.04 τ ($CH_3-\overset{|}{\underset{|}{C}}-$), as well as two high field peaks at 9.60 and 10.03 τ. The high-field peaks have τ-values that are strikingly similar to those for the CH_2- protons in *trans*- and *cis*-1,2-dimethylcyclopropanes (~9.6 and 10.2 τ, respectively),[11] and these peaks very likely signify the presence of analogous cyclopropyl groups in the polyisoprene chain. Supporting evidence for the formation of such groups is provided by the appearance of the 9.8 μ infrared band (Fig. 1*C*) that is considered to be a characteristic cyclopropane ring vibration.[12] The NMR spectrum also shows, besides unambiguous *cis–trans* isomerization (which is very difficult to assess with infrared spectroscopy in the present system), the formation of vinylidene units, and saturated double bonds. Although the 5.34 τ peak represents exomethylene groups generally, from both a mechanism standpoint (see below) and a quantitative examination of the relative areas of the various peaks in Figure 2, it appears that virtually all the $>C=CH_2$ groups are present in $-C(CH_3)=CH_2$ units instead of in nonspecific structures such as $-CH_2-C(=CH_2)-CH<$.

The microstructural analysis of the irradiated *cis*- and *trans*-1,4-polyisoprenes was carried out as follows. The vinylidene content was estimated from the relative area of the 5.34 τ peak; the vinyl content was estimated from the ratio of intensities of the 11.0 and 11.3 μ bands and multiplying the ratio by the vinylidene content just determined; the residual 1,4 content was estimated from the relative area of the broad 4.92 τ peak, correction being made for the olefinic protons in 1,2-polyisoprene; the cyclopropyl groups were estimated on the assumption that each such group contributes two protons to the high field peaks either at 9.60 or at 10.03 τ; and the *cis–trans* content was obtained from the ratio of the areas of the 8.33 and 8.40 τ peaks, correction being made for the $CH_3-\overset{|}{C}=$ protons in vinylidene units which appear coincidentally at 8.40 τ.

A convenient way to monitor the photoinduced changes in the polyisoprene films by using infrared spectroscopy was to measure the quantity $(A_{12.0}/A_{7.3})_t/(A_{12.0}/A_{7.3})_0 = R_p$, in the case of the perprotio polymers, and $(A_{14.7}/A_{7.3})_t/(A_{14.7}/A_{7.3})_0 = R_d$, in the case of the deuterated polymer, where the A are the base-line absorbances at the indicated wavelengths (in microns), and the subscripts t and zero designate the irradiated and unirradiated films, respectively.

RESULTS

Table I presents typical results obtained from the microstructural analysis of a number of ultraviolet-irradiated films of hevea, balata, and *cis*-

TABLE I

Microstructural Changes in Ultraviolet-Irradiated Polyisoprenes

		Double bonds						Relative intensity R_p of 12 μ band[b]	
Polymer	Irradiation time, hr.	1,4, %	Vinylidene, %	Vinyl, %	Conversion to cyclopropyl groups, %	Not accounted for, %	*cis*, %[a]	Obsd.[c]	Calcd.[d]
Hevea	4	84.4	4.4	0.8	4.4	6.0	91	0.74	0.82
	8	78.7	5.9	1.2	5.2	9.0	90	0.73	0.76
	20	63.2	10.5	2.9	15.7	7.7	88	0.44	0.60
	40	53.9	8.8	2.5	25.7	9.1	84	0.44	0.51
	50	47.2	12.0	3.3	31.2	6.3	80	0.31	0.44
Polyisoprene-3-*d*	4	75.8	7.2	2.0	7.4	7.6	89	0.65[e]	0.73[e]
Balata	24	63.5	12.1	3.0	15.3	6.1	28	0.57	0.74

[a] Based on residual 1,4 double bonds (col. 3).

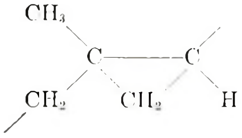
[b] See text for description of R_p.

[c] Based on infrared spectrum of original unirradiated film.

[d] Based on residual *cis* and *trans* 1,4 units, and assuming that the ratio of their extinction coefficients, ϵ_c/ϵ_t, at 12.0 μ (or at 14.7 μ, for the deuterated polyisoprene) is 1.6.[1]

[e] Relative intensity of the 14.7 μ band, R_d (see text).

polyisoprene-3-*d*. The data given for the 50 hr. irradiation of hevea correspond to the infrared and NMR spectra shown in Figures 1*C* and 2, respectively. In this particular case, of the original 100% *cis*-1,4 double bonds in hevea, 47.2% 1,4 units remain after irradiation (80% of which are in the *cis* configuration), 31.2% end up as *cis* or *trans* trisubstituted cyclopropyl structures (I), 12.0% as vinylidene double bonds, 3.3% as vinyl double bonds, and 6.3% are unaccounted for and presumably lost in various endlinked or crosslinked structures.



I

Although the spectra of balata are not shown here, it should be noted that this polymer yielded, on extensive ultraviolet irradiation, virtually the same infrared spectrum as that of irradiated hevea (Fig. 1*C*) and also the same NMR spectrum (Fig. 2), except that the relative intensities of the 8.33 and 8.40 τ peaks were reversed, indicating different *cis–trans* contents. It was not practicable to carry the photoisomerization of 1,4-polyisoprene to equilibrium, but it seems that the ultimate *cis/trans* ratio should be in the range 70/30 to 50/50, comparable to that observed in the photoisomerization of 1,4-polybutadiene.[5]

Values of R_p (or R_d) obtained for various irradiated films are shown in Table I along with the corresponding values calculated on the assumption that Beer's law applies to the absorption of the residual *cis*- and *trans*-1,4 double bonds at 12.0 (or 14.7) μ. The small discrepancies noted between the observed and calculated values of R_p (or R_d) are due, in part, to the fact that the 7.3 μ band is far from an ideal internal standard, and, in part, to the fact that the sol fraction (which is the source for the NMR spectrum and hence also the estimate of residual 1,4 unsaturation) of the irradiated polymer usually shows somewhat less decrease in unsaturation than the original film. Evidence for this is the observation that the infrared spectrum of a film cast from the NMR solution generally shows a somewhat higher R_p (or R_d) value than the original film, and therefore yields a better agreement with the calculated value. However, the relative intensity data for the original irradiated films (prior to dissolution for NMR purposes) are shown in Table I to provide an idea of the kind of results that are encountered when the photolysis is monitored by infrared spectroscopy.

The quantum yields at 2537 A. for the most important photochemical processes in polyisoprene were estimated on the basis of comparative irradiation runs on hevea and *cis*-polybutadiene by using the Pen-Ray lamp and noting the yields obtained for polybutadiene. Unfortunately, the latter were reported incorrectly in the previous paper:[5] instead of 0.09 and 0.07 for *cis–trans* isomerization and loss of 1,4 double bonds, respectively,

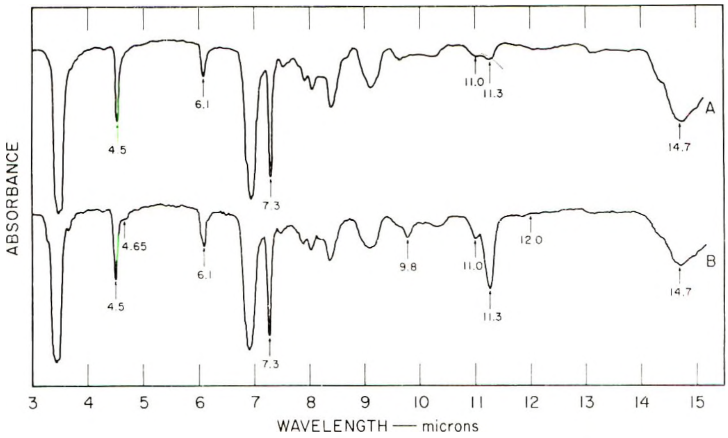
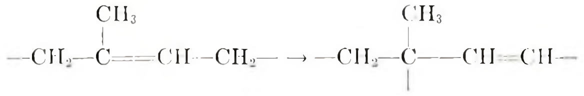


Fig. 3. Typical infrared spectrum of a *cis* 1,4-polyisoprene-3-*d* film (*A*) before and (*B*) after ultraviolet irradiation *in vacuo*.

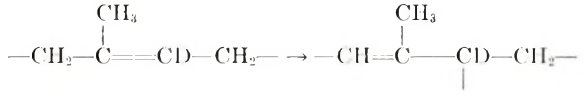
the yields should have been 0.036 and 0.061, respectively. In the present study, the following quantum yields were obtained for polyisoprene: loss of 1,4 double bonds, 0.083; *cis–trans* isomerization, 0.041; and formation of cyclopropyl groups, 0.018. Because the polymer films were inclined to become cloudy on ultraviolet irradiation, with attendant light-scattering problems, the quantum yields reported here have only qualitative, or at best, semiquantitative significance.

Additional information on the photolysis of polyisoprene is obtained from further consideration of Figure 1*C*, as well as from examination of Figure 3, showing analogous infrared changes in *cis*-polyisoprene-3-*d*. Thus, the absence of absorption at 10.3 μ (*trans* —CH=CH— units) in Figure 1*C* indicates that the double-bond migration [eq. (1)] has either not



$$\mathrm{—CH_2—}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{{=}CH—CH_2—} \rightarrow \mathrm{—CH_2—}\underset{|}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}\mathrm{—CH{=}CH—} \qquad (1)$$

occurred in polyisoprene or has occurred to a negligible extent. Likewise, the absence of a 12.0 μ band in Figure 3*B* shows that double-bond migration in the opposite direction [eq. (2)] does not occur to any perceptible extent either.



$$\mathrm{—CH_2—}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{{=}CD—CH_2—} \rightarrow \mathrm{—CH{=}}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{—}\underset{|}{\mathrm{CD}}\mathrm{—CH_2—} \qquad (2)$$

This lack of double-bond migration in the photochemistry of polyisoprene is not only in keeping with the situation in the photochemistry of polybutadiene,[5] but is also in line with the situation in the radiation chemistry of these diene polymers.[1,13]

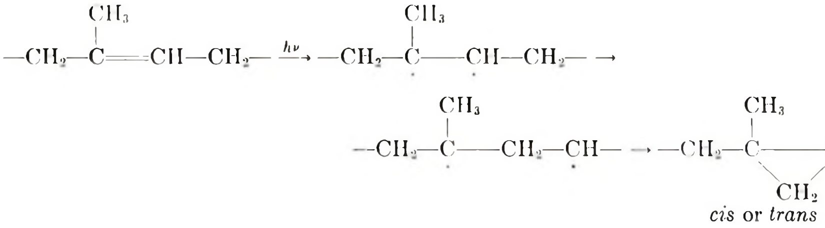
The diminution of the 14.7 μ band [—C(CH$_3$)=CD— units, whether *cis* or *trans*], the development of absorption bands at 11.3 and 11.0 μ, and the appearance of the characteristic 9.8 μ band, in the spectrum of the irradiated polyisoprene-3-*d*, are completely analogous to the infrared changes observed for hevea. It should be noted, in passing, that the 9.8 μ band was previously observed also in the infrared spectra of ultraviolet-irradiated polybutadiene, but its interpretation was not given then.[5] The small peak at 4.65 μ (C—D stretching vibration for a saturated carbon atom), which grows at the expense of the 4.5 μ band (C—D stretching vibration for an olefinic carbon atom), attests to the replacement of some of the original 1,4 double bonds in polyisoprene-3-*d* by saturated structures. Figure 3 is included in this paper because it provides an informative contrast to the corresponding spectra for the electron-irradiated polymer (Figure 3, ref. 1). It can be seen from these figures that the photochemistry of polyisoprene differs significantly from the radiation chemistry in at least several respects; thus, the former involves the production of considerable vinylidene, vinyl, and cyclopropyl groups, whereas the latter does not. It should be remarked that the infrared spectra of the electron-irradiated polyisoprenes[1] show a weak 11.3 μ band (very much weaker than that observed here for the ultraviolet-irradiated polymers) which is considered to be due to exomethylene units $\left(>C{=}CH_2\right)$ in cyclized structures rather than to the vinylidene double bonds [$-C(CH_3){=}CH_2$] assumed to be formed in the ultraviolet case.

DISCUSSION

The occurrence of photoinduced *cis–trans* isomerization in films of purified polyisoprene, by analogy to polybutadiene studied previously,[5] is assumed to result from the excitation of the $-C(CH_3){=}CH-$ double bonds to a triplet state ($\sim$74 kcal./mole) in which free rotation and hence geometrical interconversion can take place. Although this reaction proceeds in the absence of any deliberately added sensitizer, it is possible that there are adventitious impurities present in the polymer (e.g., trace amounts of carbonyl groups formed during slow aging of the raw polymer) which absorb at or below 3000 A. ($\geq$95 kcal./mole) and which can function as sensitizers by transferring excitation energy thus acquired to the polymer double bonds, in the manner depicted recently for the photosensitized isomerization of polybutadiene films.[14] Alternatively, it is quite likely that the smooth, structureless, absorption tail extending to around 3100 A. observed in the ultraviolet spectrum of the purified polyisoprene film, is associated in some way with the trisubstituted ethylenic unit in this polymer,[15–17] perhaps as a weak singlet–triplet transition of this double bond.[18] In that event, the excitation of the polyisoprene double bond could involve direct absorption of the incident ultraviolet photon without the intervention of an inter- or intramolecular energy transfer process. Such a point of view was invoked by Bateman[6,7] and by Hart and Matheson[8] to account for the effect of ultraviolet light on pure polyisoprene. Regardless of the exact physical process(es) involved in the photoexcitation of polyisoprene, it is noteworthy that our film, which was probably as pure as Bateman's (on the basis of the similarity of our ultraviolet spectrum to his[19]), showed no photochemistry above 3000 A. while he reported measurable effects at wavelengths as high as 3650 A.

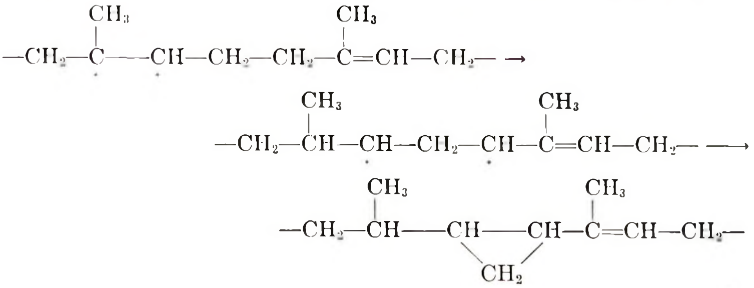
The same type of photochemical excitation of the polyisoprene double bonds which leads to their *cis–trans* isomerization is probably responsible for the formation of cyclopropyl groups in the polymer chain. Apparently the only other examples of the formation of such rings in an existing polymer chain involves the dechlorination of poly(vinyl chloride) by treatment with zinc dust[20] or the reaction of a diene polymer with a carbene;[21] by contrast, the present work reports the first example of the formation of cyclopropyl rings in a macromolecule by a direct photochemical reaction.

This process can be visualized [eq. (3)] as involving photoinduced formation of a biradical, followed by a 1,2-hydrogen migration and then ring closure.*



cis or *trans* (3)

This novel and indeed surprising photocyclization in an unsaturated macromolecule is without precedent, although there have been a few examples recently of such a biradical reaction in small olefin molecules. Thus, *trans*-1,3-diphenylpropene was found to undergo in solution an unsensitized photocyclization to *cis*- and *trans*-1,2-diphenylcyclopropanes, along with isomerization to the *cis* form of the starting olefin,[22] while butene-1 was found to undergo in the vapor phase a mercury-photosensitized cyclization to methylcyclopropane.[23] A 1,4-hydrogen migration was indicated for the butene-1 photocyclization,[23,24] but a 1,2-migration is equally likely, both processes being considered thermoneutral.[25] In the case of polyisoprene, although the 1,4-hydrogen migration with ring closure can be written as in eq. (4), this reaction probably does not occur. If it did, the resulting



(4)

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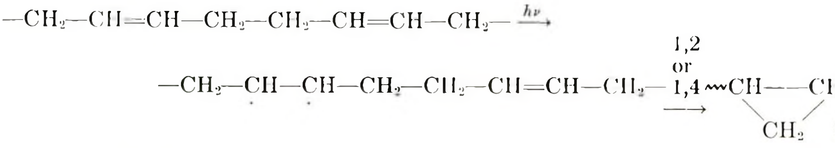
* Besides the 1,2-migration shown, there is also a 1,4 migration that can lead to essentially the same trisubstituted cyclopropyl group. However, although two additional possible hydrogen migrations (one 1,2- and one 1,4-) can be written, these are discounted because they lead to structures that are incompatible with the NMR results.

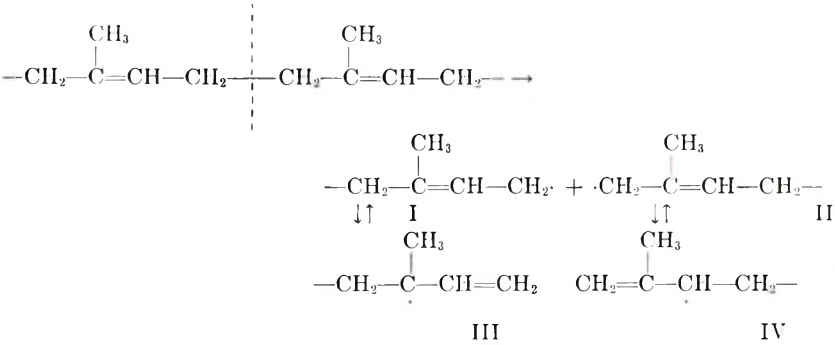
cyclopropyl groups would have virtually the same NMR peaks as the corresponding groups formed in extensively ultraviolet-irradiated polybutadiene [eq. (5)], but this was not the case. Instead, polybutadiene gave two



(5)

distinctive NMR peaks at 9.4 and 10.3 τ that were significantly displaced from the two high field peaks at 9.6 and 10.0 τ in irradiated polyisoprene, indicating that the *cis*- and *trans*-substituted cyclopropane rings formed in the two polymers were quite different. In order to throw more light on the structures of these cyclopropyl groups, we intend to carry out a detailed study of the photochemistry of dihydromyrcene, which is a diisoprene model compound for hevea.

The photochemical production of vinylidene and vinyl double bonds in polyisoprene presumably results from the rupture of the C—C bond connecting two successive isoprene units [eq. (6)]. That particular bond is



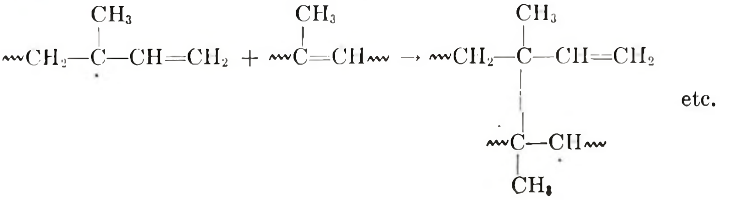
$$-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2 \,\vdots\, CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2- \rightarrow$$

$$\underset{\text{I}}{-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\cdot} + \underset{\text{II}}{\cdot CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-}$$

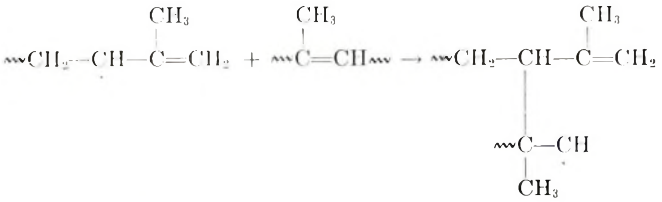
$$\updownarrow \qquad\qquad \updownarrow$$

$$\underset{\text{III}}{-CH_2-\overset{CH_3}{\overset{|}{\dot{C}}}-CH=CH_2} \qquad \underset{\text{IV}}{CH_2=\overset{CH_3}{\overset{|}{C}}-\dot{C}H-CH_2-} \qquad (6)$$

considered to be the "weak link" in the chain, with a strength of only ~43 kcal./mole,[26] due to the resonance energy contributed by the two allyl radicals formed on chain scission. The energy required for this rupture probably "spills over" from the energy-rich 1,4 double bonds in polyisoprene, just as was assumed for polybutadiene.[5] The fate of the radicals I–IV is to recombine (in any of four different ways) or to add to double bonds in the same or other macromolecular chain: the overall effect would be to produce some endlinks (or crosslinks) and some new vinylidene and vinyl double bonds in the irradiated polyisoprene, through reactions such as those shown in eqs. (7) and (8).



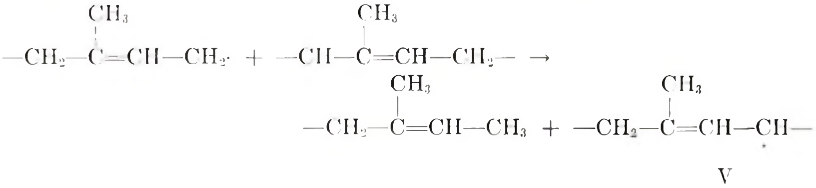
(7)



$$\sim CH_2-\underset{\cdot}{C}H-\overset{\overset{CH_3}{|}}{C}=CH_2 + \sim\overset{\overset{CH_3}{|}}{C}=CH\sim \longrightarrow \sim CH_2-\underset{\underset{\sim\underset{\underset{CH_3}{|}}{C}-\dot{C}H}{|}}{CH}-\overset{\overset{CH_3}{|}}{C}=CH_2 \quad \text{etc.} \qquad (8)$$

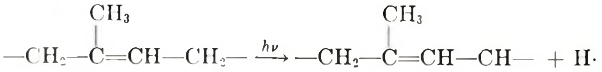
That the formation of vinylidene units is about three to five times that of the vinyl double bonds (Table I) is an indication that radical IV is that much more reactive than radical III, inasmuch as radicals I and II on further reaction merely retain the original double bonds. To the extent that radicals I–IV "polymerize" onto nearby double bonds to form endlinks, there is an added loss of double bonds over and above those which form the vinylidene, vinyl, or cyclopropyl structures, and these "lost" double bonds contribute to the number unaccounted for (Table I).

Besides recombination or addition to double bonds, another reaction that the radicals I–IV could undergo is hydrogen abstraction (or chain transfer) to produce shortened chains and new allyl radicals [eq. (9)].

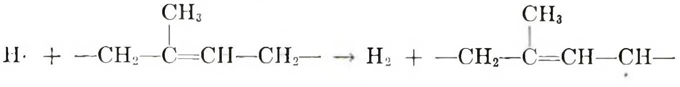


$$-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2\cdot + -CH-\overset{\overset{CH_3}{|}}{C}=CH-CH_2- \longrightarrow -CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_3 + \underset{\text{V}}{-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-\dot{C}H-} \qquad (9)$$

That this reaction does not occur to any important extent in this system is indicated by the absence of a characteristic 8.51 τ peak (associated with the terminal methyl protons in $-CH_2-C(CH_3)=CH-CH_3$, as in dihydromyrcene)[27] in the NMR spectrum of extensively irradiated polyisoprene and by the failure of polyisoprene-3-*d*, as noted earlier, to show any perceptible double-bond migration, which could result from the presence of the 3-*d* analog of radical V. This is not to say, however, that the radicals V are not formed at all in the photolysis of polyisoprene, but if they are formed they occur in an amount well below that required to produce definite infrared and NMR spectral changes, and hence they are unimportant relative to the other entities obviously formed in this system. In fact, hydrogen is evolved from hevea with a quantum yield $\leq 10^{-3}$ (in the ultraviolet range 2350–2850 A.),[6–8] whereas the yield obtained for *cis–trans* isomerization or loss of 1,4 double bonds is at least 40 to 80 times as large. Thus, if the main route for hydrogen production involves rupture of the α-methylenic C—H bonds and formation of allyl radicals, as Bateman suggested [eqs. (10) and (11)],[6,7]



$$-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2- \xrightarrow{h\nu} -CH_2-\overset{\overset{CH_3}{|}}{C}=CH-\dot{C}H- + H\cdot \qquad (10)$$



$$H\cdot + -CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2- \longrightarrow H_2 + -CH_2-\overset{\overset{CH_3}{|}}{C}=CH-\dot{C}H- \qquad (11)$$

the effects of double bond migration resulting from these allyl radicals would be below spectroscopic detection in our work.

The present study thus shows that both rupture of the C—C bonds between isoprene units and formation of biradical structures are considerably more important than rupture of α-methylenic C—H bonds in producing primary radical sites for initial oxidative attack. We hope in subsequent research to assess the relative importance of these various radical sites in the overall photooxidation of polyisoprene. Meanwhile, it is worth noting that the sum of the quantum yields for *cis–trans* isomerization, loss of 1,4 double bonds, and cyclopropyl formation ($\sim$0.14), which can be taken as a rough measure of the yield of reactive sites, is well below the initial quantum yield of 0.54 obtained in the photooxidation of hevea at 2537 A., where about 0.4% oxygen combined with the rubber and where the oxidation has probably entered the autocatalytic region.[8]

To sum up the findings on the photolysis of polyisoprene, we find that this polymer in common with polybutadiene[5] shows important loss of 1,4 unsaturation, *cis–trans* isomerization, and formation of cyclopropyl groups in the chain along with some vinyl double bonds, with polyisoprene showing in addition the formation of vinylidene units. Although isomerization and loss of double bonds are observed also in the radiolyses of these diene polymers, there is negligible formation of vinylidene and/or vinyl groups, and there is absolutely no formation of cyclopropyl rings, in the radiolysis. Unfortunately, we have no explanation for these particular differences between the photochemistry and radiation chemistry of the diene polymers.

Note added in proof: Further support for our proposed photocyclization of polyisoprene is seen in very recent work by Pinazzi and Levesque[28] on the preparation and characterization of cyclopropane derivatives of polyisoprenic compounds. They observed infrared absorption at 9.8 μ and NMR peaks at 8.70, 9.02, 9.72, 10.00, and 10.20 τ in model compounds containing structure I. Except for the 10.20 τ peak, which is apparently too weak to be detected in our Figure 2, these spectroscopic data are virtually the same as those reported in this paper and which we have attributed to cyclopropyl ring formation.

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Polyaryläther-Kondensationsprodukte des 4,4′-Bis(chloromethylphenyl)äthers mit manchen Diphenolen

MARIA TOKARZEWSKA, *Chemische Anstalt-Oświęcim, Poland*

Synopsis

Poly(aryl ethers) as products of the polycondensation of 4,4′-bis(chloromethylphenyl) ether with sodium salts of various phenols have been prepared in the Williamson reaction. The reaction was carried out at three different temperatures (78, 140, and 185°C.) in ethanol, xylene, and tetralin, respectively. The effect of the polycondensation and the nature and composition of initial components on the properties of the products has been studied. The molecular weights and the melting temperatures of the synthesized resins increased with increasing reaction temperature. The structure and molecular weight have a pronounced effect on the properties of the resins. Resins prepared from 4,4′-dihydroxydinaphthyl had the highest melting temperature and were practically insoluble, while the resins prepared from 2,2′-dihydroxydinaphthylmethane had the lowest melting temperature and were soluble in practically all organic solvents. On the basis of the experimental data a reaction scheme appropriate for the synthesis of poly(aryl ethers) from the phenolates as well as from the free phenols in the presence of NaOH has been proposed. Some thermal and mechanical properties of poly(aryl ethers) have been determined. Thermal treatment of the resins above their softening temperature resulted in an elevated softening point too. This is explained by the supplementary condensation of both chlorine or hydroxyl endgroups in the molten resins.

Einführung

Eine der grössten Ergebnisse der letzten Jahre auf den Gebiet der Makromolekularverbindungen ist die Entwicklung von temperaturbeständigen Polymeren, unter welchen die Gruppe der aromatischen Substanzen von Typus der Polyphenylene verschiedener Struktur eine der wichtigsten Stellen einnimmt.

Die bisherigen Untersuchungen haben gezeigt, dass die vorteilhaften Eigenschaften in dieser Gruppe gehören diejenigen Harze, die eine Struktur von aromatischen Äther besitzen. Zu solchen Polymeren gehören die heute schon in technischen Masstabe hergestellten Polyäther: PPO[1] d.h. poly(phenylen oxyd) und DPO[2,3] d.h. Poly(diphenylen oxyd). Diese wertvolle ätherische Bindung tritt immer öfter auch als Bindungselement von Benzolringen aromatischen Mischpolymerisaten wie z.B. Polyarylsulfone,[4] Polychinoxaline,[5] Polyarylsilane[6] u.A. auf.

Die Einführung der Ätherbindung in der Polymerkette wird durch die Anwendung von difunktionelle Äthern, meistens von Homologen des Diphenyläthers, oder durch Durchführung typischen Reaktionen die zur poly-ätherische Struktur führen, z.B. Einwirkung von Phenolate auf Chlorabkömlingenverbindungen, erreicht.

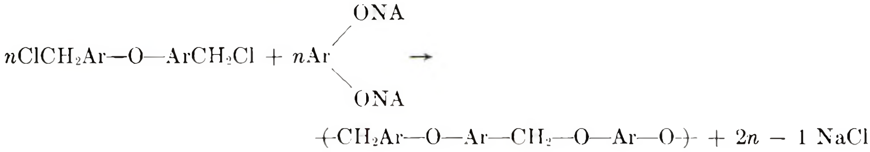
Den Polymeren des Diphenyläthers widmet die Literatur viel Aufmerksamkeit und es wurden grundlegende Arbeiten durchgeführt, welche durch verschiedene Synthesen den Einfluss von Strukturen und Art der Bindungen mit dem Grundmolekül des Diphenyläther auf die Eigenschaften des erhaltenen Polymeren untersuchen.[3,5]

Der Ziel dieser Arbeit war die Synthese und Untersuchung den Eigenschaften von Polyäthern deren Grundmolekül Bausteine enthält, die entweder von einzelnen aromatischen Ringen oder aus kondensierten mit Äthergruppen gebundenen aromatischen Ringen von Typ Ar—O—Ar und Ar—CH_2—O—Ar bestehen.

Experimentaller Teil

Die obengenannten Polymeren wurden durch Kondensation von 4,4′-Bis(chlormethylphenyl)äther mit Natriumsalze von Diphenolen, d.h. Hydrochinon, Rezorcin, Pyrokatechin, Phenolphtalein, 4,4′-Dihydroxydinaphtyl, 2,2′-Dihydroxydinaphtyl und 2,2′-Dihydroxydinaphtylmethan, in neutralen, wasserfreiem Medium erhalten.

Die Synthese wurde nach der klassischen Williamsonreaktion[7,8] durchgeführt. Es wurde der folgenden hypothetischen Verlauf der Polykondensationsreaktion angenommen:



$$n\mathrm{ClCH_2Ar{-}O{-}ArCH_2Cl} + n\mathrm{Ar}\begin{matrix} \diagup \mathrm{ONA} \\ \\ \diagdown \mathrm{ONA} \end{matrix} \rightarrow$$

$$\mathrm{\lbrace CH_2Ar{-}O{-}Ar{-}CH_2{-}O{-}Ar{-}O \rbrace} + 2n - 1\ \mathrm{NaCl}$$

Präliminare Untersuchungen über den Verlauf dieser Reaktionstyp in Äthanol wurden schon beschrieben.[9] Zu den Versuchen wurden 4,4′-Bis(chlormethylphenyl)äther, nach Tomito und Kimura[10] erhalten, und Diphenole, bezw. Phenolate, welche entweder Handelsprodukte waren oder in Laborskale selbst synthetisiert wurden, benützt.

Die Polykondensation wurde in zwei Varianten durchgeführt: (a) bei Anwendung von Phenolen unter gleichzeitiger Zugabe von Alkalilösungen bezw. festem Natriumoxyd, (b) mit Phenolaten bei Anwendung neutraler, nicht wässeriger Lösungsmittel.

In erstem Falle wurde die Polykondensation durch Erwärmung unter einem Rückflüssküler, in Stickstoffatmosphäre, in Äthylalkohol bezw. Xylen (in 300 g. Menge) als Reaktionsemdium äquimolaler Mengen Diphenol (0.1 Mol), Natriumoxyd (0.2 Mol), und 4,4′-Bis(chlormethylphenyl) äther (0.1 Mol) durchgeführt. Es wurde energisch gemischt.

In zweitem Falle wurden unter ähnlichen Bedingungen äquimolare Molmengen an Natriumsalzen einiger Diphenole, d.h., 4,4′-Dihyroxydinaphtyl, 2,2′-Dihydroxydinaphtyl, 2,2′-Dihydroxydinaphtylmethan, sowie 4,4′-Dihydroxydiphenyldimethylmethan (0.1 Mol) und 4,4′-Bis(chlor-

TABELLE I. Ergebnisse der Elementaranalyse und Molekulargewichte der Harze bei Anwendung von freien Phenolen in Alkalianwesenheit synthesiert

		Elementaranalyse								Molekulargewicht		
		Erhalten				Gerechnet					Gerechnet	
Phenol	Reaktions-medium	C, %	H, %	Cl, %	O, %	C, %	H, %	O, %	OH gruppen, %	Erhalten	OH End-gruppen	Cl End-gruppen
1,4-Dihydroxybenzol	Äthanol	77.61	5.24	1.66	15.49	78.94	5.26	15.46	0.71	—	1900	2100
	Xylol	78.24	5.02	1.12	15.62				0.55		2700	2600
1,3-Dihydroxybenzol	Äthanol	78.10	5.30	0.73	15.87	78.84	5.26	15.46	0.54		4100	2800
	Xylol	79.06	5.27	—	15.67				1.12			2500
2,1-Dihydroxybenzol	Äthanol	76.70	5.34	2.23	15.73	78.94	5.26	15.46	1.15		1300	1300
	Xylol	78.62	5.11	1.22	15.05				0.63		2400	2300
Phenolphtalein	Äthanol	77.13	4.70	2.05	16.12	79.68	4.70	15.62	0.96	1650	1600	1600
	Xylol	79.20	4.98	—	15.82				0.98			3200
4,4′-Dihydroxydimethylodiphenylomethan	Äthanol	81.14	5.98	1.40	11.48	82.46	6.16	11.37	0.65		2400	2500
	Xylol											
4,4′-Dihydroxydinaphtyl (1,1)	Äthanol	82.40	4.86	1.91	10.83	85.00	5.00	10.00	0.82		1700	1700
	Xylol											
2,2′-Dihydroxydinaphtyl (1,1)	Äthanol	82.78	4.90	1.90	10.42	85.00	5.00	10.00	0.79	1660	1700	1700
	Xylol											
2,2′-Dihydroxydinaphtylmethan (1,1)	Äthanol	83.24	5.40	1.23	10.13	85.00	5.26	9.71	0.73	2080	2200	2200
	Xylol											

TABELLE II

Ergebnisse der Elementaranalyse und Molekulargewichte der Harze, bei Anwendung von Diphenolnatriumsalze synthesiert

Phenol	Reaktions-medium	Elementaranalyse							OH gruppen, %	Molekulargewicht		
		Erhalten				Gerechnet					Gerechnet	
		C, %	H, %	Cl, %	O, %	C, %	H, %	O, %		Erhalten	OH End-gruppen	Cl End-gruppen
4,4-Dihydroxydimethyl diphenyl methan	Äthanol	79.91	5.96	2.65	11.48	—	—	—	1.40	1140	1200	1300
	Xylol	82.00	6.30	—	11.70	82.46	6.16	11.37	1.18	—	2700	—
	Tetralin	82.12	6.20	—	11.68	—	—	—	1.04	—	3000	—
4,4′-Dihydroxydinaphtyl (1,1)	Äthanol	82.50	4.90	2.55	10.15	—	—	—	0.99	—	1600	1400
	Xylol	84.78	5.02	—	10.20	85.00	5.00	10.00	1.25	—	2400	—
	Tetralin	83.67	4.85	0.98	10.50	—	—	—	0.47	—	3300	3400
2,2′-Dihydroxydinaphtyl (1,1)	Äthanol	82.00	5.00	2.68	10.32	—	—	—	1.1	1019	1500	1250
	Xylol	84.60	4.80	—	10.60	85.00	5.00	10.00	1.4	2230	2400	—
	Tetralin	84.53	4.40	—	10.07	—	—	—	1.1	2750	2800	—
2,2′-Dihydroxydinaphtylmethan (1,1)	Äthanol	82.70	5.40	1.77	10.13	—	—	—	0.85	1500	1600	1900
	Xylol	85.10	5.32	—	9.58	85.00	5.26	9.71	1.15	2600	2500	—
	Tetralin	84.54	5.21	—	10.25	—	—	—	1.02	3100	3400	—

TABELLE III
Schmelztemperatur und Löslichkeit der Polyaryläther von freien Phenolen und NaOH synthesiert

Phenol	Reactionsmedium	Schmelztemperatur, °C	Löslichkeit in Ac, B. D, X, Tr, Tt[a]
Hydrochinon	Äthanol	210	Unlöslich
	Xylol	240	Unlöslich
Rezorcin	Äthanol	200	Unlöslich
	Xylol	230	Unlöslich
Pyrokatechin	Äthanol	180	Unlöslich
	Xylol	215	Unlöslich
Phenolphtalein	Äthanol	160	Unlöslich in Al,
	Xylol	265	löslich in Ac, B, D, X, Tr, Tt
Dian	Äthanol	160	Unlöslich
4,4′-Dihydroxy-dinaphtyl (1,1)	Äthanol	280	Unlöslich
2,2′-Dihydroxy-dinaphtyl	Äthanol	210	Löslich
2,2′-Dihydroxy-dinaphtyl-methan (1,1)	Äthanol	120	Löslich

[a] Lösungsmittel: Ac = Aceton, B = Benzol, D = Dioxan, X = Xylol, Tr = Trichlorethan, Tt = Tetrachlorethan.

methylphenyl)äther (0.1 Mol) der Reihe nach in Äthylalkohol, Xylol, und Tetralin (300 g.) erwärmt. Die Reaktionzeit betrug in allen Versuche 24 Stunden.

Der Wecksel der Medien von Äthylalkohol bis Tetralin bezweckte eine Stufenweise Erhöhung der Reaktionstemperatur und die Untersuchung ihres Einflusses auf die Eigenschaften der erhaltenen Produkte- Dabei wurde es angenommen dass eine Steigerung der Temperatur in den untersuchten Systemen zu einem besseren Reaktionsumzatz und zur Erhöhung des Molekulargewichtes des Polykodensate führt.

Je nach der Löslichkeit der erhaltenen Harze in Reaktionsmedium, wurden die Endprodukte auf zweifache Weise abgesondert: unlösliche Produkte wurden von Dispersionsmittel abfiltriert und nacheinander mit Diäthyläther (um die nichtdurchreagierte Diphenyläther auszuwaschen), dann mit Äthylalkohol und schliesslich mit Wasser (um Phenolate und das entstehende Kochsalz zu entfernen) gewaschen. Das Waschen wurde bis zum Verschwinden der Chlorionen in Filtrat durchgeführt. Die in Reaktionmedium lösliche Polymere wurden durch Abdampfen des Lösungsmittel unter vermindertem Druck isoliert und wie zuvor angegeben gewaschen. Die, so gereinigten Harze trocknete mann danach bis konstanten Gewicht bei 50°C. unter vermindertem Druck.

Um die chemische Konstitution der Harze festzustellen wurde die elementare Zusammenzetzung der Polymere, das Molekulargewicht, der prozentuelle Gehalt am Chlor und Hydroxylgruppen bestimmt. Das Molekulargewicht der löslichen Polymere erklärte mann nach der kryoskopische Methode in Nitrobenzol, im Fall unlöslichen Produkte benutzte mann für die Molekularbestimmung die Anwesenheit der Chlor und Hydroxyl Endgruppen. In Tabellen I und II wurden die Ergebnisse der Elementaranalyse, der Prozentgehalt am Chlor und Hydroxylgruppen und die Molekulargewichte, der bei verschiedenen Reaktionstemperaturen erhaltenen Produkte zusammengestellt.

TABELLE IV
Schmelztemperatur und Löslichkeit der Polyaryläther aus Phenolaten synthesiert

Phenol	Reaktions- medium	Schmelz- temperatur, °C	Löslichkeit in Ac, B, D, X, Tr, Tt[a]
Dian	Äthanol	120	Löslich
	Xylol	223	Unlöslich
	Tetralin	280	Unlöslich
4,4'-Dihydroxy-dinaphtyl (1,1)	Äthanol	250	Unlöslich
	Xylol	295	Unlöslich
	Tetralin	320	Unlöslich
2,2'-Dihydroxy-dinaphtyl (1,1)	Äthanol	189	Löslich
	Xylol	318	Löslich
2,2'-Dihydroxy-dinaphtylmethan	Äthanol	103	Löslich
	Xylol	220	Löslich

[a] Lösungsmittel: Ac = Aceton, B = Benzol, D = Dioxan, X = Xylol, Tr = Trichlorethylen, Tt = Tetrachlorethylen.

TABELLE V
Thermische und Mechanische Eigenschaften der Harze

Ausgangs- phenol	Schmelz- temperatur, °C	Thermische wiederstadsfähigkeit nach Vicat °C	Reissfefestigkeit, kg/cm²	Schlagfestigkeit, kg-cm/cm²	Härte, kg/cm²
Hydrochinon	210	243	76.0	2.5	11.7
Resorzin	200	192	80.0	2.7	7.7
Pyrokatechin	180	190	79.0	2.5	11.2
Dian	223	230	133.5	3.2	23.4
Phenolphtalein	160	134		Spröde	
4,4'-Dihydroxy-dinaphtyl	228	288	50.7	2.2	25

Zwecks genauerer Charakteriesierung der untersuchten Polyaryläther wurden einige wichtige Eigenschaften der Harze bestimmt, d.h. die Schmelztemperatur und die Löslichkeit in einigen typischen Solvenzien. In Tabellen III und IV sind die erhaltenen Werte zusammengestellt.

In Tabelle V sind nach Vicat erhaltenen Prüffergebnisse der Harztemperaturbeständigkeit und die mechanische Eigenschaften der gepressten Prüflinge zusammengestellt.

Diskussion der Ergebnisse und Schlussfolgerung

Die nach der Williamsonsreaktion durchgeführte Polyaryläthersynthese liefert eine Reihe von Harzprodukte, die die Mokekularstrukturen der Ausgangskomponente zeigt.

Die hier dargestellten Untersuchungsergebnisse haben gezeigt, dass der Anwendung von freien Phenolen im alkalischem Medium analogisch die Anwendung von Diphenolnatriumsalze zum Erhalten von Polymerisation mit dem hypothetisch aufgestellten Reaktionsschema ubereinstimmt. Die mittels der Elementaranalyse bestimmte Zusammensetzung der erhaltenen Endprodukte fällt mit der auf dem theoretischen Wege berechneten überein. Die Molekulargewichte, die kryometrisch oder bei Endgruppenbestimmung erhalten wurden, entsprechen dem Polykondensationsgrad von $n = 3$–9.

Die untersuchten Harzpräparate stellen Pulverform von weisser bis brauner Farbe. Ihre Eigenschaften hängen von den Reaktionsbedingungen der Synthese ab. Die, bei tieferen Temperaturen durchgeführten Polykondensationsreaktionen (in Äthanolmedien) geben niedermolekulare Produkte. Die Erhöhung der Reaktionstemperatur auf 140 und 180°C ergibt Produkten mit viel höheren Molekulargewichten, etwa 2000–3500.

Die Molekularstruktur sowie das Molekulargewicht des Harzes üben einen starken Einfluss auf ihren Eigenschaften wie z.B. Fliesstemperatur und Löslichkeit aus. Die 4,4′-Dihydroxydinaphtylharze sind in den gewählten Lösungsmittel praktisch unlöslich. Die Löslichkeit der Polymerisate von 4,4′-Dihydroxydiphenylmethan Derivaten hängt von Mokekulargewicht des Harzes ab. Die niedermolekularen im Äthanol polykondersierte Produkte sind in aromatischen Kohlenwasserstoffverbindungen, Ketonen sowie ihren Chlorderivaten löslich, sind aber im Äthylalkohol unlöslich. Die höhermolekularen in Xylol oder Tetralin synthetisierten Produkte sind aber in der untersuchten Lösungsmittel auch unlöslich. Die Polymere, welche Derivate von 2,2′-Dihydroxydinaphtyls und 2,2′-Dihydroxydinaphtylmethan sind, sind in alle Untersuchungsgebrauchten Lösungsmittel, mit Ausnahme von Äthylalkohol, löslich, unabhangig vom Molekulargewicht.

Die Schmelztemperaturen steigen mit der Erhöhung von Polykondensationstemperatur und auch mit dem Molekulargewicht, wobei analogisch zu vorangehenden Untersuchungen, die Harze, die Derivate von 4,4′-Dihydroxydinaphtyls darstellen, sich mit mit höhsten Schmelztemperaturen auszeichnen. Dann folgen die Dianharze, während die Derivate von 2,2′-Dihydroxydinaphtylmethan sich bei den tiefsten Schmelztemperaturen charakteriesieren.

Die gepressten Prüflinge der Harzen zeichnen sich durch vorteilhafte Härte und eine thermische Widerstand fähigkeit nach Vicat, welche bis 300°C reicht, aus. Die beste Eigenschaften besitzen die Harze, die symetrisch aufgebaut sind.

Man beobachtet eine Steigerung der thermischen Wiederstandsfähigkeit der Harze nach ihrer Erwärmung bis über die Schmelztemperatur. Nach der thermischen Behandlung wiesen die Harze eine Erniedriegung der Chlorgehaltes bezw. sein völliges Fehlen, sowie eine Erniedriegung des Gehaltes von Hydroxylgruppen auf.

Diese Erscheinung kann man durch die Steigerung des Molekulargewichtes des ursprünglichen Polymeres durch eine zusätzliche Kondensation der Chlor- und Hydroxylgruppen in geschmolzenen Zustande erklären.

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Synthesis of Polyamideamines from 5-Oxazolones

YOSHIO IWAKURA, FUJIO TODA, YOSHINORI TORII,
and KATSUAKI MURATA, *Department of Synthetic Chemistry,
Faculty of Engineering, The University of Tokyo, Tokyo, Japan*

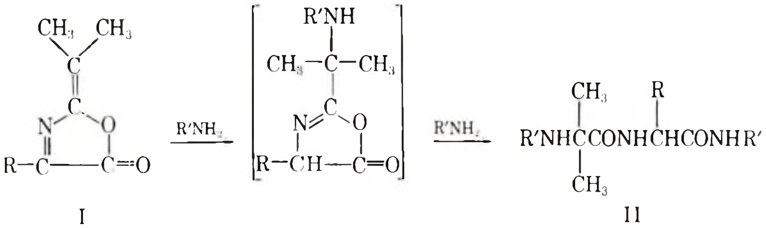
Synopsis

Polyamideamines with a sequence of two amide and one amine linkages in a main chain were synthesized from the polyaddition of 2-isopropylidene-4-alkyl-3-oxazolin-5-ones and primary diamines. The polyaddition reaction proceeded through 1,4-conjugate addition of an amine group to 3-oxazolin-5-one and subsequent ring opening of the intermediate addition product with another amine. Although aliphatic diamines gave oily polymers, xylylenediamines afforded amorphous solid polymers. The reduced viscosities and polymer melt temperature of the polymers were 0.05-0.12 and 90-130°C., respectively.

INTRODUCTION

In recent years, much investigation has been carried out on the polyaddition reaction of cyclic compounds, such as bissuccinimides,[1,2] bisglutarimides,[3] bislactones,[4] and bisoxazolones,[5] with diamines in order to obtain alternating polyamides.

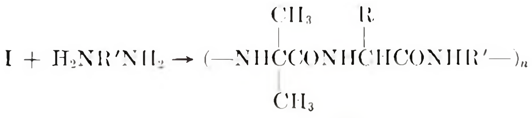
In a previous paper,[6] 2-isopropylidene-4-alkyl-3-oxazolin-5-ones (I, pseudoxazolones)[7,8] were found to react with two moles of aliphatic and aromatic primary amines to give compound II in good yields. This indicates the possibility of polymer formation[9] from compound I and primary diamines, and the resulting polymer has a sequence of two amide and one amine linkages in the polymer chain.



I II

a: R = Me, b: *i*-Pr, c: *i*-Bu

The present work describes the synthesis of linear polyamideamines (III) from compound I and aliphatic and aromatic diamines and some properties of the polymer obtained.



$$\mathrm{I} + \mathrm{H_2NR'NH_2} \rightarrow (\text{—}\mathrm{NH}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CONH}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{HCONHR'}\text{—})_n$$

III

EXPERIMENTAL

Materials

2-Isopropylidene-4-methyl-3-oxazolin-5-one (Ia), 2-isopropylidene-4-isopropyl-3-oxazolin-5-one (Ib), and 2-isopropylidene-4-isobutyl-3-oxazolin-5-one (Ic) were prepared by the same method described earlier[6,7] and distilled twice in a nitrogen stream and stored in ampules equipped with rubber stoppers in order to avoid the formation of polymeric peroxides with oxygen in the air.[10]

Xylylenediamines were distilled twice before use.[11] Physical constants were as follows: mixed xylylenediamine (XD, b.p. 111.5–113°C./4 mm. (*para* isomer, ca. 30%; *meta* isomer, ca. 70%); *p*-xylylenediamine (PXD, b.p. 106°C./3 mm.); *m*-xylylenediamine (MXD, b.p. 134°C./7 mm.).

Bisaminomethylcyclohexane (BAC) prepared by the catalytic hydrogenation of xylylenediamine with Ru catalyst, was distilled under reduced pressure. BAC thus obtained was a mixture of *cis*-1,3 isomer (87%) and 1:1 *cis*-, *trans*-1,4 isomers (13%), and its boiling point was 93–94°C./4 mm.[12]

Benzidine (Bzd) (commercial extra pure grade) was used without further purification, m.p. 128°C. 4,4-Diaminodiphenylmethane (DPM) was recrystallized from ethanol–water, m.p. 91.5–92°C.

All solvents were purified by the usual methods.[13–15]

Polyaddition Procedure

The polyaddition reaction was carried out in a sealed system. An ampule (30 ml.) was flushed thoroughly with nitrogen and sealed with a rubber stopper. A calculated amount of I (0.01 mole) was introduced through the rubber stopper by use of a syringe, and the weight of I was measured. After I was solidified by cooling with a Dry Ice–acetone bath, a solution of an equimolar amount of diamine (0.01 mole) in a solvent (10 ml.) was added to it. The ampule was sealed and placed in a hot water bath and shaken vigorously. The mixture was allowed to stand in a constant temperature bath for 14–45 hr. The polyaddition reaction was stopped by cooling the ampule. The reaction mixture was then poured into water with stirring. The polymer precipitated was filtered and washed thoroughly with water and further purified by reprecipitation in methanol to water, and dried in a vacuum oven for two days. Nitrogen analyses of the polymers are as follows.

ANAL. IIIa from Ia and XD. Calcd. for $C_{15}H_{21}N_3O_2$: N, 15.26%. Found: N, 14.88%. IIIb from Ib and XD. Calcd. for $C_{17}H_{25}N_3O_2$: N, 13.85%. Found: N, 13.99%. IIIc from Ic and XD. Calcd. for $C_{18}H_{27}N_3O_2$: N, 13.24%. Found: N, 12.28%.

Model Reaction

A mixture of Ib (0.05 mole) and benzylamine (0.10 mole) in toluene (10 ml.) was allowed to stand overnight at room temperature and the resulting crystals were then collected by filtration and recrystallized from benzene; m.p. 89–92°C.; 91% yield.

Anal. Calcd. for $C_{23}H_{31}N_3O_2$ (1:2 adduct): C, 72.41%; H, 8.19%; N, 11.02%. Found: C, 72.71%; H, 7.94%; N, 11.02%.

Infrared studies showed the following bands: ν_{NH} 3340, 3230 cm.$^{-1}$; $\nu_{C=O}$ (amide I) 1680 (shoulder), 1650 (shoulder), 1635 cm.$^{-1}$ in nujol.

A mixture of Ia (10.7 g.) and aniline (7.55 g.) in toluene (10 ml.) was kept at 60°C. for 24 hr. in a sealed tube. The resulting crystals were recrystallized from toluene, m.p. 142°C., 43% yield.

Anal. Calcd. for $C_{19}H_{23}N_3O_2$ (1:2 adduct): C, 70.13%; H, 7.12%; N, 12.91%. Found: C, 70.12%; H, 6.77%; N, 12.83%.

Infrared studies showed bands at ν_{NH} 3380, 3300 cm.$^{-1}$; $\nu_{C=O}$ (amide I) 1690, 1650, 1605 cm.$^{-1}$ in nujol. NMR results were: (s) δ = 1.60 (6H, *gem*-dimethyl), (d) δ = 1.44 ppm (3H, $>$CH—CH$_3$, J = 6.6 cps) in pyridine.

Instruments

Differential thermal analyses and thermogravimetric analyses were carried out in the air with a Thermoflex differential thermal and thermogravimetric analyzer of the high-temperature type, Rigaku Denki Co., at a heating rate of 10°C./min.

The x-ray diffraction patterns of the powdered polymer were taken with a Rigaku Denki Co., Model D2-F diffractometer, at room temperature by use of Ni-filtered CuKα radiation.

RESULTS AND DISCUSSION

Although the reaction of aliphatic primary diamines, such as ethylene-trimethylene-, tetramethylene- and hexamethylenediamine with I occurred rapidly, oily polymers were obtained. On the contrary, diamines which have a ring structure in the molecule, such as xylylenediamine, bisaminomethylcyclohexane, and aromatic diamines gave solid polymers. The results of polymerization are summarized in Table I. The reaction time (24 hr.) was confirmed to be enough to complete the polyaddition reaction of I with aliphatic amines, but a prolonged period was needed for the completion of the reaction of I with aromatic amines.[6] Therefore, periods of 24 hr. for aliphatic diamines and 45 hr. for aromatic diamines were adopted here.

As the reaction of I with diamines evolved so much heat, a solvent was necessary for dispersing heat of the initial reaction. Acetone, benzene, dimethylformamide (DMF), chloroform, dioxane, dimethyl sulfoxide

TABLE I
Polyaddition of 3-Oxazolin-5-ones with Diamines[a]

Run no.	3-Oxazolin-5-one	Diamine	Solvent	Polyaddition		Yield, %	PMT, °C.[b]	Viscosity η_{sp}/c[c]
				Temp., °C.	Time, hr.			
1	Ia	XD	Dioxane	80	24	68	88–114	0.075
2	Ib	"	"	80	24	62	91–125	0.080
3	Ic	"	"	80	24	57	95–120	0.093
4	Ib	"	Acetone	80	24	63	86–104	0.066
5	Ib	"	Benzene	80	24	58	84–102	0.071
6	Ib	"	DMSO	80	24	70	89–116	0.050
7	Ib	"	NMP	80	24	56	93–121	0.066
8	Ib	"	Sulfolane	80	24	59	92–121	0.084
9	Ic	"	Dioxane	60	24	86	96–116	0.082
10	Ic	"	DMF	60	24	75	92–118	0.073
11	Ic	"	NMP	60	24	81	87–116	0.076
12	Ic	"	Sulfolane	60	24	81	90–123	0.124
13	Ib	PXD	Dioxane	80	24	84	90–108	0.075
14	Ib	MXD	"	80	24	76	85–107	0.079
15	Ib	BAC	"	60	24	86	90–113	0.076
16	Ib	Bzd	DMF	60	45	42	92–118	0.060
17	Ib	DPM	Dioxane	60	45	55	88–111	0.073

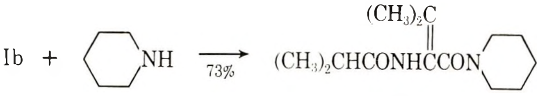
[a] All polyaddition reactions were carried out at the concentration of each 0.01 mole of monomer in 10 ml. solvent.

[b] Determined by heating a sample sealed in a capillary tube.

[c] Measured at a concentration of 0.5 g./100 ml. in DMF at 30°C.

(DMSO), *N*-methylpyrrolidone (NMP), and tetramethylene sulfone (TMS) were examined as solvents. Although dioxane and TMS seemed to give satisfactory results, marked differences were not found among those solvents.

In the reaction of I with amines, aliphatic secondary amines, such as piperidine, gave somewhat peculiar results. If the reaction was carried out under the same reaction condition with primary amines, 1:1 adduct, such as compound (IV), was obtained as a major product through the direct ring opening reaction of Ib attacked at the carbonyl group, prior to the conjugate addition reaction of Ib. The resulted compound (IV) could not add further amine. Consequently, the fact that the polymer was obtained from I and primary amines indicates that the first step of the reaction is addition of amine to the exo double bond of I. However, in the reaction of primary amines, a direct ring-opening reaction as a first step could not be denied completely. The ring-opening reaction as a first step engenders chain termination because there is no further chain growth of the product. The cause of the low molecular weight of the polymers obtained would be attributable primarily to such a chain termination reaction.



IV

(IV)

The reduced viscosities of the polymers obtained at various temperatures in DMF are shown in Table II. No marked effect of temperature on the viscosity of the polymer obtained, was noted. However, a systematic change with temperature in viscosities of the polymers was observed. It may be that some side reactions described above were suppressed at lower temperatures.

The infrared spectra of the polyamideamines showed peaks characteristic of amide and amine at 3320 (NH), 1650 (amide I), and 1520 cm.$^{-1}$ (amide II) and resembled to those of the corresponding model compound (Fig. 1).

The polyamideamines were soluble in DMF, DMSO, NMP, methanol, dioxane, acetone, tetrahydrofuran, chloroform, and *m*-cresol, but were

TABLE II
Effect of Temperature on Polyaddition[a]

Temperature, °C.	η_{sp}/c[b]
150	0.045
80	0.067
60	0.082
30	0.115
0	0.106
−20	0.098

[a] Reaction time, 24 hr.

[b] Measured at a concentration of 0.5 g./100 ml. in DMF at 30°C.

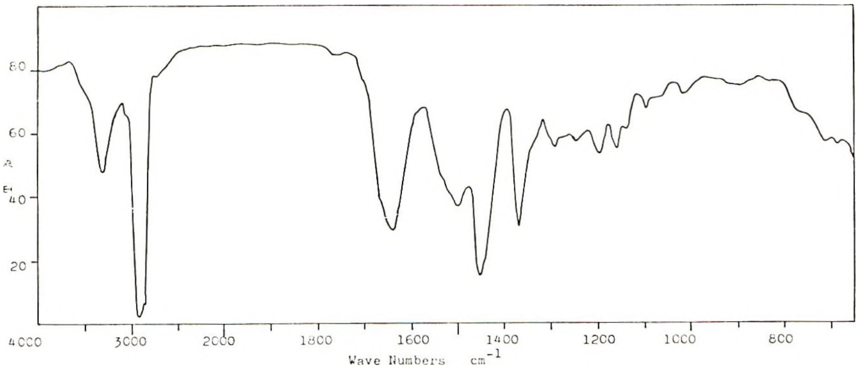


Fig. 1. Infrared spectrum of polyamideamine (No. 12).

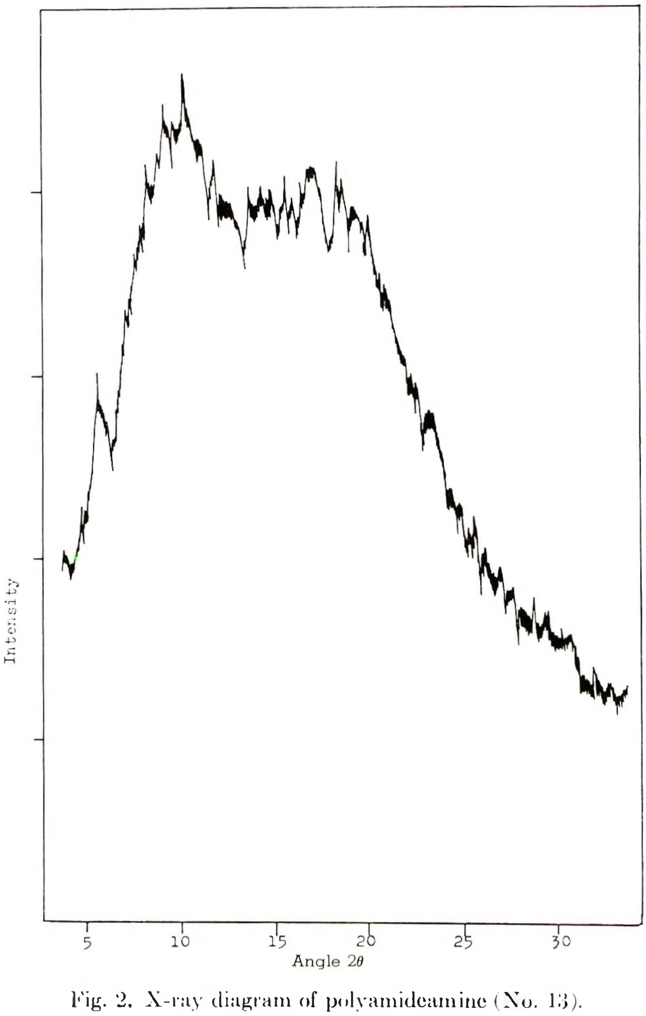


Fig. 2. X-ray diagram of polyamideamine (No. 13).

insoluble in nonpolar solvents, such as benzene, toluene or *n*-hexane. The polymers were insoluble in water, but soluble in 1*N* aqueous hydrochloric acid. The polymers were reprecipitated by neutralizing the acidic solution with 10% aqueous sodium hydroxide; this probably indicates the presence of amine linkages in the polymers.[16]

The x-ray diffraction pattern of the powdered polymer (No. 13) is shown in Figure 2. Some peaks are observed in the pattern, but the crystallinity of the polymer appears not to be high. This would be attributable in part to the steric hindrance of bulky side chains to the formation of intermolecular hydrogen bond formation and partially to the random distribution of head-to-tail and head-to-head structures in a polymer chain. The polymer melt temperatures (PMT) of polymers obtained were in the range of 90–130°C. and large differences in PMT were not seen because of the amorphous character of the both polymers.

In the thermogravimetric analysis of the polymer (No. 13) a weight loss began near at 200°C., and about 78% of the original weight of the polymer was lost in air until the temperature was raised up to 400°C. In the differential thermal analysis, a marked endotherm was found at about 140-150°C. which was interpreted as a melting region of the polymer.

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Polymerization of Isocyanates. IV. Polymerization by Aqueous Initiator Systems

YOSHIO IWAKURA, KEIKICHI UNO, and NORIO KOBAYASHI,
The Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo, Japan

Synopsis

Isocyanates were polymerized by aqueous solutions of numerous alkali salts at a low temperature. Polymer could be obtained even in the presence of a large excess of water to monomer in the polymerization system. The initiating species was proposed to be hydroxide ion.

INTRODUCTION

Isocyanates were found by Shashoua and co-workers[1] to undergo anionic polymerization. Since then other methods of isocyanate polymerization such as cationic,[2] thermal,[3] radiation-induced,[3,4] and electrochemically initiated polymerization[5] have been reported. However, anionic polymerization is the most common method for isocyanate polymerization. The literature contains several references to anionic initiator systems.[1,2,6]

On the other hand, isocyanates are well known to react with water easily to give carbon dioxide and substituted ureas, and the reaction is very fast in homogeneous systems.[7] Moreover, active hydrogen compounds such as water have been known to stop an anionic polymerization. So it has been emphasized that in the polymerization of isocyanates all the apparatus and solvents must be dried before use.[8]

We have found that isocyanates can be polymerized to a linear polymer even in the presence of water. In the present paper the active species and the role of water in the polymerization of isocyanates by aqueous initiator systems are described.

RESULTS AND DISCUSSION

Phenyl isocyanate was polymerized to a linear polymer at −50°C. by aqueous solutions of a variety of inorganic compounds. They are summarized in Table I. All the polymers obtained gave infrared spectra identical with those of the polymers prepared by sodium cyanide in a nonaqueous system.

TABLE I
Polymerization of Phenyl Isocyanate by Aqueous Solutions of Inorganic Compounds[a]

No.	Initiator: Name	Initiator: Formula	Initiator: Amt., mole × 10^{-4}	Yield, %
1	Sodium hydroxide	$NaOH$	1.5	68
2	Potassium hydroxide	KOH	2.1	76
3	Sodium iodide	NaI	0.6	0
4	Sodium azide	NaN_3	0.5	58
5	Sodium nitrite	$NaNO_2$	1.9	38
6	Sodium cyanide	$NaCN$	1.0	74
7	Potassium cyanate	$KCNO$	1.4	30
8	Potassium thiocyanate	$KSCN$	2.1	0
9	Sodium phosphate, monobasic	NaH_2PO_4	1.3	0
10	Sodium phosphate, dibasic	Na_2HPO_4	1.0	18
11	Sodium phosphate, tribasic	Na_3PO_4	1.3	72
12	Sodium bicarbonate	$NaHCO_3$	1.1	7
13	Sodium carbonate	Na_2CO_3	1.5	64
14	Sodium bisulfite	$NaHSO_3$	1.2	0
15	Sodium sulfite	Na_2SO_3	1.5	64
16	Sodium phosphite	Na_2HPO_3	1.2	11
17	Sodium arsenate, monobasic	NaH_2AsO_4	1.2	0
18	Sodium aluminate	$NaAlO_2$	1.4	76
19	Sodium tungstate	Na_2WO_4	1.0	3
20	Sodium tellurite	Na_2TeO_3	1.7	74

[a] Polymerization condition: Phenyl isocyanate, 0.042 mole; DMF, 50 ml.; Water, 0.056 mole; Polymerization, by method A and at −50°C. for 10 min.

Aqueous sodium hydroxide as an initiator gave polymer in good yield. Since only three kinds of ions, such as Na^+, H_3O^+, and OH^- are present in this system, it would be reasonable to consider that the initiating species for the isocyanate polymerization is hydroxide ion.

When the aqueous salt solution was acidic or neutral, the polymerization did not take place.

As the alkaline character of the aqueous salt solution increased, the yield of the polymer increased. This trend is shown in Figure 1, where the polymer yields are plotted against the pK_a value of inorganic acid components. Since the amount of hydroxide ion in aqueous salt solution increases along with pK_a value of the acid component, and since hydroxide ion can initiate the polymerization of isocyanates as described above, it would be most probable to conclude that hydroxide ion is an initiating species also in the polymerization by aqueous solution of salts.

When initiator systems were extended to the aqueous solution of alkali metal salts of carboxylic acids, a more marked effect of pK_a values on polymer yields was observed. They are listed in Table II and III. From the results, the following information is obtained. First, the catalytic activity of alkali salt of dicarboxylic acid depends on the pK_2 value and not on the

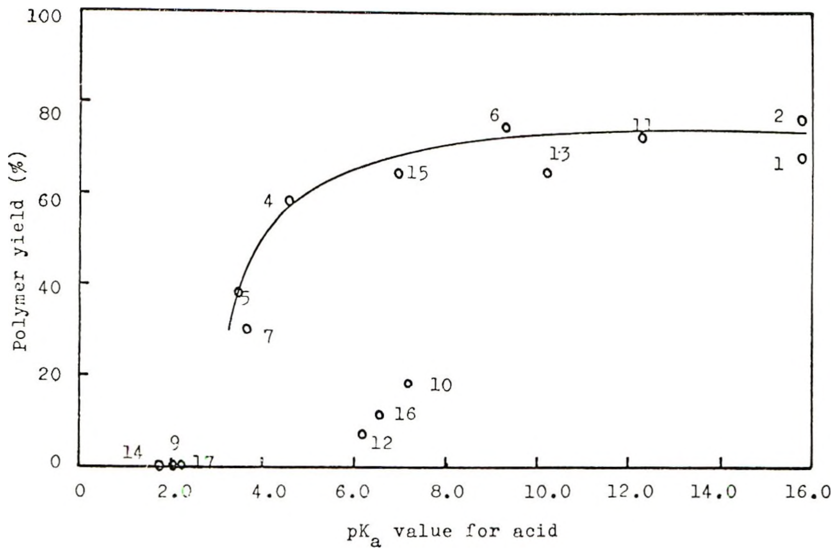

Fig. 1. Effect of pK_a value for acid on polymer yield. The numbers represent the experiment numbers in Table I.

pK_1 value. Thus the contribution of carboxylate anion to the initiation seems to be improbable and the active species here may also be regarded as hydroxide ion. Also there is a difference of 0.3 between the pK_a values of the alkali salts of monocarboxylic acids and those of dicarboxylic acids at which polymer can be obtained in a moderate yield. The catalytic activity of salts was studied; in the monocarboxylic acid series the pK_a value was above 4.2, and in the dicarboxylic acid series the pK_2 value was above 4.5. On the basis of statistical corrections, a comparison between the proton-donating ability of the monobasic sodium salt of a dicarboxylic acid and that

TABLE II

Polymerization of Phenyl Isocyanate by Sodium Salts of Monocarboxylic Acids[a]

No.	Initiator (MX) Formula	Initiator (MX) Amt., mole × 10^{-4}	pK_a values for acid (HX)[b]	Yield, %
21	$C_6H_5SO_2Na$	1.0	1.29	0
22	Cl_2CHCO_2Na	1.2	1.29	0
23	$ClCH_2CO_2Na$	1.1	2.86	0
24	HCO_2Na	2.6	3.77	2
25	$HOCH_2CO_2Na$	1.4	3.83	Trace
26	$C_6H_5CO_2Na$	1.1	4.20	30
27	$C_6H_5CH{=}CHCO_2Na$	1.3	4.43	56
28	CH_3CO_2Na	1.3	4.76	68
29	$CH_3CH_2CO_2Na$	1.2	4.88	50

[a] Polymerization conditions same as in Table I.

[b] In water at 25°C.

TABLE III
Polymerization of Phenyl Isocyanate by Alkali Metal Salts of Dicarboxylic Acids[a]

	Initiator (MXM or MXH)		pK_i values for acid (HXH)[b]		
No.	Formula	Amt., mole $\times 10^{-4}$	pK_1	pK_2	Yield, %
31	KO_2CCO_2K	1.3	1.23	4.19	0
32	$NaO_2CCH(OH)CH(OH)CO_2H$	1.3	2.96	4.24	0
33	$NaO_2CCH(OH)CH(OH)CO_2Na$	1.2	2.96	4.24	0
34	$NaO_2CCH{=}CHCO_2Na$ (*trans*)	1.0	3.0	4.5	66
35	$NaO_2CCH_2CO_2Na$	1.2	2.85	5.85	72
36	$NaO_2CCH{=}CHCO_2Na$ (*cis*)	1.0	1.91	6.6	82

[a] Polymerization conditions same as in Table I.
[b] In water at 25°C.

of monocarboxylic acid requires that the ionization constant of the former be multiplied by 2, resulting in a lowering of the pK_2 value by 0.3.[9] This is consistent with the above results.

The effects of water concentration and initiator concentration were investigated with the use of *p*-methoxyphenyl isocyanate as a model, because the polymer is soluble in several organic solvents. Figure 2 depicts the influence of the ratio of water to monomer on the yield and molecular weight of the *N*-*p*-methoxyphenyl 1-nylon obtained with NaCN as an initiator. In this case the polymerization was carried out by a method involving dropping of monomer into the reaction mixture (method B),

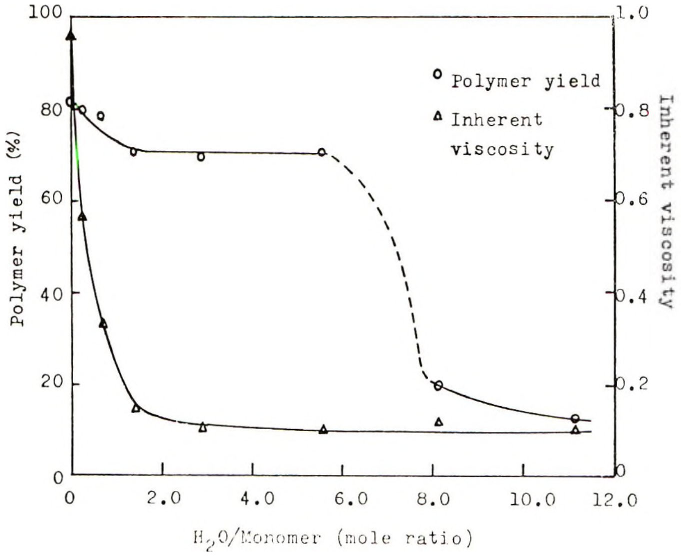

Fig. 2. Effects of water:monomer ratio on (○) polymer yield and (Δ) inherent viscosity. Polymerization conditions: *p*-methoxyphenyl isocyanate, 2.0×10^{-2} mole; DMF, 50 ml.; NaCN, 1.0×10^{-4} mole; polymerization by method B at −50°C. for 10 min.

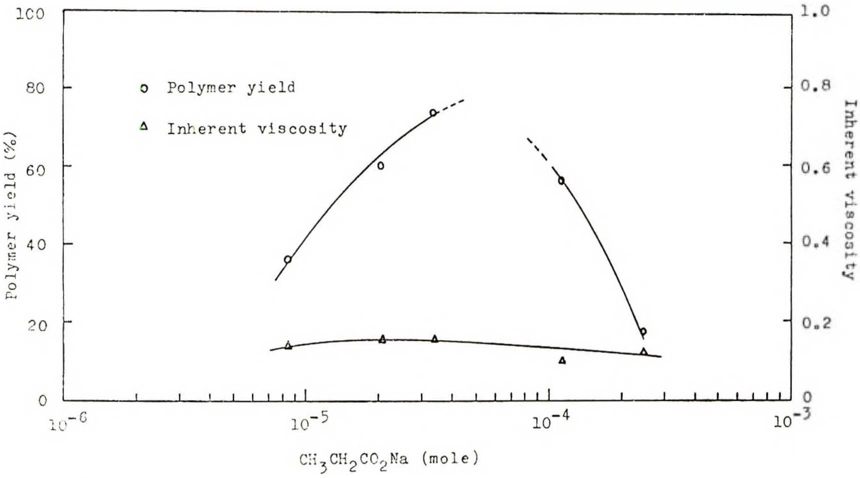

Fig. 3. Effects of initiator concentration on (○) polymer yield and (△) inherent viscosity. Polymerization conditions: *p*-methoxyphenyl isocyanate, 2.0 × 10^{-2} mole; DMF, 50 ml.; water, 0.056 mole; polymerization by method A at −50°C. for 10 min.

since the method involving dropping in of initiator (method A), which is in general for isocyanate polymerization, was not suitable to determine the effect of water because of the high polymerization rate of isocyanate. The molecular weight of the polymer decreases markedly with an increase in water ratio. On the other hand, polymer yield is less affected by water. It is important to note that polymer with inherent viscosity of about 0.1 was obtained even in the presence of water over eleven times the (molar) quantity of monomer. This evidence would be ascribed to the following factors. Since initiation is faster than propagation, and propagation in turn is faster than termination, the rate-determining step of the polymerization would be the diffusion of the monomer. In addition, the monomer concentration is relatively high just after its addition into the polymerization system.

Figure 3 shows the influence of the initiator concentration on the yield and molecular weight of the polymer, an aqueous solution of $CH_3CH_2CO_2Na$ being used as the initiator system. In this case polymerization was carried out by method A. It is seen that there is an optimum concentration range of initiator for the highest yield. On the other hand, the molecular weight of the polymers is very low over the entire range of initiator concentration, presumably because of a high concentration of water around the propagating species in method A.

EXPERIMENTAL

Materials

Commercial phenyl isocyanate was distilled, b.p. 59°C./19 mm. *p*-Methoxyphenyl isocyanate was synthesized from *p*-methoxybenzoic hydrazide, and then distilled, b.p. 115°C./25 mm.

Commercial grade dimethylformamide (DMF) was first distilled with about 10% added benzene to remove water. Then the solvent was purified by distillation from calcium hydride. It was redistilled before use, b.p. 59°C./24 mm.

All the inorganic materials were obtained commercially.

Preparation of Polymers

Polymerization of isocyanate was carried out in DMF at −50°C. by using aqueous solutions of numerous alkali metal salts. The procedure was much more simple than that given by Shashoua.[1] Two polymerization methods were employed; one was an initiator-dropping method (method A) and the other a monomer-dropping method (method B). The following sections describe typical polymerization procedures.

Polymerization of Phenyl Isocyanate with Aqueous Sodium Hydroxide (Method A). A 200-ml., three-necked round-bottomed flask was equipped with a stirrer and a thermometer. In the flask were placed 50 ml. of DMF and 5 g. of phenyl isocyanate and the contents cooled to −50°C. A solution of 0.0060 g. of sodium hydroxide in 1.0 ml. of water was added dropwise through an injector with vigorous stirring. The mixture became highly viscous immediately. After 10 min., 100 ml. of methanol was added to quench the reaction. The precipitated polymer was filtered, washed with methanol, dried under vacuum, extracted with boiling acetone for 3 hr. in a Soxhlet apparatus, and dried again. The yield was 68%.

Polymerization of *p*-Methoxyphenyl Isocyanate by Aqueous Sodium Cyanide (Method B). In a 200-ml., three-necked, round-bottomed flask were placed 50 ml. of DMF and a solution of 0.0049 g. of sodium cyanide in 1.0 ml. of water. The contents were cooled to −50°C. To the reaction system was added 3 g. of *p*-methoxyphenyl isocyanate through a dropping funnel with vigorous stirring. The reaction mixture became highly viscous immediately. After 10 min., 100 ml. of methanol was added. The precipitated polymer was filtered, washed with methanol, dried under vacuum, reprecipitated from chloroform solution into methanol. The yield was 69%.

Characterization of the Polymers

The infrared spectra were obtained by a double-beam Hitachi EPI-S2 infrared spectrophotometer. The inherent viscosity was measured at 30°C. in an Ostwald viscometer.

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Preparation of Highly Branched Graft Copolymers by the Ceric Ion Method

YOSHIO IWAKURA, YOHJI IMAI,* and KOHJI YAGI,
Department of Synthetic Chemistry, Faculty of Engineering,
University of Tokyo, Tokyo, Japan

Synopsis

Grafting of methyl methacrylate onto poly(6-methacryloyl-D-galactose) was very rapid, and the increase in weight reached about 1500% after 2-3 min. The maximum number of branches of the graft copolymers obtained was about 50. In the closest position two adjacent grafted branches were separated from each other by about 45-50 units of 6-methacryloyl-D-galactose on the average. Susceptibility of the various polymers containing sugar residues to grafting was compared, and the importance of the hemiacetal group in the grafting was revealed. Solubility of the backbone polymer in water was also important for rapid grafting by the ceric ion method.

Our previous results with grafting onto cellulose,[1] poly(vinyl alcohol),[2] and proteins[3] by the ceric ion method have demonstrated that hemiacetal or 1,2-glycol units in the backbone polymers play an important role in the grafting and that the number of branches per backbone polymer is 2 at the most. The fact that the graft copolymers have only a small number of branches is fairly common in the case of graft copolymers prepared by a free-radical mechanism. The maximum number of branches reported so far is 15 among the comparatively well-characterized graft copolymers[4] prepared by a free-radical mechanism.

The present paper is concerned with preparation of graft copolymers having a large number of branches in high density. The backbone polymers used were rather special; they contain sugar moieties in the pendant side chains, and the preparation of those polymers will be reported in a separate paper. It was our idea that a water-soluble polymer containing hemiacetal or 1,2-glycol groups would be most susceptible to grafting by the ceric ion method. In fact, grafting of methyl methacrylate onto poly(6-methacryloyl-D-galactose) yielded graft copolymer having up to 50 branches.

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* Present address: Institute for Medical and Dental Engineering, Tokyo Medical and Dental University, Surugadai, Kanda, Chiyoda-ku, Tokyo, Japan.

EXPERIMENTAL

Materials

The backbone polymers used were poly(6-methacryloyl-D-galactose), poly(1-*O*-methacryloyl-D-galactose), poly(6-methacryloyl-D-glucose), poly-(1-*O*-methacryloyl-D-glucose), and poly(*N*-methacryloyl-D-glucosamine). The method of their preparation will be reported in a subsequent paper. Methyl methacrylate monomer was purified by the usual method and stored in the dark at −20°C. Reagent grade ceric ammonium nitrate from G. F. Smith Co. was used without further purification.

Preparation of Graft Copolymer

An aqueous solution of the backbone polymer and methyl methacrylate were placed in a three-necked flask equipped with a condenser and a gas inlet tube. Nitrogen was bubbled through the solution for 30 min. at 30°C., and then grafting was started by adding ceric ammonium nitrate solution in 1*N* nitric acid. Polymerization was terminated by pouring the resultant mixture into methanol containing hydroquinone. The precipitate was filtered and dried *in vacuo*.

Conventional extractive treatment of the polymerization products in a Soxhlet apparatus with acetone gave no homopolymer of methyl methacrylate (MMA). Only a trace of homopolymer of MMA was obtained by filtration and repeated washings with hot acetone on Hyflo Super-Cel (Johns-Manville Sales Co.) filter bed. The amount of the homopolymer was practically negligible under the conditions studied here. The percentage weight increase was calculated from [(total weight of graft copolymer—weight of original backbone polymer)/weight of original backbone polymer] × 100.

Separation of Grafted Branches

Poly(6-methacryloyl-D-galactose)–methyl methacrylate graft copolymer was suspended in acetone and aqueous solution of paraperiodic acid added. After the mixture was allowed to stand at room temperature for 24 hr., it was filtered on Hyflo Super-Cel filter bed and washed with acetone many times. The filtrate and washings were combined and evaporated almost to dryness under reduced pressure. The materials obtained were dissolved in acetone and the grafted poly(methyl methacrylate) was reprecipitated with methanol.

Molecular Weight Determinations

The number-average molecular weight of the grafted poly(methyl methacrylate) separated by paraperiodic acid treatment was calculated from the intrinsic viscosity in benzene at 30°C. by using the equation, $[\eta] = 8.69 \times 10^{-5}\bar{M}_n^{0.76}$.[5]

The degree of polymerization of poly(6-methacryloyl-D-galactose) was determined on the basis of the number-average molecular weight of its parent, poly(1,2,3,4-diisopropylidene-6-methacryloyl-D-galactose), which in turn was determined by a high-speed membrane osmometer of Mechrolab. Inc. The degree of polymerization of material used for grafting was 1400, 1900, 2200, and 2700.

RESULTS AND DISCUSSION

Grafting of Methyl Methacrylate onto Poly(6-methacryloyl-D-galactose)

Grafting of methyl methacrylate (MMA) onto poly(6-methacryloyl-D-galactose) (6-PMGa) was very rapid; the reaction mixture became gradually turbid, and then the polymer precipitated. Both poly(methyl methacrylate) (PMMA) and 6-PMGa were soluble in dimethylformamide, but the graft copolymers obtained were insoluble in DMF and only swelled. In order to make the 6-PMGa component soluble in ordinary organic solvents, the graft copolymers were acetylated with acetic anhydride in

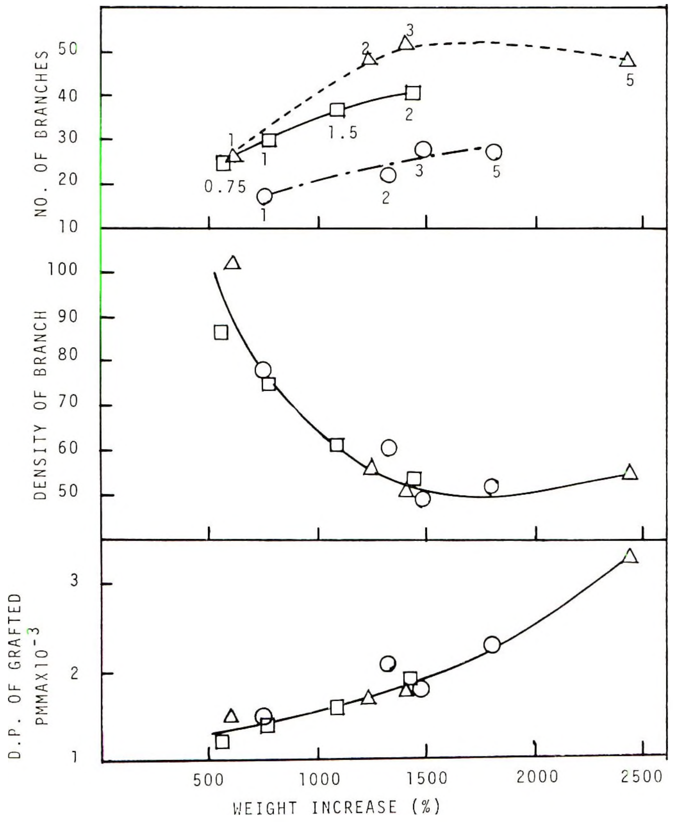

Fig. 1. Effect of degree of polymerization of 6-PMGa on grafting of MMA onto poly(6-methacryloyl-D-galactose) (6-PMGa): (○) DP = 1400; (□) DP = 2200; (△) DP = 2700. Grafting conditions: 6-PMGa, 25 mg.; MMA, 5 ml.; Ce^{+4}, 0.67 × 10^{-3} mole/l.; HNO_3, 0.01 mole/l.; total volume, 30 ml.

pyridine, but the acetylated graft copolymers obtained also only swelled with acetone, benzene, and chloroform.

In order to separate the grafted PMMA branches from 6-PMGa, the graft copolymers were treated with paraperiodic acid in acetone at room temperature for 24 hr. More than 90% of the grafted PMMA were separated, but not all the grafted PMMA could be separated completely by this treatment. Acid hydrolysis with hydrochloric acid or sulfuric acid or alkaline hydrolysis were all unsatisfactory.

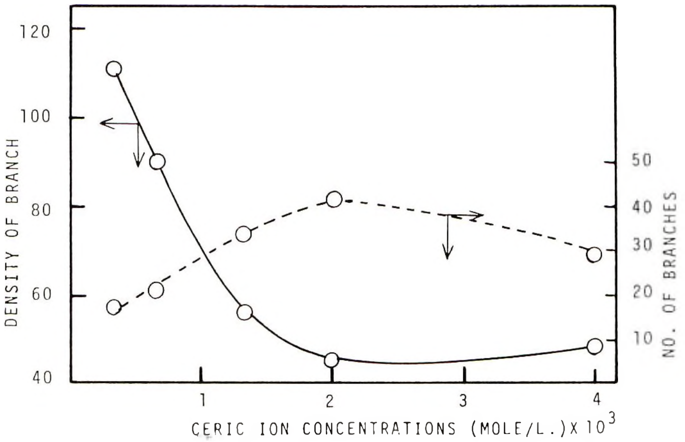

Fig. 2. Effect of initial ceric ion concentration on (——) branching and (- - -) number of branches. Grafting conditions: DP of 6-PMGa used, 1900; grafting time, 1 min.

The results of grafting are summarized in Figure 1. This figure shows the effect of grafting time and degree of polymerization of 6-PMGa. The degree of polymerization of PMMA branches, number of branches, and branching density are plotted against percentage weight increase. Figures shown in the plots of the number of branches are grafting time in minutes.

The branching density is defined as follows:

$$\text{Branching density} = \frac{\text{degree of polymerization of backbone polymer}}{\text{number of branches}}$$
$$= \text{number of monomer units of backbone polymer per branch}$$

Even if some graft copolymers have the same branching density, the number of branches depends on the degree of polymerization of the backbone polymers. Therefore, it is difficult to estimate uniformly various kinds of graft copolymers by the number of branches, but uniform estimation of various graft copolymers is possible by comparing the branching density. Among the graft copolymers hitherto prepared by a free-radical mechanism, cellulose acetate–styrene graft copolymers prepared by the radiation method by Stannett et al.[6] have had a minimum value of about 70–100, as roughly calculated by us on the basis of the data presented in

TABLE I
Grafting of MMA onto Crosslinked 6-PMGa[a]

Time, min.	% Weight increase of crosslinked 6-PMGa sample of varying ethylene dimethacrylate contents[b]			
	0	0.1 wt.-%	1 wt.-%	10 wt.-%
2	1300	156	—	—
5	2000	304	64	24

[a] Grafting conditions, see Fig. 1.

[b] Samples which contain 0, 0.1, 1, 10 wt.-% of ethylene dimethacrylate have regenerated hemiacetal group contents of 90, 89, 74, and 84%, respectively.

the literature.[6] This means that the branches are attached to a backbone polymer at intervals of 70–100 monomer units, on the average.

The plots of degree of polymerization of grafted PMMA and branching density are on a single curve, even though the degree of polymerization of 6-PMGa ranged from 1400 to 2700. This means that the probability of participation of sugar residues in the grafting is the same, regardless of the degree of polymerization of 6-PMGa. The number of branches reached to a maximum after about 2–3 min. and the maximum number of branches obtained was about 50.

Figure 2 shows the effect of ceric ion concentration on the density of branch or number of branches. The molar ratio of ceric ion to 6-methacryloyl-D-galactose units ranged from 1:10 to 1:0.83. This figure shows that in the closest position two adjacent branches were separated by 45–50 monomer units, on the average. This value of the branching density of 45–50 was thought to be a limit for the system studied, and is at the same time the lowest value hitherto obtained for graft copolymers prepared by a free-radical mechanism.

Thus the graft copolymers which have a large number of branches in high density were prepared. A typical example is one having a degree of polymerization of backbone (6-PMGa) of 1900, a degree of polymerization of grafted PMMA of 1000, and 42 branches.

Table I shows the results of grafting of MMA onto crosslinked 6-PMGa and the effect of solubility or swelling in water on grafting. The crosslinked 6-PMGa was prepared by copolymerization of 1,2,3,4-diisopropylidene-6-methacryloyl-D-galactose with ethylene dimethacrylate. The crosslinked polymers were pulverized and subjected to deacetonation in formic acid.

Susceptibility of the backbone polymer to grafting decreased markedly with increasing degree of crosslinking. The insolubility of the backbone polymer in water reduced its susceptibility to grafting markedly.

Grafting of MMA onto Polymers Containing *N*-Methacryloyl-D-glucosamine Units

N-Methacryloyl-D-glucosamine (N-MAG) was homopolymerized and copolymerized with acrylonitrile, MMA, and *N*-vinylpyrrolidone in DMF.

TABLE II
Grafting of MMA onto the Polymers Containing *N*-Methacryloyl-D-glucosamine (*N*-MAG) Unit[a]

Backbone polymer	Grafting time, min.	Weight increase, %
Poly(*N*-MAG)	3	1070
N-MAG–N-vinyl pyrrolidone (20 : 80)[b]	3	920
N-MAG–acrylonitrile (16 : 84)[b]	10	15
N-MAG–MMA (1 : 99)[b]	10	0
6-PMGa	3	1400

[a] Grafting conditions, see Fig. 1.
[b] Copolymer composition in molar ratio.

Table II shows the results of grafting of MMA onto the polymers described above. Attempts to separate the grafted PMMA branches were unsuccessful.

Poly(*N*-methacryloyl-D-glucosamine) and the copolymer with *N*-vinylpyrrolidone were water-soluble, but the other copolymers were insoluble in water. Therefore, Table II demonstrates an important role of solubility in water of a backbone polymer in rapid grafting by the ceric ion method.

In addition, grafting onto such different water-insoluble copolymers as 6-methacryloyl-D-galactose–MMA (12:88) or 6-methacryloyl-D-glucose–MMA (30:70) brought only 10–20% weight increase after 10 min.

These facts are consistent with the results of grafting onto crosslinked 6-PMGa as described in the preceding section.

Grafting of MMA onto the Various Polymers Containing Sugar Residues

Table III shows the results of grafting onto a water-soluble polymers of 6-methacryloyl-D-galactose or -glucose, 1-methacryloyl-D-galactose or -glucose, and *N*-methacryloyl-D-glucosamine.

TABLE III
Grafting of MMA onto Polymers Containing Sugar Residues[a]

Backbone polymer	Grafting time, min.	Weight increase, %
Poly(6-methacryloyl-D-galactose)	2	1300
Poly(1-methacryloyl-D-galactose)	5	110
Poly(6-methacryloyl-D-glucose)	2	1070
Poly(1-methacryloyl-D-glucose)	6	57
Poly(*N*-methacryloyl-D-glucosamine)	3	1070

[a] Grafting conditions, see Fig. 1.

A marked difference between 6- and 1-methacrylates of glucose or galactose was observed. 1-Methacrylates have no hemiacetal group, but the three remaining polymers contain hemiacetal groups. Therefore, these results indicated that the hemiacetal group is important in rapid grafting by the ceric ion method. The importance of the hemiacetal group has been pointed out previously in the grafting onto cellulose.[1]

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Cationic Polymerization of Cyclic Dienes. V. Polymerization of the Methylcyclopentadiene*

SHINZO KOHJIYA, YUKIO IMANISHI, and SEIZO OKAMURA,
Department of Polymer Chemistry, Kyoto University, Kyoto, Japan

Synopsis

Methylcyclopentadiene (MCPD) has been polymerized with cationic catalysts in toluene solution at −78°C. to a white powdery polymer, whose intrinsic viscosity in benzene solution at 30°C. ranged from 0.1 to 0.5. The comparison of the rate of homopolymerization of MCPD with that of cyclopentadiene (CPD) and the copolymerization of MCPD and CPD indicated that MCPD is much more reactive than CPD. It was suggested that the high stability of cycloalkenyl cation is responsible for the high reactivity of cyclic dienes. Infrared and NMR spectroscopy on polymethylcyclopentadiene showed that almost all of the monomer units in polymethylcyclopentadiene produced under the present conditions have a trisubstituted double bond. The mechanism of the initiation reaction in the polymerization of cyclic dienes is also discussed.

INTRODUCTION

Although cationic polymerizations of cyclic dienes have long been known,[2] few investigations of the polymerization mechanism have been carried out. Recently, we reported kinetic studies of the low-temperature cationic polymerizations of cyclopentadiene[1,3] (CPD) and cyclohexadiene[4] with the use of Friedel-Crafts metal halides as a catalyst. It was found that cyclic dienes interact with metal halides strongly and as a consequence a very rapid initiation reaction and a catalyst consumption by monomer took place. The high reactivity of cyclic dienes has been recognized also in copolymerization studies with isobutene[5] and α-methylstyrene.[6]

It is interesting to note that cyclic dienes, in particular CPD, are highly reactive in cationic polymerization though they have no strongly electron-donating group like other reactive monomers in cationic polymerization. Moreover, CPD undergoes a propagation reaction in more than one way, that is, 1,2- and 1,4-propagations. The problem concerning the mode of propagation can be solved in principle by analyzing the polymer structure, but with CPD it has not been settled definitely.

Here, in an attempt to study about the reactivity of alkyl substituted cyclic dienes, the polymerization of methylcyclopentadiene (MCPD) was investigated. As far as we are aware, only a preliminary investigation on the polymerization of MCPD has been reported.[7] In the present investi-

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* For Part IV see Kohjiya et al.[1]

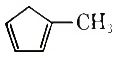
gation we directed our attention primarily to the effect of the methyl substituent on the reactivity of monomer and on the structure of the polymer obtained. Some discussion of the mechanism of the initiation reaction is also given.

EXPERIMENTAL

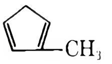
Materials

MCPD was obtained by the pyrolysis of the dimer, which was purified by vacuum distillation. The MCPD was collected and stored at −78°C. and was distilled from calcium hydride just before use (b.p. 70–71°C.). As will be shown later, the MCPD thus obtained was a mixture of two isomers. The composition of MCPD was analyzed by gas chromatography according to Csicsery[8] on a dimethyl sulfolane column at 36°C.

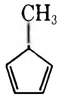
Three isomers are known for MCPD:[8] the 1-methyl-, 2-methyl-, and 5-methylcyclopentadienes.



1-Methylcyclopentadiene



2-Methylcyclopentadiene



5-Methylcyclopentadiene

The gas chromatogram of methylcyclopentadiene obtained by pyrolysis of the dimer revealed that the MCPD used for the present investigation was a mixture consisting of 52% 2-MCPD, 45% 1-MCPD, and 3% CPD. The content of CPD varied slightly, depending on the conditions of pyrolysis, but the ratio of 1-MCPD and 2-MCPD kept always unchanged.

The isomerization of monomer during the polymerization may not be important, because the polymerization rate is quite large, as is seen in Figures 1–3, whereas the isomerization rate at low temperatures has been reported to be slow.[9]

The purification of CPD has been reported by the present authors.[1]

Titanium tetrachloride ($TiCl_4$), stannic chloride ($SnCl_4$), and boron trifluoride etherate ($BF_3 \cdot OEt_2$) were used as catalysts and were distilled directly into glass ampules (in the case of $SnCl_4$, from phosphorus pentoxide). Commercial trichloroacetic acid (TCA) (guaranteed reagent) was used as a cocatalyst without further purification. The mole ratio of the acid to metal halides was always unity.

Toluene[1] and sometimes methylene chloride[10] were used as solvents. They were purified as reported previously. The water content of the solvent was 3–5 mmole/l. as determined by the Karl Fischer method.

Procedures

The polymerizations were carried out at −78°C. The polymerization apparatus and the procedures have been reported previously.[1] The intrinsic viscosity of benzene solution of polymethylcyclopentadiene (PMCPD) was measured at 30°C. Infrared spectra of the polymer were measured on the carbon disulfide solutions or KBr disks. Nuclear magnetic resonance (NMR) spectra of the polymer were measured as carbon tetrachloride solutions at 60 Mc./sec. against tetramethylsilane as an internal standard.

RESULTS

Homopolymerization of Methylcyclopentadiene

Time–conversion curves for the polymerization of MCPD with $TiCl_4$–TCA are shown in Figure 1. The polymerization was very rapid at first, but soon it stopped at a certain conversion which depended on the initial catalyst concentration. It is therefore evident that the polymerization is of typical nonstationary-state type started with a fast initiation reaction accompanied with some termination reaction. Further addition of $TiCl_4$ to the dormant system reinitiated the rapid polymerization, which stopped again at a higher conversion. The same phenomenon was observed in the polymerization of CPD with the same catalyst.[3]

As is seen in Figure 1, 6 mmole/l. of $TiCl_4$ was needed to reach 30% conversion of MCPD, while in the case of CPD only 1 mmole/l. was needed to get the same conversion under comparable conditions.[3] These findings may be explained by either a lower reactivity of MCPD than CPD or the more violent catalyst consumption with MCPD than with CPD.

The time–conversion curves for the polymerization of MCPD with $SnCl_4$–TCA are shown in Figure 2. Here again, a rapid initial polymerization and a saturation phenomenon of the conversion curve were observed. Hence, the polymerization of MCPD catalyzed by $SnCl_4$–TCA is also of a typical nonstationary-state polymerization started with a fast initiation reaction accompanied with some termination reaction. This is in contrast to the polymerization of CPD catalyzed by $SnCl_4$–TCA,[1] where the time–

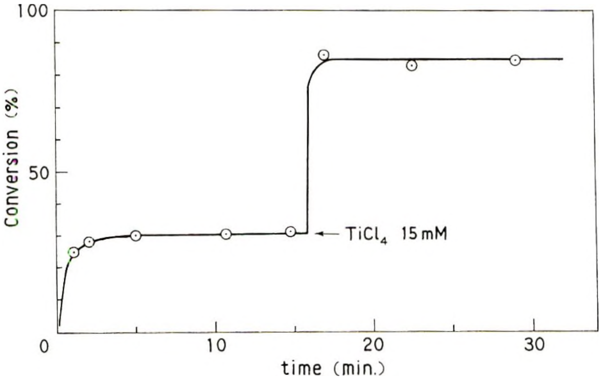


Fig. 1. Polymerization of MCPD with $TiCl_4$–TCA at −78°C. $[M]_0$ = 1.2 mole/l. $[C]_0$ = 6.0 mmole/l.; Solvent, toluene. Additional $TiCl_4$ added as indicated in the figure.

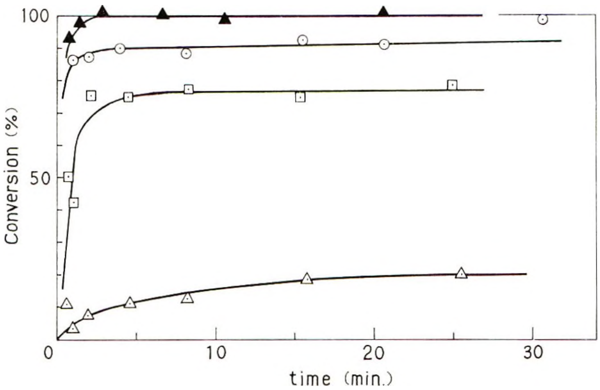


Fig. 2. Polymerization of MCPD with $SnCl_4$–TCA at −78°C.: (△) $[C]_0 = 0.53$ mmole/l.; (□) $[C]_0 = 1.1$ mmole/l.; (○) $[C]_0 = 2.4$ mmole/l.; (▲) $[C]_0 = 6.0$ mmole/l. $[M]_0 = 1.2$ mole/l.; solvent, toluene.

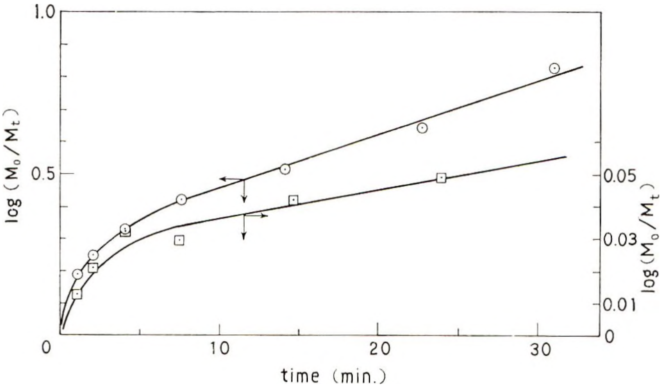


Fig. 3. Polymerization of MCPD with $BF_3.OEt_2$ at −78°C. (first-order plot): [□] $[C]_0 = 2.0$ mmole/l.; (○) $[C]_0 = 5.0$ mmole/l. $[M]_0 = 1.2$ mole/l.; solvent, toluene.

conversion curve did not level off but reached 100% conversion. As compared with the CPD–$SnCl_4$–TCA system,[1] a much smaller amount of catalyst was enough to bring the polymerization of MCPD to higher conversions under comparable conditions. Therefore, it seems that MCPD is more reactive than CPD.

In the polymerization of MCPD with $BF_3 \cdot OEt_2$, the initial polymerization was rapid but the polymerization rate decreased towards the end. However, the polymerization proceeded without stopping before 100% conversion. The plots of log $([M]_0/[M]_t)$ against t, where $[M]_0$ and $[M]_t$ represent the initial monomer concentration and the residual monomer concentration at time t, respectively, are shown in Figure 3. Here, the curves can be divided into two parts. One of them is the first curved section which represents a nonstationary-state polymerization, and the other is the latter linear section which represents a stationary-state polymerization. The same situation was met in the polymerization of CPD

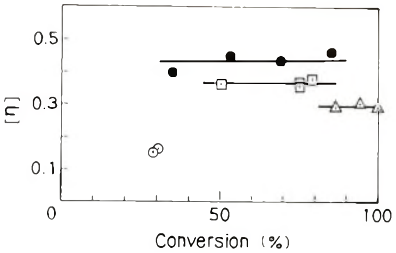


Fig. 4. Intrinsic viscosity at 30°C. of benzene solution of PMCPD obtained by cationic catalysts: (○) $TiCl_4$–TCA, 6.0 mmole/l.; (△) $SnCl_4$–TCA, 2.4 mmole/l.; (□) $SnCl_4$–TCA, 6.0 mmole/l.; (●) $BF_3 \cdot OEt_2$, 5.0 mmole/l. $[M]_0 = 1.2$ mole/l.; polymerization solvent, toluene.

catalyzed by $SnCl_4$–TCA.[1] With $BF_3 \cdot OEt_2$, a larger amount of catalyst was required in CPD polymerization[1] than in MCPD polymerization to attain the same conversion under the comparable conditions. Therefore, MCPD appeared to be more reactive than CPD.

Figure 4 shows intrinsic viscosities of PMCPD. Since the catalyst concentration was not always constant in these polymerizations, this cannot be discussed on a quantitative level. However, it is evident that the intrinsic viscosity of the polymer is not affected by the conversion, but that it was affected by the nature of catalyst and decreased in the order $BF_3 \cdot OEt_2$ > $SnCl_4$–TCA > $TiCl_4$–TCA. This is in complete agreement with the order found with polycyclopentadiene (PCPD).[1,3] It can be said that the more acidic, the catalyst, the lower the molecular weight of PMCPD.

Copolymerization of Methylcyclopentadiene and Cyclopentadiene

Investigation of the homopolymerization of MCPD demonstrated that MCPD was more reactive than CPD. However, polymerizations catalyzed by $TiCl_4$–TCA seemed to be an exception, where more catalyst was needed than in the polymerization of CPD to get the same conversion.

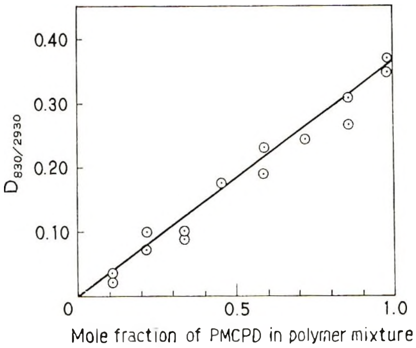


Fig. 5. Calibration curve for the determination of copolymer composition of MCPD and CPD.

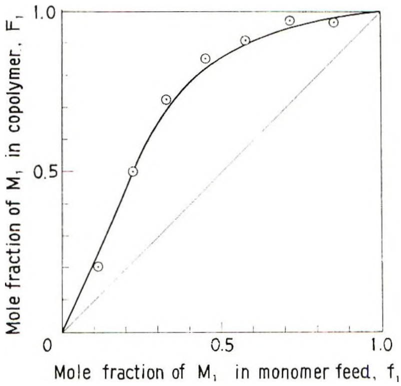


Fig. 6. Copolymer composition curve of MCPD (M_1) and CPD (M_2) catalyzed by $TiCl_4$–TCA at −78°C. Total monomer concentration, 15 vol.-% (1.8–2.0 mole/l.); $[C]_0$ = ca. 1.0 mmole/l.; solvent, toluene.

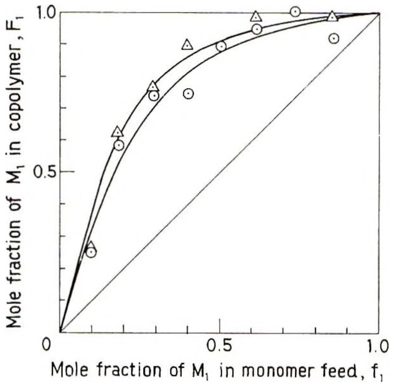


Fig. 7. Copolymer composition curves of MCPD (M_1) and CPD (M_2) catalyzed by $SnCl_4$–TCA at −78°C.: (○) in toluene, $[C]_0$ = ca. 0.6 mmole/l.; (△) in methylene chloride, $[C]_0$ = ca. 0.4 mmole/l. Total monomer concentration, 20 vol.-% (2.4–2.7 mole/l.).

The reasons are considered as the lower reactivity of MCPD or the more important catalyst-consuming reaction with MCPD than CPD. To know which is actually the reason copolymerizations of MCPD (M_1) and CPD (M_2) were carried out; in such reactions we can eliminate the factor of catalyst consumption.

The copolymer composition was analyzed by infrared spectroscopy, the absorption at 830 cm.$^{-1}$ being used as a key band. This absorption was ascribed to C—H out-of-plane deformation of trisubstituted ethylene[11] which exists only in PMCPD. The mixtures of PCPD and PMCPD of known mole fractions were prepared and subjected to infrared spectroscopy to get the calibration curve. Figure 5 shows the calibration curve which was used to analyze the copolymer compositions throughout this work. The copolymer composition determined by this method is in good agreement with that determined by NMR measurement of the copolymer, thus supporting the reliability of the infrared method.

The compositions of copolymer obtained by $TiCl_4$–TCA in toluene are plotted against the monomer feed in Figure 6. It was found that MCPD is more reactive in the propagation reaction than CPD. The intrinsic viscosities of the copolymers lay in the range of 0.3–0.5.

The effect of solvent polarity on the monomer reactivity ratio was investigated with copolymerization catalyzed by $SnCl_4$–TCA. As is seen in Figure 7, no serious effect of solvent dielectric constant was observed. Since in all copolymerizations the conversion was kept below 10%, the Mayo-Lewis differential equation was used to calculate the monomer reactivity ratio; in toluene, $r_1 = 8.5 \pm 3.5$ and $r_2 = 0.36 \pm 0.26$; in methylene chloride, $r_1 = 14.9 \pm 5.6$ and $r_2 = 0.42 \pm 0.23$. Comparison of Figure 6 with Figure 7 showed that the catalyst had little effect on the monomer reactivity ratio.

Structure of Polymethylcyclopentadiene

The infrared spectrum of PMCPD obtained with $TiCl_4$–TCA is shown in Figure 8. PMCPD obtained with other catalysts gave almost the same spectrum. In Figure 8 the infrared spectrum of PCPD[12] is also shown for the comparison. Three distinct differences were observed between the two spectra. Firstly, the C—H stretching absorption at 3030 cm.$^{-1}$ was weaker in PMCPD than in PCPD. Secondly, the C=C stretching absorption of PMCPD appeared at 1680 cm.$^{-1}$, while that of PCPD appeared at 1640 cm.$^{-1}$. Thirdly, C—H out-of-plane deformation absorption appeared at 830 cm.$^{-1}$ with PMCPD, but at 720 cm.$^{-1}$ with PCPD. These differences are attributed to trisubstitution of the double bond in PMCPD and *cis* disubstitution of that in PCPD.[11] The absorption band at 1030 cm.$^{-1}$ is detectable with PMCPD. Its absorbance was proportional to the concentration of PMCPD. However, the assignment is not clear.

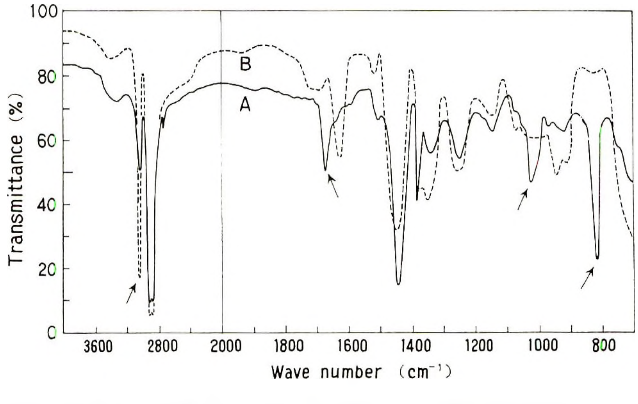
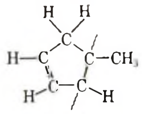
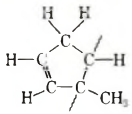
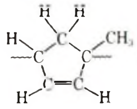
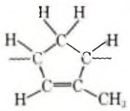
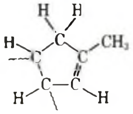
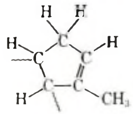


Fig. 8. Infrared spectra of PMCPD and PCPD: (*A*) PMCPD obtained with $TiCl_4$–TCA; (*B*) PCPD obtained with $TiCl_4$–TCA. Measured as KBr pellet.

TABLE I
Structure of Polymethylcyclopentadiene

	1—MCPD			2—MCPD		
		Structure	$A/(B + C + D)$		Structure	$A/(B + C + D)$
1,2 Addition	I		$^1/_3$	II		$^1/_3$
1,4 Addition	III		$^1/_3$	IV		$^1/_7$
3,4 Addition	V		$^1/_7$	VI		$^1/_7$

The NMR spectrum of PMCPD obtained with $TiCl_4$–TCA is shown in Figure 9. The spectrum is almost identical with that obtained with $SnCl_4$–TCA. The NMR spectrum of PCPD[12] is also shown for the comparison. A sharp peak at τ 8.4 (peak *D*) is due to methyl protons, which is shifted downfield. A peak at τ 4.9 (peak *A*) is due to olefin protons, which is shifted upfield. Furthermore, the ratio of peak area $A/(B + C + D)$ was exactly 1/7. These facts confirm that the methyl group is in conjugation with double bond, that is, the double bond is trisubstituted.[13] A small shoulder appeared at τ 4.9 (peak *A*). Similar splitting was sometimes observed with PCPD.[12] Since MCPD as well as CPD undergoes a propagation reaction in several ways (see below), a multiplicity of the environment of the olefinic proton may have caused the splitting of the absorption peak. Two peaks at τ 8.0 (peak *C*) and 7.5 (peak *B*) may be assigned to methylene protons and methyl protons, respectively. It is possible that there is some contribution of β-methylene protons to peak *D*.

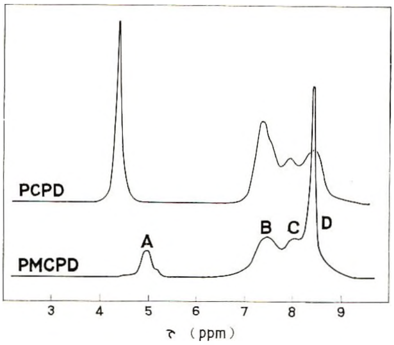


Fig. 9. NMR spectra of PMCPD and PCPD. PMCPD obtained with $TiCl_4$–TCA; PCPD obtained with $BF_3 \cdot O(C_2H_5)_2$. Measured in carbon tetrachloride solution at room temperature at 60 Mc./sec., tetramethylsilane used as internal standard.

The MCPD used in the present investigation was the mixture of two isomers. For each isomer, 1,2-, 1,4-, and 3,4-propagation reactions, are possible, thus giving six basic structures of monomer unit in polymer, as shown in Table I. However, infrared and NMR spectra indicated that only structures IV, V, and VI are possible. If complete assignment of the peaks *B* and *C* is made and the degree of contribution of β-methylene protons to peak *D* is estimated, the relative abundance of structures IV, V, and VI can be quantitatively determined. However, this was not the case. Yen assigned peak *B* to α-protons, peak *C* to β-protons, and peak *D* to methyl protons. Calculating the ratio α-H/β-H Yen concluded that the polymer has almost entirely a 1,4 structure.[7] However, the assignment of Yen for PMCPD as well as for PCPD is open to question.[12] Hence, the quantitative analysis of the polymer structure is not yet completed.

DISCUSSION

The copolymerization of MCPD with CPD showed that MCPD was about ten times as reactive as CPD. This is accounted for in terms of an electron-releasing effect of a methyl group. In fact, with 1-methylcyclopentadiene the $\mathrm{p}K_a$ value of its conjugate cation is calculated to be -5.3,[14,15] and with CPD it is -8.7.[14,15] These values mean that the MCPD cation is more stabilized by the action of a methyl group than the CPD cation. The effect of the polymerization conditions on the monomer reactivity ratio was negligibly small.

The present investigation of homopolymerization and copolymerization of MCPD demonstrates that MCPD as well as CPD is a reactive monomer. It may generally be said that five-membered cyclic dienes are reactive in cationic polymerization. As the CPD ring does not suffer internal strain,[16] the release of strain by conversion from a cyclic diene into a cyclic olefin at a polymerization does not explain their high reactivity. The high stability of a cyclopentenyl cation seems attractive as a reason. Thus, the $\mathrm{p}K_a$ value for protonated CPD (a cyclopentenyl cation) is larger than those of a protonated isobutene (a tertiary butyl cation, $\mathrm{p}K_a = -15.5$[14]) and of a protonated 2,4,6-trimethyl-α-methyl-styrene ($\mathrm{p}K_a = -12.2$[17]). These facts imply that a cyclopentenyl cation is relatively stable and cyclopentadienes are easily converted into protonated forms, which leads to a very rapid initiation reaction. The nucleophilicity of the monomer is another important factor in determining the monomer reactivity, that is, the reactivity in the propagation reaction. In this connection, some experiments are currently being carried out to determine the nucleophilicity of cyclic dienes; results will be published in the future.

Study of the polymer structure indicates that the polymerization of MCPD did not proceed via a stable tertiary carbonium ion, that is, the addition of incoming monomer did not occur at a carbonium ion bearing a methyl group. This is explained in terms of steric hindrance of a methyl group if one takes into account that trisubstituted ethylenes are reluctant to be polymerized.[18] It is quite interesting that with 1-methylcyclopentadiene there is a convenient pathway for the propagation reaction which is facilitated by the electronic effect of a methyl group and without involving

TABLE II

Shape of Time–Conversion Curves

Monomer	Catalyst	Type of time–conversion curve[a]
MCPD	$TiCl_4$–TCA	A
MCPD	$SnCl_4$–TCA	A
MCPD	$BF_3 \cdot OEt_2$	B
CPD	$TiCl_4$–TCA	A
CPD	$SnCl_4$–TCA	B
CPD	$BF_3 \cdot OEt_2$	C

[a] Shapes shown in Fig. 10.

steric hindrance of a methyl group, because the reaction site is in conjugation with but distant from the methyl group.

In the investigations on the homopolymerization of MCPD with various catalysts, the shape of the time–conversion curve was strongly dependent on the catalyst used (Fig. 10). These curves are classified in Table II, in which CPD is also listed for comparison. In Table II and Figure 10 type A is for a typical nonstationary-state polymerization (fast initiation and propagation with diminishing numbers of active species), type B is for concomitant nonstationary- and stationary-state polymerization, and type C is for a nearly stationary-state polymerization. The mechanism of the initiation reaction was investigated and is discussed in more detail in the previous papers of this series.[1,3] It is interesting to note that the more reactive MCPD brought about a fast initiation reaction (type A) even with a less electrophilic Lewis acid ($SnCl_4$).

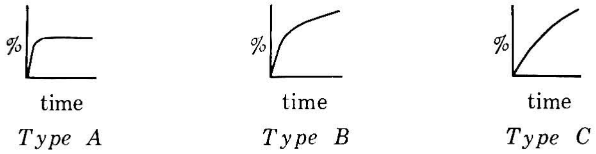


Fig. 10. Time–per cent conversion curves.

Note Added in Proof: After this paper was completed the polymerization of a mixture of methyl cyclopentadienes and some remarks on the structurs of its polymer were reported, see C. Aso and O. Ohara, *Makromol. Chem.*, **109**, 161 (1967).

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Effect of Polymer Structure on Ease of Hydrogen Abstraction by Cumyloxy Radicals

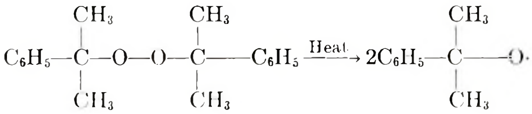
JOGINDER LAL, JAMES E. McGRATH,* and ROBERT D. BOARD,†
Research Division, The Goodyear Tire & Rubber Company,
Akron, Ohio 44316

Synopsis

Vulcanizates of five elastomers having different chemical structures were prepared with recipes comprising dicumyl peroxide. Cumyl alcohol/acetophenone molar ratios were determined by gas–liquid chromatography (GLC) on acetone extracts of vulcanizates. Diphenyl ether was used as the internal standard. The ease of hydrogen abstraction by cumyloxy radicals, reflected by the cumyl alcohol/acetophenone ratio, decreases in the following order: *cis*-1,4-polyisoprene > poly(propylene oxide) > poly(vinyl *n*-butyl ether) > poly-1-heptene ≃ EPR. This order is in qualitative agreement with the order based on calculated relative rates of hydrogen abstraction by methyl and *tert*-butoxy radicals and literature data on oxygen absorption of some of these polymers as a result of hydrogen abstraction by peroxy radicals.

INTRODUCTION

Interest in the use of peroxide curing agents has increased with the availability of saturated rubbers. The mechanism of crosslinking of a variety of rubbers with peroxides has been reviewed recently by Loan.[1] Dicumyl peroxide has received considerable attention due to its low volatility, ease of handling, and usefulness as a source of free radicals which perform effectively in hydrogen abstraction reactions. The unimolecular thermal decomposition of dicumyl peroxide results in the formation of cumyloxy radicals which may then abstract hydrogen from a substrate to give α,α-dimethylbenzyl alcohol (cumyl alcohol) or undergo dismutation by β-scission to acetophenone and methyl radicals.



$$C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-O-O-\overset{CH_3}{\underset{CH_3}{C}}-C_6H_5 \xrightarrow{\text{Heat}} 2C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-O\cdot \qquad (1)$$

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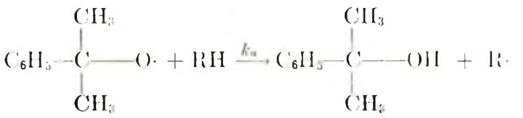
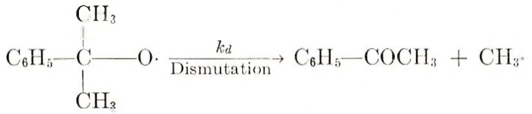
* Present address: Union Carbide Corp., Chemicals and Plastics Division, Bound Brook, New Jersey.

† Present address: Chemistry Department, Purdue University, Lafayette, Indiana.



$$C_6H_5-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-O\cdot + RH \xrightarrow{k_a} C_6H_5-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH + R\cdot \tag{2}$$



$$C_6H_5-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-O\cdot \xrightarrow[\text{Dismutation}]{k_d} C_6H_5-COCH_3 + CH_3\cdot \tag{3}$$

$$\frac{r_a}{r_d} = \frac{k_a}{k_d}[RH] \tag{4}$$

Where RH is a hydrogen-bearing substrate, r_a and r_d are rates of hydrogen abstraction and dismutation reactions, respectively, and k_a and k_d are the corresponding rate constants. The molar ratio of cumyl alcohol to acetophenone determined experimentally gives the ratio r_a/r_d. The higher the value of this ratio for a polymer the greater is the ease of hydrogen abstraction. We were interested in assessing the effect of chemical structure of polymers on the ease of hydrogen abstraction during vulcanization with a dicumyl peroxide-sulfur curing system. For this study, we selected four saturated and one unsaturated polymer, namely, poly(propylene oxide), ethylene–propylene rubber (EPR), poly-1-heptene, poly(vinyl *n*-butyl ether), and *cis*-1,4-polyisoprene.

EXPERIMENTAL

Materials

The preparation of poly(vinyl *n*-butyl ether), poly-1-heptene and poly(propylene oxide) has been described previously.[2] EPR was obtained from Enjay Chemical Company and contained about 46 mole-% propylene (designated as Enjay 404). Synthetic *cis*-1,4-polyisoprene was obtained from Shell Chemical Corporation and was selected for this work because of its low catalyst residue. All polymers were free from antioxidant, either by design or as a result of continuous extraction with acetone for 16 hr. The number-average molecular weights of the four saturated rubbers before compounding are given in Table I.

TABLE I
Number-Average Molecular Weights (Osmotic) of Polymers

Polymer	$\overline{M}_n$
Poly(propylene oxide)	91,000
EPR	59,000
Poly-1-heptene	138,000
Poly(vinyl *n*-butyl ether)	166,000

Dicumyl peroxide was purified by recrystallizing Di-Cup R (95%, Hercules Powder Co.) from methanol.

Vulcanization

The saturated rubbers were compounded by milling with 2 phr (weight parts per 100 parts of rubber) dicumyl peroxide and 0.2 phr sulfur (Table II). To determine the effect of sulfur on cumyl alcohol/acetophenone ratio, EPR was also compounded with only dicumyl peroxide (2 phr). The *cis*-1,4-polyisoprene was compounded with 2 phr dicumyl peroxide for use as a standard and for comparison with data in the literature. Vulcanizate samples were prepared by curing in a press for 80 min. at 295°F. (146°C.). The press was then chilled by circulating cold water to minimize volatilization of cumyl alcohol and acetophenone during subsequent handling of samples.

TABLE II
Effect of Polymer Structure on Cumyl Alcohol/Acetophenone Molar Ratio During Vulcanization with Dicumyl Peroxide[a]

Polymer	Sulfur in compounding recipe, phr	Wt.-% in vulcanizate		Recovery, %	Molar ratio of cumyl alcohol to Acetophenone
		Cumyl alcohol	Acetophenone		
cis-1,4-Polyisoprene	—	0.031	0.004	100	6.83[b]
Poly(propylene oxide)	0.20	0.016	0.003	87	4.70
EPR	0.20	0.021	0.014	81	1.32
EPR	—	0.031	0.018	97	1.52[c]
Poly-1-heptene	0.20	0.014	0.008	77	1.54
Poly(vinyl *n*-butyl ether)	0.20	0.020	0.008	82	2.20

[a] Curing at 146°C. for 80 minutes. All recipes contained 2 phr dicumyl peroxide.
[b] Literature value: 5.55.[3]
[c] Literature values: 2.5,[4] 0.86.[5]

Extraction and Analysis

Accurately weighed specimens (about 1–2 g.) of vulcanizates were placed separately in tightly capped, wide-mouthed 4-oz. bottles containing 100 ml. of distilled acetone. The extraction was allowed to continue for 13 days at 25°C. An F and M 1609 instrument with a flame ionization detector was used to determine very low concentrations of cumyl alcohol and acetophenone present in the acetone extracts Recrystallized diphenyl ether was found to be useful as an internal standard. The following instrument conditions were found suitable for the analysis: column, 5 ft., 10% Carbowax 5000M on 60/80 mesh Gaschrom Z; column temperature, 165°C.; injection point temperature, 200°C.; detector temperature, 200°C.; sample size, 4–10 μl.

Two mixtures of known compositions A and B were analyzed to determine the response factors for cumyl alcohol and acetophenone (Table III).

TABLE III

	Composition		Response factor[a]	
Component	Mixture A	Mixture B	Mixture A	Mixture B
Cumyl alcohol	0.10 g.	0.10 g.	1.11 ± 0.03	1.14 ± 0.02
Acetophenone	0.05 g.	0.15 g.	1.05 ± 0.03	1.10 ± 0.02
Diphenyl ether	0.10 g.	0.15 g.	1.00	1.00
Acetone	100 ml.	100 ml.	—	—

[a] $$\text{Response factor for cumyl alcohol} = \frac{\text{Peak area of } (C_6H_5)_2O}{\text{Wt. of } (C_6H_5)_2O} \bigg/ \frac{\text{Peak area of cumyl alcohol}}{\text{Wt. of cumyl alcohol}}$$

These response factors were used to convert area per cent values for given components to weight per cent values. The response factors were occasionally checked and were the same within experimental error.

For a typical experiment, duplicate results were as follows: cumyl alcohol, 0.0237, 0.0244 g.; acetophenone, 0.0147, 0.0148 g.

RESULTS

In Table II, data are given for weight per cent cumyl alcohol and acetophenone extracted from vulcanizates, their molar ratio R, and per cent recovery based on the total amount of these two components. For calculating per cent recovery, it was assumed that 91% of dicumyl peroxide had decomposed[6] under our experimental conditions. The recovery is quantitative for the polyisoprene and nearly so in the case of EPR cured with dicumyl peroxide only. The presence of sulfur in the compounding recipe for the saturated elastomers reduced the recovery to 77–87%, presumably due to some ionic decomposition[5] of dicumyl peroxide. For the vulcanization of Shell polyisoprene at 146°C. we obtained a value of 6.83 for the ratio R. This value is in fair agreement with the corresponding literature value of 5.55[3] for natural rubber vulcanization at 154°C. and an extrapolated value of about 8.3 at 146°C. obtained from the data of Thomas.[6] Parks and Lorenz[7] have reported that the ratio R was about 4.4 for the reaction of dicumyl peroxide with 2,6-dimethyl-2, *trans*-6-octadiene, a model polyisoprene. The R value for 2,6-dimethyloctadiene is expected to be lower than that for *cis*-1,4-polyisoprene, since the latter contains twice as many secondary allylic hydrogens per unit weight. Our value of the ratio R for EPR was 1.52. This value is between the values of 0.86 reported by Robinson et al.[5] for vulcanization at 160°C. and 57% recovery of cumyl alcohol plus acetophenone and 2.5 reported by Loan[4] for vulcanization at 153°C. (no recovery figure given). Qualitatively speaking, the value of R is expected to decrease with increasing temperature of vulcanization.[3] Since ethylene–propylene rubbers of reasonably similar composition (40–50 mole-% propylene) were used in these three investigations the differences in the value of R are not due to overall composition. These differences presumably lie in other factors which include the analytical methods and per cent recovery of acetophenone and cumyl alcohol.

The R values for the four saturated elastomers cured with the peroxide-sulfur recipe indicate that the ease of hydrogen abstraction decreases in the following order:

poly(propylene oxide) > poly(vinyl *n*-butyl ether) > poly-1-heptene ≅ EPR

The R value for EPR decreased about 13% when sulfur was included in the curing recipe. This may not be significant in view of the limited data. If this adjustment is made for vulcanizates of polyisoprene obtainable with the peroxide-sulfur recipe the R value is estimated to be about 5.9. Therefore, the ease of hydrogen abstraction by cumyloxy radicals decreases in the following order for the five polymers investigated:

cis-1,4-polyisoprene > poly(propylene oxide) >
poly(vinyl *n*-butyl ether) > poly-1-heptene ≅ EPR

DISCUSSION

A qualitative estimate of the relative ease of hydrogen abstraction in these polymers may be obtained from literature data on relative rate constants for abstraction of various types of hydrogen atoms in model compounds by free radicals. It would be desirable to make such an estimate with cumyloxy radicals; however, model compound data with cumyloxy radicals are quite limited. In Table IV, relative rate constants are given for abstraction of various types of hydrogen atoms in two different classes of compounds by using *tert*-butoxy radicals which are reasonably similar to cumyloxy radicals. Similar data are not available for ethers. In Table V, we have listed the various types of hydrogen atoms in the five synthetic elastomers investigated. The vinylic hydrogen in the 1,4-polyisoprene is considerably less[9] active and consequently has been omitted from this table. For the three hydrocarbon polymers, the relative rates of

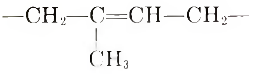
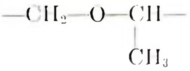
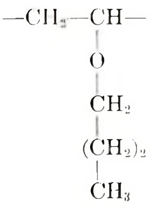
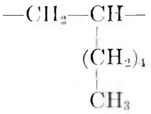
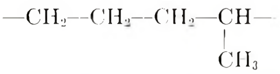
TABLE IV
Relative Rate Constants for Abstraction of Various Types of Hydrogen Atoms by *tert*-Butoxy Radicals[a]

Type of hydrogen atom	Class of organic compound	
	Alkane	Alkene[b]
Primary	1	20 (*p*, *s*)
Secondary	12.2	93 (*s*, *s*)
Tertiary	44	176 (*t*, *p*)

[a] Values from Walling and Thaler (Table VII).[8]

[b] (*p*,*s*) refers to an allylic radical in which the odd electron is delocalized between primary and secondary carbons; (*s*,*s*) if delocalized between two secondary carbons. Value for (*s*,*t*) type abstraction [expected to be higher than the (*s*, *s*) type] is not available.

TABLE V
Types of Hydrogen Atoms in Various Polymers Investigated

Polymer	Structural repeat unit in polymer	Type of hydrogen atom[a]								
		Non-activated			Activated by double bond			Activated by ether group		
		P	S	T	P	S	T	P	S	T
cis-1,4-Polyisoprene[b]	 $—CH_2—C(CH_3)=CH—CH_2—$	—	—	—	3	4	—	—	—	—
Poly(propylene oxide)	 $—CH_2—O—CH(CH_3)—$	3	—	—	—	—	—	—	2	1
Poly(vinyl *n*-butyl ether)	 $—CH_2—CH(O—CH_2—(CH_2)_2—CH_3)—$	3	6	—	—	—	—	—	2	1
Poly-1-heptene	 $—CH_2—CH((CH_2)_4—CH_3)—$	3	10	1	—	—	—	—	—	—
EPR (50 mole-% propylene)[c]	 $—CH_2—CH_2—CH_2—CH(CH_3)—$	3	6	1	—	—	—	—	—	—

[a] P, S, and T designate primary, secondary, and tertiary hydrogen atoms, respectively.
[b] 100% 1,4-structure assumed to simplify calculations.
[c] This average composition unit is employed here to simplify calculations.

hydrogen abstraction by *tert*-butoxy radicals were calculated by the following relationship:

$$\text{Relative overall rate of hydrogen abstraction} = X[k_1Z_1 + k_2Z_2 + k_3Z_3 + \ldots] \quad (5)$$

where X is the number of gram molecules of polymer repeat unit per 100 g of rubber, $k_1,k_2,k_3, \ldots$ are relative rate constant values for various types of hydrogen atoms (Table IV), and $Z_1,Z_2,Z_3, \ldots$ are the number of hydrogen atoms of a given type per polymer repeat unit (Table V).

The calculated relative rates of hydrogen abstraction from *cis*-1,4-polyisoprene, polyheptene, and EPR are 410, 172, and 171, respectively (Table VI). The order of these rates is in accord with the experimental data in Table II.

The extraction of hydrogen atoms from a variety of substrates by methyl radicals has been extensively investigated. Relative rate constants for

TABLE VI
Calculated and Experimental Relative Rates for Hydrogen Abstraction from Various Polymers

Polymer	Molar ratio[a] of cumyl alcohol to acetophenone	Calculated relative rates of hydrogen abstraction by Methyl radical	Calculated relative rates of hydrogen abstraction by *tert*-butoxy radical	R_0[b]
cis-1,4-Polyisoprene	6.83	635	410	7.0
Poly(propylene oxide)	4.70	176	—	5.9[c]
Poly(vinyl *n*-butyl ether)	2.20	144	—	—
Poly-1-heptene	1.54	126	172	—
EPR	1.52, 1.32	136	171	2.1

[a] Data from Table II.

[b] Values from Norling et al. (Table I).[10]

[c] Obtained on a copolymer of propylene oxide, which contained unsaturation[11] for vulcanization. A somewhat lower value would be expected for the homopolymer.

abstraction of various types of hydrogen atoms pertinent to the polymers under consideration are listed in Table VII. The calculated relative rates of hydrogen abstraction by methyl radicals from five elastomers are given in Table VI. Again, the order of these rates is in accord with the experimental data in Table II.

TABLE VII
Relative Rate Constants for Abstraction of Various Types of Hydrogen Atoms by Methyl Radicals[a]

Type of hydrogen atom	Class of organic compound: Alkane	Alkene	Ether
Primary	1	17	5
Secondary	7	57	18[b]
Tertiary	50	177	63

[a] Values from Trotman-Dickenson (Table 7).[9]

[b] Value assumed for this article by employing the empirical relationship: $k_2 = (k_1k_3)^{1/2}$, where k_1, k_2, and k_3 denote rate constants for primary, secondary, and tertiary hydrogen atoms, respectively.

Tobolsky and co-workers[10] have studied peroxide-initiated oxidation of several elastomers at 80°C. Their experimental values of R_0 are listed in Table VI for three polymers. R_0 is a measure of the relative ease of hydroperoxide formation as a result of hydrogen abstraction by peroxy radicals:

$$RO_2\cdot + RH \rightarrow ROOH + R\cdot$$

Qualitatively, the oxidation rates of these polymers follow the same order as obtained from our study of the ease of hydrogen abstraction by cumyloxy radicals by determining the cumyl alcohol/acetophenone molar ratio.

This is contribution No. 385 from the Research Laboratories, The Goodyear Tire & Rubber Company, Akron, Ohio.

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Polymerization of D-α-Methylbenzyl Methacrylate by *n*-Butyllithium and the Tacticity and Optical Rotation of the Polymer

HEIMEI YUKI and KOJI OHTA, *Department of Chemistry, Faculty of Engineering Science,* KATSUHIRO UNO and SHUNSUKE MURAHASHI, *Department of Polymer Science, Osaka University, Toyonaka, Osaka, Japan*

Synopsis

D-α-Methylbenzyl methacrylate, $[\alpha]^{25}_{589} = +51.3°$ (neat), was polymerized by *n*-butyllithium in toluene–tetrahydrofuran mixtures of various solvent ratios at −78°C. The polymers obtained were converted into poly(methyl methacrylate)s, which were analyzed for tacticity by high resolution NMR spectroscopy. A linear relationship was obtained between the optical rotation and the isotacticity of poly(D-α-methylbenzyl methacrylate). The extrapolation of the data gave +120° and +99° for $[\alpha]^{15}_{589}$ of the fully isotactic and syndiotactic polymers, respectively. The copolymerization of the D- and L-isomers in toluene gave copolymers which were less isotactic than the homopolymer of the D-isomer. The optical rotation of the copolymer was proportional to the excess of one isomer in the polymer.

INTRODUCTION

A number of investigations on the relation between the tacticity and optical rotation of optically active polymers have been reported. It has been found that some isotactic polymers have extremely large optical rotations compared to the corresponding monomers, and the causes of these large rotations have been discussed. The large optical rotations of isotactic poly[(*S*)-3-methylpentene-1] and its higher homologs[1] have been ascribed to the helical conformation of the polymers predominantly in one screw sense. Similar investigations have been made on various optically active vinyl compounds, e.g., α-olefins,[2–5] vinyl ethers,[6] aldehydes,[7] methacrylates,[8–12] and acrylates.[11,12] However, few investigations have been concerned with the quantitative treatment of the relation between the tacticity and the optical rotation of the optically active polymer.

Methacrylates are one of the types of monomer which are known to be polymerized to both isotactic and syndiotactic polymers. This work was done to investigate the change in the optical rotations of a series of polymers, whose stereoregularities vary successively from the isotactic to the syndiotactic configuration. D-α-Methylbenzyl methacrylate (D-MBMA), which was considered to be practically optically pure, was polymerized at

-78°C. in mixtures of various ratios of toluene and tetrahydrofuran (THF), *n*-butyllithium (BuLi) being used as a catalyst.

The copolymerization of D- and L-MBMA was also carried out, at varying ratios of D- and L-isomers, to study the influence of the optical antipode on the stereospecific polymerization of an optically active monomer.

EXPERIMENTAL

Materials

D-α-Methylbenzyl Methacrylate. According to Kenyon,[13] D,L-α-methylbenzyl hydrogen phthalate (m.p., 110°C.) was resolved into fractions rich in the D-isomer and in the L-isomer through the brucine salt. In this work, 87 g. of the D,L-phthalate and 127 g. of anhydrous brucine in 300 ml. of dry acetone gave 108 g. of the D salt and 98 g. of the L salt. From the salts, 42 g. of the D-phthalate ($[\alpha]_{589}^{25}$, $-20.5°$; m.p., 93°C.) and 38 g. of the L-phthalate ($[\alpha]_{589}^{25}$, $+23.7°$; m.p., 92°C.) were obtained by hydrolysis.

The phthalate rich in one isomer was fractionally recrystallized from solution in a benzene–cyclohexane mixture (1:4 v/v). Finally, 16.2 g. of the D-phthalate having $[\alpha]_{589}^{15} = -36.5°$ was recrystallized from 100 ml. of the mixed solvent to give 11 g. of the phthalate having $[\alpha]_{589}^{15} = -36.9°$ ($c = 3.84$ dl./g., ethanol) and m.p. = 86.5°C. (lit.[13] $[\alpha]_D = +36.5°$ for the L-isomer, m.p., 86.0°C.). This fraction appeared to be practically optically pure, since its optical rotation and melting point were not changed by repeated recrystallizations.

By the acid hydrolysis of the D-phthalate, D-α-methylbenzyl alcohol was obtained almost quantitatively; α_{589}^{15}, $+44.6°$ (neat); b.p., 66°C./2 mm. Hg; n_D^{20}, 1.5280, (lit.[14] $[\alpha]_D^{30} = -45.0°$ for the L-isomer).

The reaction between D-α-methylbenzyl alcohol and methacryloyl chloride gave the methacrylate in 82% yield; $[\alpha]_{589}^{25}$, $+51.3°$ (neat); b.p., 56°C./0.4 mm. Hg; n_D^{20}, 1.5031.

ANAL. Calcd. for $C_{12}H_{14}O_2$: C, 75.76%; H, 7.42%. Found: C, 75.80%; H, 7.62%.

D,L-α-Methylbenzyl Methacrylate. D,L-MBMA was prepared from methacryloyl chloride and the D,L-alcohol; b.p., 70°C./0.7 mm. Hg; n_D^{20}, 1.5059.

Methyl Methacrylate. Methyl methacrylate (MMA) was purified by the usual method and vacuum-distilled just before use with calcium hydride as a drying agent.

Solvents. The toluene and THF used in the polymerization reaction were distilled into a reaction vessel attached to a vacuum system with BuLi and lithium aluminum hydride as drying agents, respectively.

***n*-Butyllithium.** *n*-BuLi was prepared as a solution in toluene according to Ziegler's method.[15] The concentration (0.5 mole/l.) was determined by the double titration method.[16]

Polymerization

All the polymerization reactions were done in ampules. BuLi (0.36 mmole) was added to a solution of 0.01 mole of monomer in 20 ml. of solvent at −78°C. After reaction for 48 hr. at −78°C., the reaction mixture was poured into a large amount of methanol. The polymer thus obtained was reprecipitated from toluene–methanol.

Conversion of Poly(α-methylbenzyl Methacrylate) into Poly(methyl Methacrylate)

Dry hydrogen bromide was bubbled through a solution of 0.4 g. of poly(α-methylbenzyl methacrylate) (PMBMA) in 100 ml. of toluene for 6 hr. at room temperature. After hydrogen bromide was purged off with dry nitrogen, the reaction mixture was poured into a large amount of acetone. The precipitates were collected, washed with acetone, and dried *in vacuo*. Poly(methacrylic acid) was obtained almost quantitatively. It showed no absorption bands due to the phenyl group in the infrared spectrum.

A large excess of diazomethane dissolved in THF was added to the suspension of poly(methacrylic acid) (about 0.18 g.) in THF (30 ml.) with stirring at room temperature. The reaction mixture was poured into a large amount of methanol. The product was reprecipitated from toluene–methanol. The polymer thus obtained was confirmed to be poly(methyl methacrylate) (PMMA) by elementary analysis, infrared spectroscopy, and NMR spectroscopy.

ANAL. Calcd. for $C_5H_8O_2$: C, 59.98%; H, 8.05%. Found: C, 59.65%; H, 8.14%.

Measurements

Optical rotations were measured on a Yanagimoto OR-10 polarimeter with the use of a 0.5 dm. cell. The concentration of polymer solution was about 2% and the accuracy of the readings was ±0.003°.

Solution viscosities were measured in an Ostwald viscometer on a 0.5% solution of polymer in toluene at 30°C.

Infrared spectra were taken on a JASCO IR–S Infrared spectrometer with the use of a polymer film cast on a NaCl plate from a solution in carbon tetrachloride.

High-resolution NMR spectra were obtained with a JNM–4H-100 spectrometer at 100 Mc./sec. with the use of 10% solution of the polymer in chloroform at 50°C.

RESULTS

D-MBMA was polymerized by BuLi in mixtures of toluene and THF at −78°C. The results are shown in Table I. In each case the yield of polymer was higher than 90%. The molecular weight of the polymer, represented by its solution viscosity, changed independently of the compo-

TABLE I

Polymerization of D-MBMA in a Mixture of Toluene and THF by BuLi at −78°C.[a]

		P-D-MBMA				PMMA derived		Tacticity		
Expt. no.	THF/solvent, vol.-%	Yield, %	$[\alpha]_{589}^{15}$ [b]	η_{sp}/c [c]	D_{1255}/D_{1236}	Yield, %	η_{sp}/c [c]	I, %	H, %	S, %
1	0	91	+116.5	0.66	1.68	81	0.65	78.4	16.6	5.0
2	2.5	94	+116.6	0.28	1.45	80	0.42	76.1	13.7	10.2
3	5	92	+116.9	0.19	1.42	73	0.36	76.5	12.3	11.2
4	10	94	+112.0	0.26	1.14	78	—	54.7	16.1	29.2
5	15	97	+106.6	0.39	0.89	84	—	26.4	22.9	50.7
6	25	94	+104.2	0.37	0.81	81	—	15.6	30.1	54.3
7	50	93	+104.0	0.30	0.75	96	0.37	10.6	28.2	61.2
8	100	93	+104.7	0.23	0.80	90	0.29	11.5	28.4	60.1

[a] Monomer, 2.04 g. (11 mmole); total volume of solvent, 20 ml.; BuLi, 0.36 mmole.

[b] In toluene at 15°C.; c = 2.0 g./100 ml.

[c] In toluene at 30°C.; c = 0.5 g./100 ml.

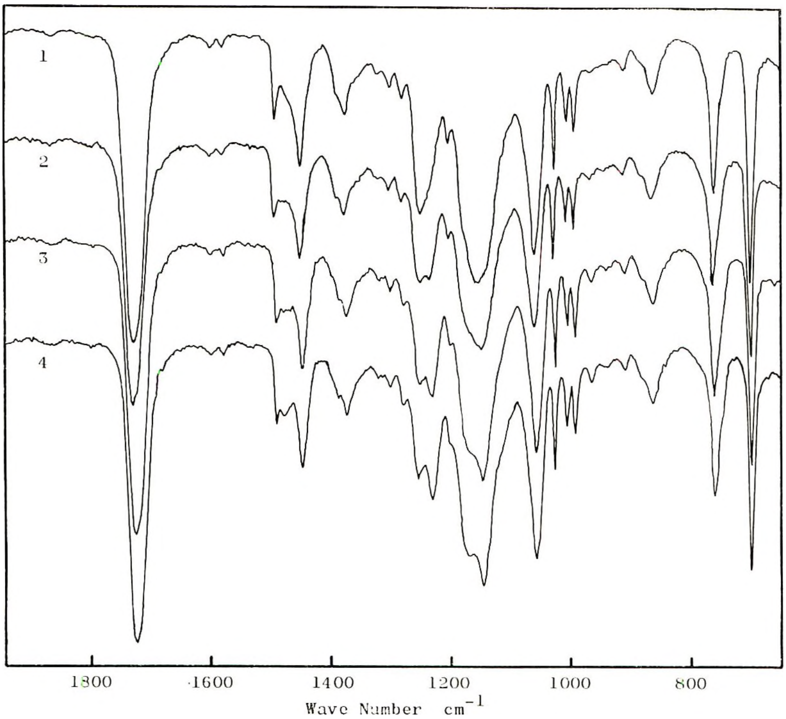

Fig. 1. Infrared spectra of P-D-MBMA at various contents of THF in the polymerization solvent: (*1*) 0%; (*2*) 10%; (*3*) 15%; (*4*) 100%.

sition of the solvent used in the polymerization reaction. However, with the variation of the solvent composition from pure THF to pure toluene, the optical rotation $[\alpha]_{589}^{15}$ changed gradually from +104° to +116°. As shown in Figure 1, the relative intensities of some absorption bands in the infrared spectrum of the polymer also changed with the composition of the solvents used in the polymerization. For example, a successive change was observed in the ratio of the optical densities of the bands at 1255 and 1236 cm.$^{-1}$ Matsuzaki et al.[17] reported similar observations for the polymers of D,L-MBMA prepared by different initiators.

The polymers of D-MBMA were converted into PMMA as described in the experimental section. The tacticities of the derived polymers were determined from their high-resolution NMR spectra.[18,19] The results are also listed in Table I. It is well known in the chemistry of peptide synthesis that debenzylation and methylation reactions cause no racemization of an α-amino acid under similar reaction conditions. In a polymer synthesis no change in the tacticity of poly(benzyl vinyl ether) was observed during the conversion into poly(vinyl acetate) via poly(vinyl alcohol).[20] Therefore, it would be expected that no change occur in the configuration of the α-carbon during the conversion from PMBMA into PMMA. The PMMA's were obtained in fairly good yields, and the changes in the tactic contents caused by the partial losses of the products might be negligible.

The PMMA derived from P-D-MBMA, produced in toluene, showed the highest isotacticity and the lowest syndiotacticity. The replacement of a part or the whole of the polymerization solvent with THF caused a decrease in the isotactic content (I) and an increase in the syndiotactic content (S) of the polymer. At low THF concentrations, from 0 to 5% by volume, the isotactic content of the polymer changed only a little, but the syndiotactic and heterotactic contents changed relatively significantly; the syndiotactic content increased and the heterotactic content (H) decreased with increase in the THF concentration. Large amounts of THF, above 50%, gave highly syndiotactic polymers having almost the same tactic contents as that of the polymer obtained in pure THF.

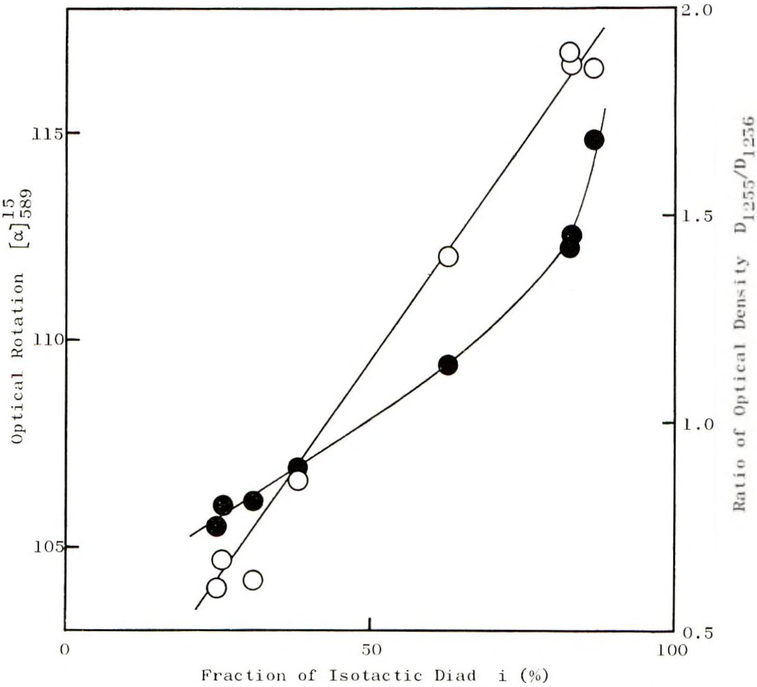

Fig. 2. Isotactic diad i vs. (○) $[\alpha]^{15}_{589}$ and (●) D_{1255}/D_{1236} of P-D-MBMA.

The relationship between the specific rotation $[\alpha]^{15}_{589}$ and the isotactic diad content i ($= I + H/2$) of P-D-MBMA is plotted in Figure 2. In this figure the ratio of the optical densities of the bands at 1255 and 1236 cm.$^{-1}$ in the infrared spectrum is also plotted against i. A linear relationship was obtained between $[\alpha]^{15}_{589}$ and i, and by the extrapolation of this straight line +120° and +99° were obtained for $[\alpha]^{15}_{589}$ at $i = 100\%$ and $i = 0\%$ ($s = S + H/2 = 100\%$), respectively. The ratio D_{1255}/D_{1236} also increased with increasing isotactic content, showing this to be a measure of the tacticity, but the ratio versus i showed a concave curve.

The optical rotation and the solution viscosity of P-D-MBMA were measured in a toluene–cyclohexane mixture (2:3 v/v) and in THF. The

TABLE II
Optical Activity and Solution Viscosity of P-D-MBMA in Toluene–Cyclohexane (2:3) and THF

Expt. no.	Toluene–cyclohexane		THF	
	$[\alpha]_{589}^{15}$ [a]	η_{sp}/c [b]	$[\alpha]_{589}^{15}$ [a]	η_{sp}/c [b]
1	+106.2	0.44	+90.0	0.76
2	+108.2	0.21	+93.5	0.29
3	+107.7	0.16	+93.2	0.22
4	+102.7	0.19	+86.4	0.30
5	+97.3	0.24	+78.3	0.44
6	+96.4	0.23	+73.8	0.43
7	+95.9	0.20	+71.9	0.36
8	+96.4	0.16	+73.7	0.26

[a] At 15°C.; c = 2.0 g./100 ml.

[b] At 30°C.; c = 0.5 g./100 ml.

results are shown in Table II. Compared with the data obtained in toluene solution (Table I) both the optical rotation and the solution viscosity were low in the toluene–cyclohexane mixture, while the optical rotation was further depressed but the solution viscosity increased in THF.

The racemic monomer was also polymerized by BuLi in toluene–THF mixtures under the same conditions as those employed in the polymerization of the D-isomer. The polymers obtained were converted into PMMA and the tacticities were determined from their high resolution NMR spectra. The results are shown in Table III. The effect of THF on the stereospecific polymerization was similar to that on the polymerization of the D-monomer, but some minor differences were observed as described below.

MMA was also polymerized in toluene–THF mixtures by BuLi under the same conditions as those employed in the polymerization of MBMA, and the tacticities of the polymers were determined. The results are shown in Figure 3 together with the data obtained from the polymerizations of D- and D,L-MBMA. In this figure are plotted the dependences of the isotactic diad contents and the heterotactic triad contents of the polymers on the compositions of the solvent mixtures used in the polymerization reactions. In the polymerization of MMA a much more drastic effect of THF on the isotacticity of the produced polymer was observed than that in the polymerization of MBMA. It was also found that the isotactic diad contents of the racemic PMBMA's produced in the solvents containing small amounts of THF were remarkably lower than those of the D-polymers, and that the heterotactic content of the racemic polymer produced in toluene showed a very high value. On the other hand, the polymers obtained in the solvents containing more than 20% of THF had almost the same tacticities, regardless of the existence of the enantiomorphic isomer. The heterotactic content in the polymer of MMA was relatively high and reached a constant value (above 30%) with only 5% of THF in the polymerization solvent.

TABLE III

Polymerization of D,L-MBMA in a Mixture of Toluene and THF by BuLi at −78°C.[a]

Expt. no.	THF/solvent, vol.-%	P-D,L-MBMA		PMMA derived				
						Tacticity		
		Yield, %	η_{sp}/c[b]	Yield, %	η_{sp}/c[b]	I, %	H, %	S, %
11	0	86	0.82	86	0.93	56.2	34.6	9.2
12	5	92	0.28	79	—	65.1	15.3	19.7
13	10	91	0.31	89	—	44.2	23.5	32.3
14	15	88	0.26	90	0.50	32.7	23.7	43.6
15	25	91	0.21	85	0.31	19.8	27.6	52.6
16	50	93	0.20	75	0.18	9.0	30.3	60.7
17	100	93	0.31	85	0.38	8.4	31.4	60.2

[a] Monomer, 2.04 g. (11 mmole); total volume of solvent, 20 ml.; BuLi, 0.36 mmole.

[b] In toluene at 30°C.; $c = 0.5$ g./100 ml.

TABLE IV

Copolymerization of D- and D,L-MBMA by BuLi at −78°C. in Toluene[a]

Expt. no.	Monomer composition D/(D + L), %	Copolymer			Tacticity of PMMA derived		
		Yield, %	$[\alpha]_{589}^{15}$ [b]	η_{sp}/c [c]	I, %	H, %	S, %
1	100	91	+116.5	0.66	78.4	16.6	5.0
21	90.5	95	+95.8	0.65	68.4	24.7	6.9
22	79.8	92	+70.4	0.69	59.6	32.2	8.1
23	70.2	93	+47.5	0.50	58.7	31.5	9.7
24	60.1	92	+23.9	0.57	56.1	33.5	10.4
11	0	86	0	0.82	56.2	34.6	9.2

[a] Monomer, 1.9 g. (0.10 mmole); toluene, 18 ml.; BuLi, 0.34 mmole.

[b] In toluene at 15°C.; c = 2.0 g./100 ml.

[c] In toluene at 30°C.; c = 2.0 g./100 ml.

The copolymerization of D- and L-MBMA by BuLi was carried out in toluene at −78°C. The composition of the monomer mixture was varied from pure D to the racemic mixture using the D- and D,L-monomer. In each case the copolymer was obtained in greater than 90% yield, suggesting that the copolymer consisted of almost the same composition as that of the monomer mixture charged. The polymers obtained were also converted into PMMA in the same manner described above and the tacticities were determined. The results are shown in Table IV. The relationship between the optical rotation of the copolymer and the monomer composition charged is shown in Figure 4. In this figure, also, the tactic contents of the derived PMMA's are plotted against the monomer composition. The optical rotation was proportional to the excess of the D-isomer over the racemic mixture in the monomer charged. The isotactic content of the polymer decreased and the heterotactic content increased with the change

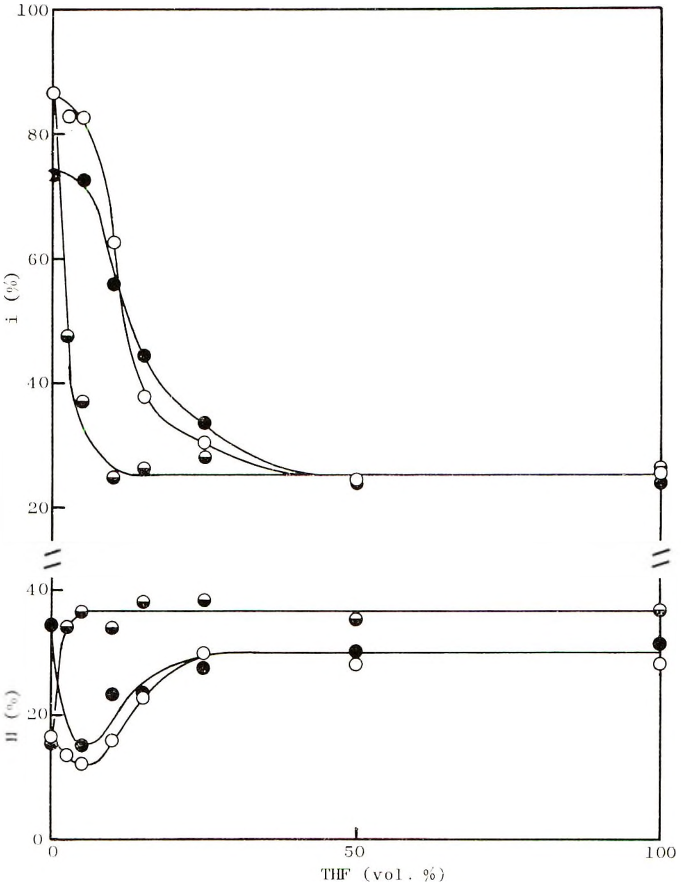

Fig. 3. Effects of THF on the stereospecific polymerizations of D- and D,L-MBMA and MMA: (○) D-MBMA; (●) D,L-MBMA; (◒) MMA.

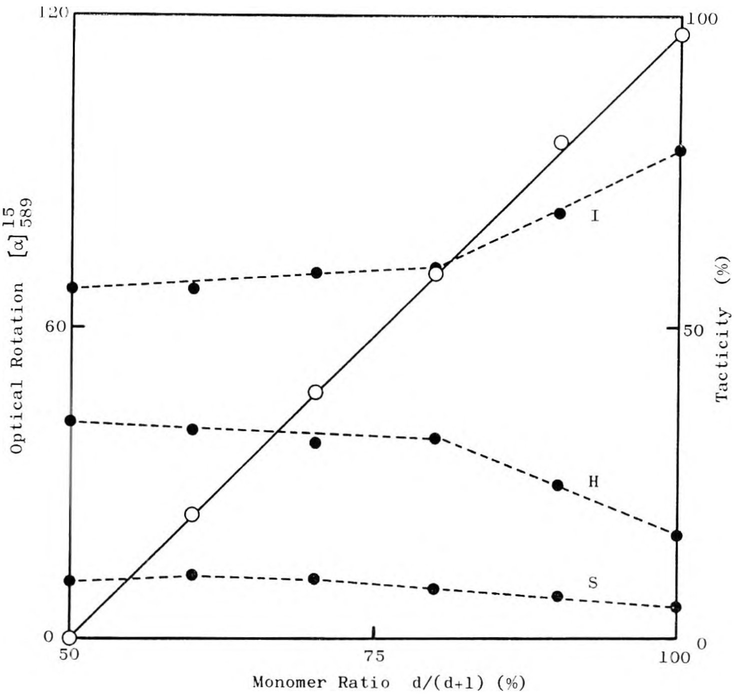

Fig. 4. Monomer composition vs. (○) optical rotation of the polymer and (●) tacticity of the polymer in the copolymerization of D- and L-MBMA.

of monomer composition from the pure D-isomer to the racemic mixture, while the syndiotactic content remained almost unchanged.

DISCUSSION

The tacticity of PMBMA shifted gradually from isotactic to syndiotactic with increase in the THF content in the solvent used in the polymerization reaction. The same has already been observed in the polymerization of MMA by alkyllithium.[21]

It was found that the optical rotation of P-D-MBMA changed linearly with the stereoregularities. In Figure 2 the relationship between i and $[\alpha]_{589}^{15}$ is shown. Linear relationships were also observed between the optical rotation and the other tactic contents, such as I and S as well as s. The extrapolation of the straight line in Figure 2 gave $[\alpha]_{589}^{15} = +120°$ and $+99°$ for the specific rotations of the fully isotactic and syndiotactic polymers, respectively. Liu et al.[9] have investigated the optical rotation and the optical rotatory dispersion of the same polymer and reported that the optical rotation of the isotactic polymer was higher than those of α-methylbenzyl pivalate and the syndiotactic and atactic polymers by about 30%, the exact difference varying to some extent with wavelength and with solvent.

The difference between the optical rotations of the isotactic and syndiotactic P-D-MBMA was significant. From the tacticities listed in Table

I it is obvious that, in the polymethacrylate, the tactic sequence lengths are so small that relatively long helices cannot exist along the chain.[22] Furthermore, the examination of molecular models shows that the steric hindrance between the α-methyl and ester groups in the polymer seems to make it difficult for the helices to be maintained, if they exist. The larger optical rotation shown by the isotactic sequence in this polymer may be due to the local asymmetric conformation in the main chain preferred by the asymmetric ester group. The linearity of the optical rotation versus tactic diad content relationship suggests that the conformation taken by one tactic diad may be independent of the conformations in the neighborhood.

With respect to the solvent, no correlation between the optical rotation and the solution viscosity of this polymer was observed, as shown in Table II. This may suggest that the change in the optical rotation does not directly reflect the change in the conformation and may be affected also by the solvation.

The stereospecificity in the isotactic polymerization of D-MBMA in toluene was just the same as that of MMA, while the isotacticity of P-D,L-MBMA produced in toluene was considerably lower than those of the D-polymer and PMMA, as shown in Figure 3. The lower isotacticity in the D,L-polymer was not accidental, because the same tendency was observed in the copolymerizations of the D- and L-monomer (Fig. 4). This lower isotacticity is attributed to the distinctly higher heterotactic content of the polymer, which suggests some prevention by the optical antipode, of the isotactic propagation of the opposite stereoisomer.

Goode et al.[23] reported that in the polymerization of MMA by alkyllithium in toluene at a low temperature, the isotactic propagation was conducted with the helical conformation of the propagating chain end. On the other hand, in the polymerization of *N*-carboxyanhydride of γ-benzyl L-glutamate[24] it has been found that the opposite enantiomorph prevents or weakens the helical configuration at the propagating chain end, and that the chain prefers to add the isomer corresponding to its terminal residue. In the polymerization of MBMA it is not certain whether the helical configuration at the chain end does exist or not. However, the results showed distinctly the effect of the asymmetric configuration of the monomer on its stereospecific polymerization.

Compared with the isotactic polymerization of MMA, the small effect of THF on that of MBMA may suggest a strong steric influence on the stereospecific polymerization of the latter monomer. At the higher THF contents in the polymerization solvents, the polymers of MBMA had the same stereoregularities, regardless of the existence of the enantiomorph. The rigid conformation at the propagating chain end, taken in toluene may be released with the solvation by THF to the extent that the propagation is not influenced by the difference between the configurations of the stereoisomers.

The copolymers of D- and L-MBMA had specific rotations proportional to the excess of the D-monomer in the mixtures polymerized. As the copolymers have less isotactic contents than the D-polymer has, they should have lower optical rotations than those observed, if the copolymerization took place randomly with respect to the tacticity. However, the differences were so small that they were comparable to the experimental errors and could not be observed, even if they existed.

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Studies on the Tacticity of Polyacrylonitrile. III. NMR Spectra of Stereoisomers of 2,4,6-Tricyanoheptane as Model Compounds of Polyacrylonitrile

MASAO MURANO and REIZO YAMADERA, *Textile Research Institute, Toyobo Company Ltd., Katata, Otsu, Japan*

Synopsis

The three stereoisomers of 2,4,6-tricyanoheptane were separated and their NMR spectra were studied as the three-unit model compounds of polyacrylonitrile. The chemical shifts and coupling constants obtained from the NMR spectra were compared to those of the two-unit model compounds. The geminal protons for the isotactic methylene are not equivalent, but the difference of the chemical shifts is smaller than that in the *meso* two-unit model. The racemic methylene signals appear at higher field than the *meso* methylene in the heterotactic three-unit model as in the case of the racemic and the *meso* two-unit models. The signals of the methinic protons in triads appear in the order isotactic CH, heterotactic CH, and syndiotactic CH from the high field. From the observed values of the vicinal coupling constants, the chain conformations of the model compounds are also discussed.

INTRODUCTION

High-resolution nuclear magnetic resonance (NMR) spectroscopy has been applied to the studies on the stereoregularity of polyacrylonitrile (PAN) by several investigators.[1–5] The authors have reported the analysis of the NMR spectra of PAN[1] and its two-unit model compounds, *meso* and racemic 2,4-dicyanopentanes (DCNP).[2]

Recently, the studies on the three-unit model compounds of vinyl polymers (2,4,6-trisubstituted heptanes[6–12] have been carried out to obtain useful information for the analysis of polymer spectra as well as two-unit model compounds.[13–21] McMahon and Tincher[15] reported the conformational energies of 2,4-disubstituted pentanes. Abe et al.[6] have interpreted the NMR spectra of poly(vinyl chloride) on the basis of the results from the analysis of the spectra of 2,4,6-trichloroheptanes. Fujiwara et al.[8] discussed the conformation of 2,4,6-heptanetriols from the analysis of the NMR spectra.

The three-unit model compounds of PAN, 2,4,6-tricyanoheptane (TCNH), have been synthesized and separated into three fractions by Takata et al.,[22] but the configurations of each fraction have not been determined.

In our preceding paper,[23] the configurations of the stereoisomers of TCNH (isotactic, heterotactic, and syndiotactic) were determined from the NMR spectra.

In this paper, the detailed analysis of the NMR spectra is given for the three kinds of stereoisomers of TCNH and compared with those of DCNP and PAN.

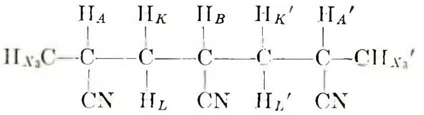
EXPERIMENTAL

The preparation of TCNH and the separation into three kinds of stereoisomers were reported in a previous paper.[23] The NMR spectra at 60 Mc./sec. were measured on Varian A-60 and HR-60 spectrometers at various temperatures. A spin-decoupling technique was used with the side-band method.

The solvents used for measurement of the spectra were chloroform and NaCNS–D_2O. The concentration was about 10%.

ANALYSIS OF THE NMR SPECTRA

The analysis of the NMR spectra of the stereoisomers of TCNH was carried out by the first-order perturbation method reported by Fujiwara et al.[13] The spin system of the model compounds is shown as I.



$$\begin{array}{ccccccccccccc} & & H_A & & H_K & & H_B & & H_{K'} & & H_{A'} & & \\ & & | & & | & & | & & | & & | & & \\ H_{X_3}C & - & C & - & C & - & C & - & C & - & C & - & CH_{X_3'} \\ & & | & & | & & | & & | & & | & & \\ & & CN & & H_L & & CN & & H_{L'} & & CN & & \end{array}$$

I

The methylenic protons are represented by the KL (or $K'L'$) part of an $ABKL$ (or $A'BK'L'$) system, and the methinic protons by the A part of an $AKLX_3$ system and the B part of a $BKLK'L'$ system.

The values of the coupling constants and chemical shifts of the three kinds of stereoisomers were estimated so as to obtain a good agreement between observed and calculated spectra.

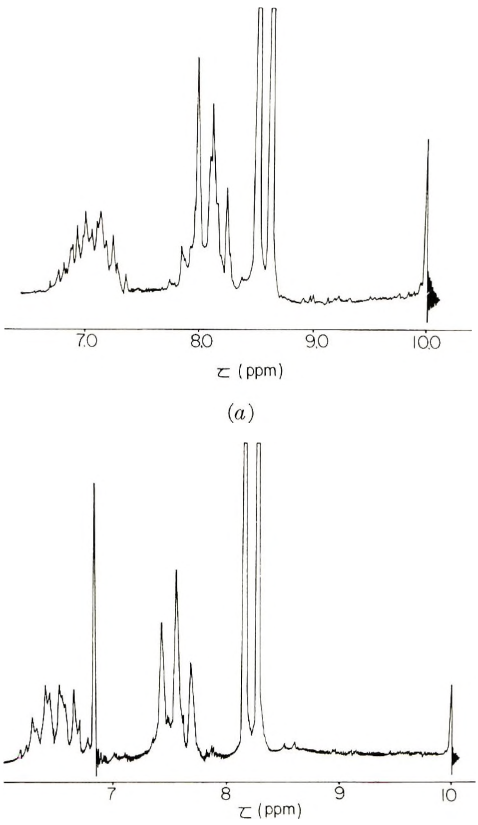
RESULTS AND DISCUSSION

Syndiotactic TCNH

The NMR spectra of syndiotactic TCNH in chloroform and NaCNS–D_2O are shown in Figures 1*a* and 1*b*, respectively. The spectra were measured at various temperatures from 25 to 120°C.

The observed and calculated spectra of the methylenic protons are shown in Figure 2. The spectra of the corresponding two-unit model compound (racemic DCNP) in both solvents are shown in Figures 3*a* and 3*b* for comparison with those of the three-unit model.

The methylenic protons show a 1:2:1 triplet at around 7.5–7.8 ppm in NaCNS–D_2O in both the two- and three-unit models, while their signals



(a)

(b)

Fig. 1. NMR spectra of syndiotactic TCNH: (a) in chloroform and (b) in NaCNS–D_2O at 25°C.

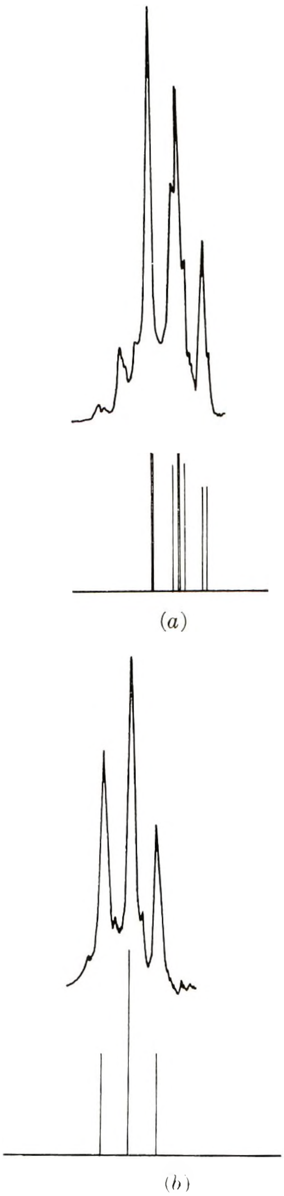
are not triplet in chloroform. However, there is a slight difference in the chemical shifts between the two geminal methylenic protons of the three-unit model in chloroform ($\nu_{KL} \neq 0$). Figure 4 shows the methylenic proton resonance decoupled from the methinic protons. In both solvents, it shows only one peak. This shows that ν_{KL} is not large.

A multiplet due to the methinic protons at lower field is a superposition of two types of spectra, one is derived from the $A(A')$ part of the $AKLX_3$ $(A'K'L'X'_3)$ system and the other the B part of the $BKLK'L'$ system.

The spectrum in NaCNS–D_2O does not show any remarkable temperature dependence, while in chloroform the value of ν_{KL} becomes slightly smaller at higher temperature.

Heterotactic TCNH

Figures 5a and 5b show the NMR spectra of heterotactic TCNH in chloroform and in NaCNS–D_2O, respectively. Figure 6 shows the observed and calculated spectra of the methylenic protons. They can be analyzed



(a)

(b)

Fig. 2. Observed (upper) and calculated (bottom) spectra of methylenic protons of syndiotactic TCNH: (a) in chloroform and (b) in NaCNS–D_2O.

as an overlap of the racemic and *meso* methylenic proton resonances. The racemic part is almost the same as that of the syndiotactic TCNH, while the *meso* part is considerably different from that of the isotactic TCNH and is similar to that of *meso* DCNP.

The signal due to the racemic methylene appears at higher field than that of the *meso* methylene. This fact was also found in the NMR spectra of DCNP.[2] The methylenic proton resonance decoupled from the methinic protons supports this result, as can be seen in Figure 7. The decoupled spectrum consists of the singlet of the racemic methylene and the quartet of the *meso* one; the former is at higher field than the latter.

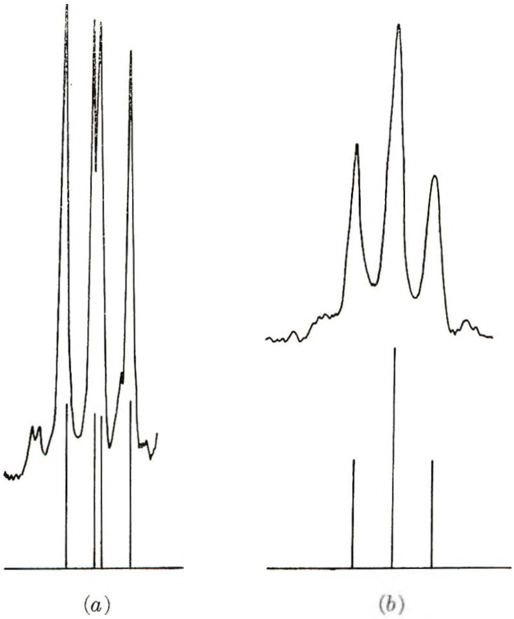


Fig. 3. Methylenic proton resonance of racemic DCNP: (*a*) in chloroform and (*b*) in NaCNS–D_2O.

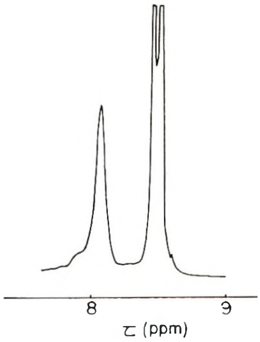
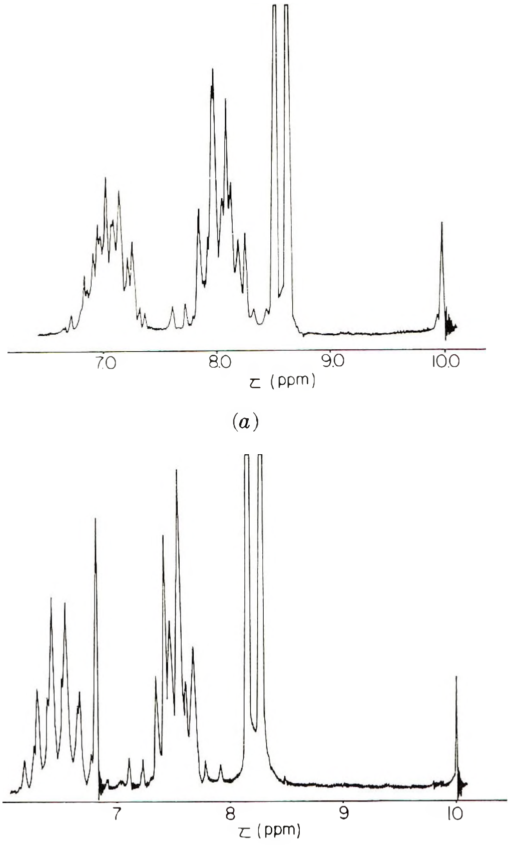


Fig. 4. Methylenic proton resonance decoupled from methinic protons of syndiotactic TCNH in chloroform.

The spectrum of the *meso* methylene does not show any remarkable temperature dependence from 25 to 120°C. in both solvents. The racemic methylene shows the same temperature dependence as in the syndiotactic TCNH.

Isotactic TCNH

The NMR spectra of isotactic TCNH are markedly different in the methylenic signals from those of the *meso* DCNP in both solvents, as shown in Figures 8–10. The difference in the chemical shifts between the geminal methylenic protons, ν_{KL}, is very small in isotactic TCNH compared to *meso* DCNP. Consequently, the methylenic proton resonance decoupled from the methinic protons shows a broad singlet as shown in Figure 11, although the decoupled spectrum of the *meso* DCNP is a quartet.[2]



(*a*)

(*b*)

Fig. 5. NMR spectra of heterotactic TCNH: (*a*) in chloroform and (*b*) in NaCNS–D_2O at 25°C.

The isotactic TCNH shows a remarkable change in the spectra of both solvents at elevated temperature.

A small peak observed at 7.9 ppm may be due to an impurity in the isotactic TCNH. This peak remains in the decoupled spectrum, as shown by the arrows in Figures 8 and 11.

Comparison between the Model Compounds and PAN

In the case of poly(vinyl chloride), Abe et al.[6] reported that the difference of the chemical shifts of the two *meso* methylene protons at 60 Mc./sec. was found to be ca. 7 cps for the isotactic three-unit model while it was ca. 16 cps for the isotactic two-unit model or heterotactic three-unit model. Recently, Doskočilová et al.[12] also reported a similar relationship. The spectrum of poly(vinyl chloride) has been interpreted reasonably on the basis of this result, although Bargon et al.[24] recently reported the non-equivalence of the *meso* methylene protons from the 100 Mc./sec. spectrum.

A similar relationship can be obtained between isotactic TCNH and *meso* DCNP, as shown in Table I.

By analogy with the ν_{KL} values in the model compounds, the *meso* methylene resonance of PAN may be analyzed to be equivalent as in the case of poly(vinyl chloride).

The methinic proton resonance spectrum decoupled from the methylenic protons in PAN is shown in Figure 12. This spectrum is almost the same as that of Bargon et al.[4] As can be seen in Figure 12, there are three kinds of methinic protons, the syndiotactic CH, heterotactic CH, and isotactic CH of triads. Analysis of the three-unit model shows that the isotactic CH appears at the highest field and the syndiotactic CH at the lowest field (Tables II and III). From this fact, the three peaks in Figure 12 can be assigned as the isotactic CH, heterotactic CH, and syndiotactic CH from the high field. This order is same as that in poly(vinyl chloride)

TABLE I
Comparison of Coupling Constants and Chemical Shifts of 2,4-DCNP and 2,4,6-TCNH

		Coupling constants, cps					Chemical shift CH_2
		CH_2—CH				CH_2	
Solvent	Isomer	J_{AK}	J_{BL}	J_{AL}	J_{BK}	J_{KL}	ν_{KL}, ppm
$CHCl_3$	Racemic DCNP	11.5	11.5	4.2	4.2	14.0	0
	Heterotactic (racemic) TCNH	9.8	10.9	6.2	5.1	14.3	3.0
	Syndiotactic TCNH	9.8	10.5	5.8	5.1	14.3	3.0
	Meso DCNP	7.2	7.2	7.2	7.2	14.0	15.0
	Heterotactic (meso) TCNH	8.5	7.5	7.5	8.5	14.3	14.5
	Isotactic TCNH	8.8	7.8	7.8	8.8	14.3	7.1
NaCNS–D_2O	Racemic DCNP	7.5	7.5	7.0	7.0	13.5	0
	Heterotactic (racemic) TCNH	7.5	7.5	7.0	7.0	13.5	0
	Syndiotactic TCNH	7.5	7.5	7.0	7.0	13.5	0
	Meso DCNP	7.5	7.5	7.5	7.5	13.5	13.0
	Heterotactic (meso) TCNH	7.5	7.5	7.5	7.5	13.5	11.2
	Isotactic TCNH	7.5	7.5	7.5	7.5	13.5	6.5

TABLE II

Chemical Shifts and Coupling Constants of 2,4,6-TCNH in $CHCl_3$

	Chemical shift, ppm				Coupling constants, cps					
			CH		CH_3–CH	CH_2	CH_2–CH			
Isomer	CH_3	CH_2	2,6	4	J_{AX}	J_{KL}	J_{AK}	J_{BL}	J_{AL}	J_{BK}
Syndiotactic	8.57	$8.12\begin{cases}8.10\\8.15\end{cases}$	7.05	7.04	7.2	14.3	9.8	10.5	5.8	5.1
Heterotactic										
Meso	8.57	$8.05\begin{cases}7.93\\8.17\end{cases}$	7.10	7.11	7.2	14.3	8.5	7.5	7.5	8.5
Racemic		$8.12\begin{cases}8.10\\8.15\end{cases}$	7.12		7.2	14.3	9.8	10.9	6.2	5.1
Isotactic	8.57	$8.08\begin{cases}8.02\\8.14\end{cases}$	7.15	7.16	7.2	14.3	8.8	7.8	7.8	8.8

TABLE III

Chemical Shifts and Coupling Constants of 2,4,6-TCNH in NaCNS–D_2O

	Chemical shifts, ppm				Coupling constants, cps					
			CH		CH_3–CH	CH_2	CH_2–CH			
Isomer	CH_3	CH_2	2,6	4	J_{AX}	J_{KL}	J_{AK}	J_{BL}	J_{AL}	J_{BK}
Syndiotactic	8.26	7.55	6.47	6.46	7.5	13.5	7.5	7.5	7.0	7.0
Heterotactic										
Meso	8.26	7.51 $\begin{cases} 7.42 \\ 7.61 \end{cases}$	6.50	6.52	7.5	13.5	7.5	7.5	7.5	7.5
Racemic		7.55	6.51		7.5	13.5	7.5	7.5	7.0	7.0
Isotactic	8.26	7.52 $\begin{cases} 7.47 \\ 7.58 \end{cases}$	6.53	6.57	7.5	13.5	7.5	7.5	7.5	7.5

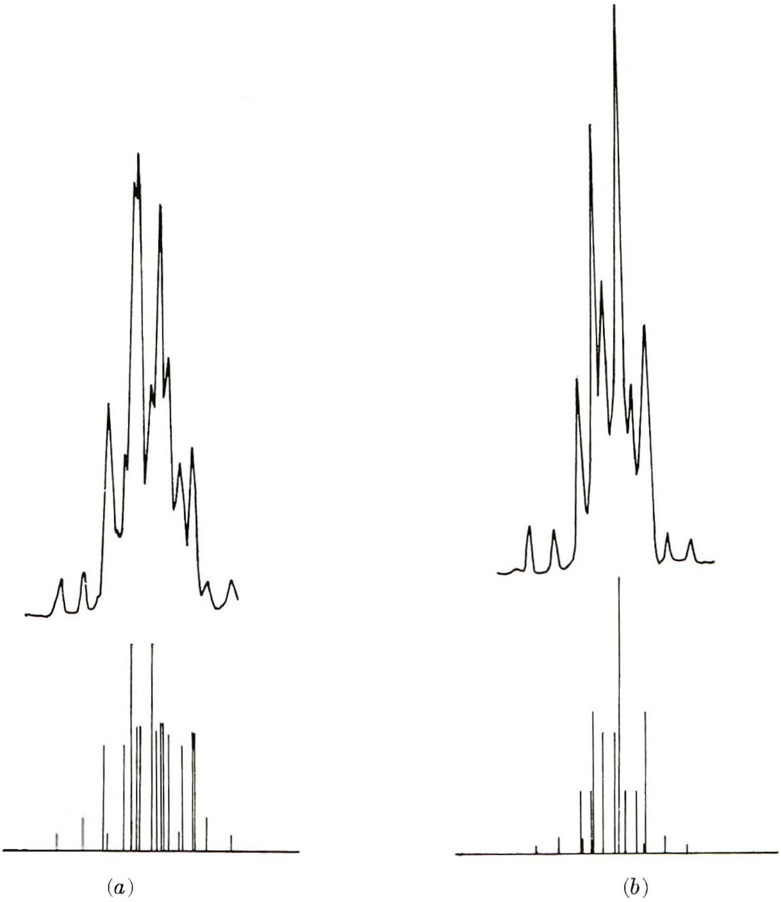


Fig. 6. Observed (upper) and calculated (bottom) spectra of methylenic protons of heterotactic TCNH: (a) in chloroform and (b) in NaCNS–D_2O.

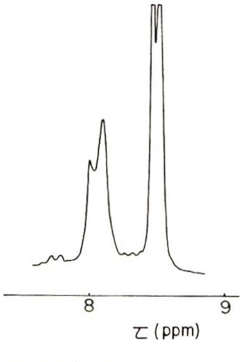
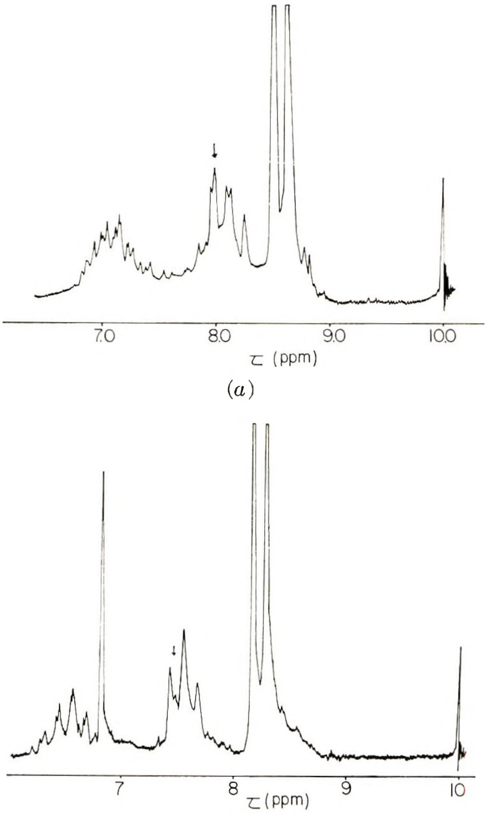


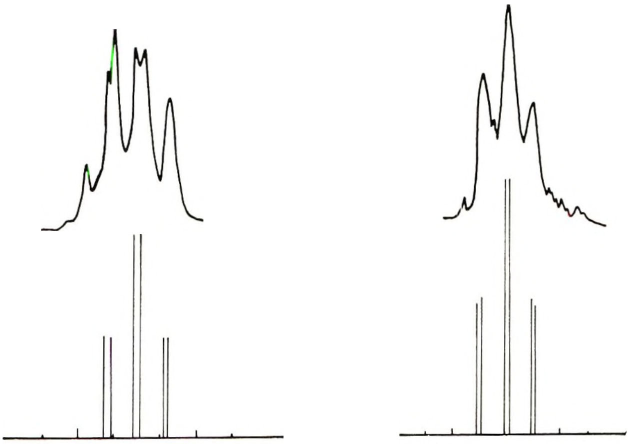
Fig. 7. Methylenic proton resonance decoupled from methinic protons of heterotactic TCNH in chloroform.



(a)

(b)

Fig. 8. NMR spectra of isotactic TCNH: (a) in chloroform and (b) in NaCNS–D_2O at 25°C.



(a) (b)

Fig. 9. Observed (upper) and calculated (bottom) spectra of methylenic protons of isotactic TCNH: (a) in chloroform and (b) in NaCNS–D_2O.

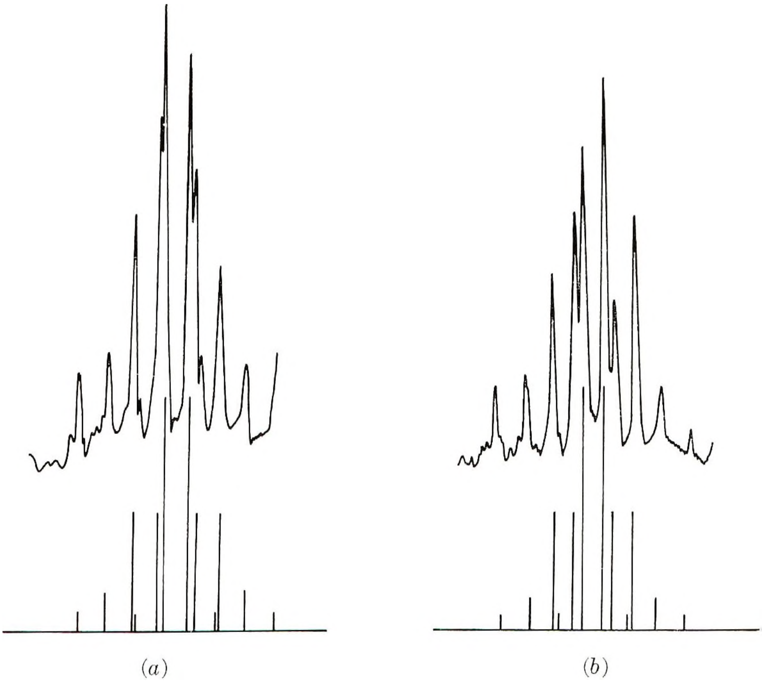


Fig. 10. Methylenic proton resonance of *meso* DCNP: (*a*) in chloroform and (*b*) in NaCNS-D_2O.

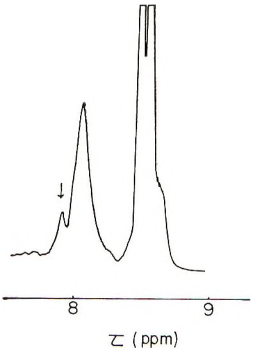


Fig. 11. Methylenic proton resonance decoupled from methinic protons of isotactic TCNH in chloroform.

Chain Conformation of the Model Compounds

Recently, the chain conformations of model compounds have been often discussed from the analysis of their NMR spectra; especially the model compounds of poly(vinyl chloride),[6,12,15] poly(vinyl alcohol),[8] and polystyrene[20] were studied in detail.

The coupling constants obtained from the NMR spectrum take the value averaged over all of the isomeric forms.[25] From this respect, the

TABLE IV
Chemical Shifts and Coupling Constants of 2,4-DCNP

		Chemical shifts, cps						
		CH_3–CH	CH_2	CH_2–CH				
Isomer	Solvent	J_{AX}	J_{KL}	J_{AK}	J_{BL}	J_{AL}	J_{BK}	ν_{KL}, ppm
Meso	$CHCl_3$	7.2	14.0	7.2	7.2	7.2	7.2	15.0
Racemic	$CHCl_3$	7.2	14.0	11.5	11.5	4.2	4.2	0
Meso	NaCNS–D_2O	7.5	13.5	7.5	7.5	7.5	7.5	13.0
Racemic	NaCNS–D_2O	7.5	13.5	7.5	7.5	7.0	7.0	0

authors have discussed the chain conformation of DCNP.[2] The NMR spectrum of the *meso* DCNP shows that $J_{AK} = J_{BL} = J_{AL} = J_{BK}$, while in the racemic form, $J_{AK} = J_{BL} \neq J_{AL} = J_{BK}$ in CCl_4, pyridine, and benzene and $J_{AK} = J_{BL} = J_{AL} = J_{BK}$ in NaCNS–D_2O and DMSO-*d*6. These results were interpreted as follows. In the solution, the *meso* DCNP is considered to have two equivalent conformations, TG and GT, which are mirror images of each other. The racemic DCNP, however, might have either the TT or GG conformation predominantly in CCl_4, pyridine, and benzene, while it has the two conformers with almost equal probability in NaCNS–D_2O and DMSO-*d*6.

The chain conformation of TCNH can be discussed in the same manner. In the isotactic TCNH, $J_{AK} = J_{BL} \approx J_{AL} = J_{BL}$ in chloroform and $J_{AK} = J_{BL} = J_{AL} = J_{BL}$ in NaCNS–D_2O. This relation is almost the same as in the *meso* DCNP, and suggests that the three-unit model takes the same conformation as the two-unit model, TGTG and GTGT, considering the possible conformations.

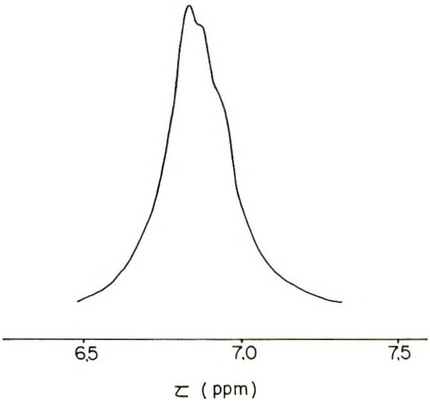


Fig. 12. Methinic proton resonance of PAN decoupled from methylenic protons.

In the heterotactic TCNH, the *meso* methylene takes the TG and GT forms, because $J_{AK} = J_{BK} \approx J_{AL} = J_{BL}$ in chloroform and $J_{AK} = J_{BK} = J_{AL} = J_{BL}$ in NaCNS–D_2O as in the case of *meso* DCNP. The racemic methylene has also the same relation as the racemic DCNP, $J_{AK} = J_{BE} \approx J_{AL} = J_{BK}$ in NaCNS–D_2O and $J_{AK} \approx J_{BL} \neq J_{AL} \approx J_{BK}$ in chloroform, so it takes TT and GG with almost equal probability in NaCNS–D_2O, and TT or GG predominantly in chloroform. Therefore, the heterotactic TCNH takes either one or two conformations in TTTG, TTGT, and GGTG in chloroform, and it takes these three forms in NaCNS–D_2O.

In the syndiotactic TCNH, the same relation can be found as that of racemic DCNP in NaCNS–D_2O, $J_{AK} = J_{BL} \approx J_{AL} = J_{BK}$, and almost the same as that for the two-unit and three-unit model in chloroform (Tables II–IV). Accordingly in chloroform, it takes the TTTT form, but in NaCNS–D_2O both TTTT and TTGG (GGTT).

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Reactions of Living Polystyrene with Difunctional Nitriles to Produce Specifically Placed Grafting Sites

J. A. GERVASI,* A. B. GOSNELL,† D. K. WOODS, and V. STANNETT,‡ *Camille Dreyfus Laboratory, Research Triangle Institute, Research Triangle Park, North Carolina 27709*

Synopsis

Graft polymers have been synthesized with two equal length branches and one or two branches of a different length or composition. The first step was a coupling reaction of living polystyrene with a difunctional nitrile. The product was hydrolyzed to form a ketone-containing backbone. Subsequently another sample of living polystyrene or of poly-2-vinylpyridine was added to the backbone to form the graft. Anionic polymerization was used for the synthesis of backbone and side chains, so all of the products are well defined. The products and reaction sequences also serve as models for a general synthesis of well-defined comb-shaped polymers, in which the length of the backbone, and the number, length, and spacing of the side chains may be controlled.

Introduction

The structure of graft polymers has generally been more or less random in terms of the number, length, and spacing of side chains on the backbone. This is a consequence of the synthesis methods. With free-radical initiation, for example, which can be induced by a number of techniques,[1] the active sites are formed in a random placement along the backbone. The side chains then grow and terminate in a generally broad molecular weight distribution.

Better-defined graft polymers have been prepared by using anionic polymerization techniques. Altares et al.[2] have synthesized comb-shaped polystyrene by placing chloromethyl groups along the backbone, then effecting a substitution reaction to replace the chlorine with a polystyrene side chain. Gervasi et al.[3] applied the same technique to synthesize a polystyrene–polyvinylpyridine graft copolymer, and Gosnell et al.[4] added living polystyrene as a side chain directly to polyvinylpyridine. Inasmuch as backbone and side chains had been prepared by anionic polymerization, they had very narrow molecular weight distributions, and, therefore, better defined structures than the earlier graft systems. Yet even in these cases the num-

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* Present address: Celanese Research Company, Summit, New Jersey.

† To whom correspondence should be addressed.

‡ Present address: Department of Chemical Engineering, North Carolina State University, Raleigh, N. C.

TABLE I
Coupling Reactions of Living Polystyrene to Form Backbones

Sample number	Coupling agent	Terminal anion	Reaction conditions	$\bar{M}_v$ of single chain	$\bar{M}_v$ of bulk coupled product	Dimer in coupled product (calcd.), wt.-%
345-19-II	*p*-Cyanobenzyl bromide	Styryl	Equivalent amount; 25°C., 10 hr.	868,000	1,030,000	31.4
345-24-II	*p*-Cyanobenzyl bromide	1,1-Diphenylethyl	Titrated at 50°C. over a 1-hr. period	69,200	70,500	3.7
345-33-II	Terephthalonitrile	1,1-Diphenylethyl	Titrated at 25°C. over 8-hr. period	31,100	36,400	29.1
345-42-I	*p*-Cyanobenzyl chloride	Styryl	Equivalent amount; at 60°C., 10 hr.	555,000	1,010,000	90.1
345-45-I	*p*-Cyanobenzyl chloride	Styryl	Equivalent amount; at 50°C.; heated at 60°C. for 10 hr.	81,300	108,000	39.8
345-45-II	*p*-Cyanobenzyl chloride	1,1-Diphenylethyl	Equivalent amount at 50°C.; heated at 60°C. for 10 hr.	81,300	86,500	12.0
345-52-II	*p*-Cyanobenzyl chloride	α-Methylstyryl	Twofold excess of living polymer; 25°C., 20 hr.; 60°C., 24 hr.	40,500	52,200[a,b]	44.8
345-56-II	Terephthalonitrile	Styryl	Equivalent amount; 25°C., 10 hr.; 60°C., 24 hr.	44,900	66,500[a,b]	65.0

345-56-III	Terephthalonitrile	α-Methylstyryl	Equivalent amount; 25°C., 10 hr.; 60°C., 24 hr.	44,900	63,900[a]	59.5
345-61-II	Adiponitrile	Styryl	Equivalent amount; 25°C., 24 hr.; 60°C., 24 hr.	105,000	107,000	Nil
345-61-III	Adiponitrile	α-Methylstyryl	Equivalent amount; 25°C., 8 hr.; 60°C., 23 hr.	105,000	106,000	Nil
345-64-II	Adiponitrile	Styryl	Equivalent amount; 25°C., 10 hr.; 60°C., 32.5 hr.	31,500	31,100	Nil
345-64-III	Adiponitrile	α-Methylstyryl	Equivalent amount; 25°C., 10 hr.; 60°C., 32.5 hr.	31,500	29,400	Nil
345-67-IV	Diethyl carbonate	α-Methylstyryl	Died due to impurities in coupling solution (very rapid loss of color)	31,500	29,200	Nil
345-67-V	Diethyl carbonate	Styryl	Equivalent amount, 25°C., 72 hr.	31,500	42,800[a,b]	52.8
345-69-VI	Sodium ethyl[c] carbonate	Styryl	Equivalent amount; 25°C., 24 hr.; 60°C., 48 hr.	31,500	26,500	Nil
345-69-VII	Sodium ethyl[d] carbonate	α-Methylstyryl	Equivalent amount; 25°C., 24 hr.; 60°C., 48 hr.	31,500	40,500[a]	44.4

[a] Fractionated.

[b] Used in addition reaction.

[c] Sodium ethyl carbonate was not soluble in benzene.

[d] Sodium ethyl carbonate solution was prepared with the use of tetrahydrofuran but was not completely soluble.

TABLE II

Addition Reactions of Living Polystyrene and Living Poly-2-vinylpyridine to the Hydrolyzed Backbones

Sample number	Backbone		Coupling agent	Side chain		Conditions	Yield of crafts, %
	Calcd. M_w	Anion		Polymer	$\bar{M}_v$		
345-76-II	81,000	α-Methyl-styryl	*p*-Cyanobenzyl[a] chloride	PS	67,900	Titrated to an excess of anions at ≈6°C.; then 25°C., 10 hr.; 62°C., 3 hr.	31.4
345-88-II	81,000	α-Methyl-styryl	*p*-Cyanobenzyl[a] chloride	P2VP	137,500	Titrated to an excess of anions; 25°C., 48 hr.	18.7[d]
345-98-V	89,800	Styryl	Terephthalonitrile[b]	PS	34,800	Titrated to an excess of anions; 25°C., 48 hr.; 70°C., 5 hr.	42.4[e]
345-105-III	89,800	Styryl	Terephthalonitrile[b]	P2VP	52,200	Titrated to an excess of anions; 25°C., 36 hr.; 70°C., 5 hr.	30.2[d]
345-108-II	63,000	Styryl	Diethyl carbonate[c]	P2VP	127,500	Titrated to an excess of anions; 25°C., 48 hr.; 70°C., 9 hr.	5.0[d]

[a] Backbone 345-52-II in Table I.

[b] Backbone 345-56-II in Table I.

[c] Backbone 345-67-V in Table I.

[d] From extraction data, based on one side chain per backbone.

[e] Per cent graft estimated from concentration vs. elution volume curve.

ber of side chains on each backbone and the distances between the side chains were randomly distributed.

The present communication is concerned with an approach to the elimination of this last degree of randomness, that is the synthesis of a comb-shaped graft in which not only the lengths of the backbone and side chains are narrowly defined, but the number of chains on each backbone and the spacing between them are known.

The backbone precursors were prepared by coupling monofunctional-living polystyrene, initiated by butyllithium, with difunctional nitriles. This gave a linear chain with one or two active sites precisely at the center. These coupled polymers were than hydrolyzed to the ketone in acid media to give backbones with the desired grafting sites. The coupling reactions were tested by using living polystyrene having styryllithium, α-methylstyryllithium, and 1,1-diphenylethyllithium endgroup anions. The nitriles investigated as possible coupling agents include *p*-cyanobenzyl chloride, *p*-cyanobenzyl bromide, *p*-cyanobenzonitrile, and adiponitrile. Other possible coupling agents tested were diethyl carbonate and sodium ethyl carbonate. After hydrolysis the backbone polymers were purified by column fractionation and used in grafting reactions with living polystyrene or living poly-2-vinylpyridine.

Experimental

The preparation of the living polystyrene and living poly-2-vinylpyridine used in this work employed materials, apparatus, and techniques already described in earlier papers of this series.[3,4] The living polystyrene in some instances was capped with α-methylstyrene or 1,1-diphenylethylene. The α-methylstyrene was purified by distillation from the blue complex of sodium and benzophenone, the diphenylethylene was purified by condensing small amounts of benzene alternately in the monomer, then back in the sodium–benzophenone solution. The capping monomers were later distilled or poured into the solution of living polystyrene. This gave a polymer which was essentially polystyrene, but which had an anion endgroup with no α-hydrogen.

The nitrile or ester coupling reagents listed in Table I were recrystallized or redistilled, then purified by the same procedure as the 1,1-diphenylethylene above. The coupling reactions were carried out by pouring the coupling agent solution into the living polymer and stirring for various times and temperatures as shown in Table I.

After the coupling reaction the reactor was opened and any remaining anions were destroyed with methanol. The polymers were precipitated in methanol, filtered and dried in a vacuum oven at 60°C. for at least 16 hr.

The expected reaction product from the nitrile was an imine which was presumably converted to the ketone by acid hydrolysis. Approximately 5 g. of the coupled polystyrene was dissolved in 30 ml. benzene to which was added 7 ml. distilled H_2O and 100 ml. of 72% H_2SO_4. After 2 hr. stirring, 200 ml. distilled H_2O was added. The mixture was refluxed for 3–4 days with occasional addition of benzene to maintain the polymer in solution. The hydrolyzed product was reprecipitated three times in methanol. After recovery from the methanol and drying, the product was fractionated by a column elution as already described.[5]

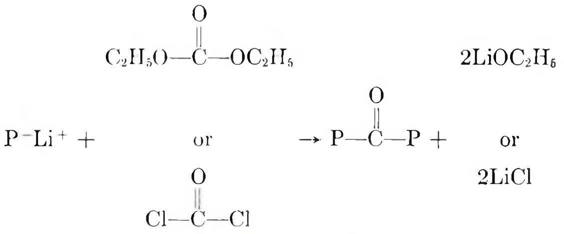
The fractionated material was then used as backbone to make the branched polymer. The backbone was placed in a reactor chamber and dried by the same procedure as the 1,1-diphenylethylene, then dissolved in the benzene. Styrene or 2-vinylpyridine was polymerized in the reactor and the living polymer solution added to the backbone solution. The conditions for the branching reaction are listed in Table II.

The grafted products were characterized by osmotic pressure molecular weight measurements and/or by solvent extraction.

Discussion

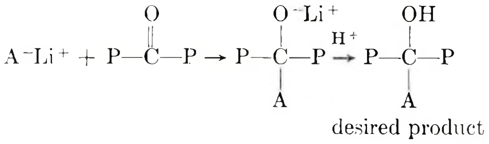
The central problem in this work was to provide a backbone of well-defined length with an attachment site at a known and predetermined position. Later, the side chain could be added to the backbone by methods already known.[3,4,6,7] The chain length may be defined by anionic polymerization, but the difficulty lies in placing the attachment site. For example, chloromethylation is incapable of a specific placement. Addition to the ester of methyl methacrylate is also unsatisfactory because there is no obvious method for placing a single methyl methacrylate unit at a specific spot along the backbone.

A possible solution to this problem would be to couple living polystyrene of narrow molecular weight distribution with phosgene or diethyl carbonate [eq. (1)].



$$P^-Li^+ + \begin{matrix} C_2H_5O-\overset{O}{\overset{\|}{C}}-OC_2H_5 \\ \text{or} \\ Cl-\overset{O}{\overset{\|}{C}}-Cl \end{matrix} \rightarrow P-\overset{O}{\overset{\|}{C}}-P + \begin{matrix} 2LiOC_2H_6 \\ \text{or} \\ 2LiCl \end{matrix} \qquad (1)$$

If the ketone-containing product could be isolated, another narrow distribution polymer could be grafted later.



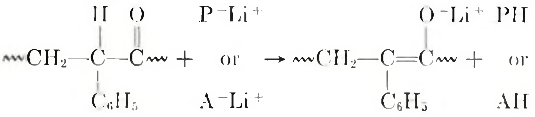
$$A^-Li^+ + P-\overset{O}{\overset{\|}{C}}-P \rightarrow P-\underset{\underset{A}{|}}{\overset{O^-Li^+}{\overset{|}{C}}}-P \xrightarrow{H^+} P-\underset{\underset{\underset{\text{desired product}}{A}}{|}}{\overset{OH}{\overset{|}{C}}}-P \qquad (2)$$

The product from reaction (2) could fulfill the stated requirements. The backbone length would be defined because the P lengths would be identical. The grafting site would necessarily be at the center of the backbone. The side chain could be within broad limits, of any desired and known length.

Finally, the carbonyl group is known[7,8] to react with living polymer to form an addition product.

There are several possible objections to this scheme, however. The most serious is the likelihood that the carbonyl group would react with living polystyrene during the backbone preparation [reaction (1)], to form a three-branched product directly. In that event, there would be no active site remaining for reaction (2).

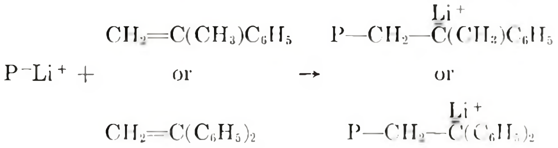
Another side reaction which can occur during reactions (1) or (2) is hydrogen abstraction [eq. (3)].



$$\sim CH_2-\overset{H}{\underset{C_6H_5}{C}}-\overset{O}{\overset{\|}{C}}\sim + \begin{matrix}P^-Li^+\\ \text{or}\\ A^-Li^+\end{matrix} \rightarrow \sim CH_2-\underset{C_6H_5}{C}=\overset{O^-Li^+}{C}\sim + \begin{matrix}PH\\ \text{or}\\ AH\end{matrix} \qquad (3)$$

After reaction (1), α-hydrogen abstraction would be enhanced because of the activation by both the neighboring phenyl and keto groups.

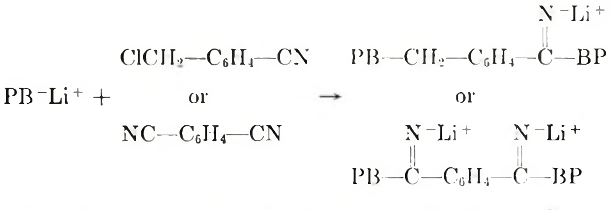
The solutions proposed for these difficulties were to use nitriles rather than esters for the backbone preparation[9] and, if necessary, to cap the living polystyrene in reaction (1) with 1,1-diphenylethylene or α-methylstyrene so that there would be no hydrogen adjacent to the addition site. The expected sequence would be as shown in eq. (4):



$$P^-Li^+ + \begin{matrix}CH_2=C(CH_3)C_6H_5\\ \text{or}\\ CH_2=C(C_6H_5)_2\end{matrix} \rightarrow \begin{matrix}P-CH_2-\overset{Li^+}{\bar{C}}(CH_3)C_6H_5\\ \text{or}\\ P-CH_2-\overset{Li^+}{\bar{C}}(C_6H_5)_2\end{matrix} \qquad (4)$$

where P^-Li^+ denotes polystyryllithium.

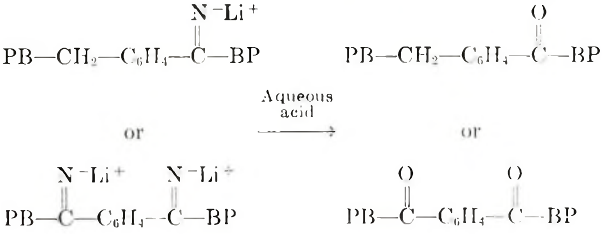
The new living polymer may then react with a nitrile [eq. (5)]:



$$PB^-Li^+ + \begin{matrix}ClCH_2-C_6H_4-CN\\ \text{or}\\ NC-C_6H_4-CN\end{matrix} \rightarrow \begin{matrix}PB-CH_2-C_6H_4-\overset{N^-Li^+}{\overset{\|}{C}}-BP\\ \text{or}\\ PB-\overset{N^-Li^+}{\overset{\|}{C}}-C_6H_4-\overset{N^-Li^+}{\overset{\|}{C}}-BP\end{matrix} \qquad (5)$$

where PB^-Li^+ denotes polystyryllithium capped with 1,1-diphenylethylene or α-methylstyrene.

No further addition takes place after the imine formation in reaction (5). The polymer could then be isolated and hydrolyzed to the ketone:



$$\begin{matrix}PB-CH_2-C_6H_4-\overset{N^-Li^+}{\overset{\|}{C}}-BP\\ \text{or}\\ PB-\overset{N^-Li^+}{\overset{\|}{C}}-C_6H_4-\overset{N^-Li^+}{\overset{\|}{C}}-BP\end{matrix} \xrightarrow{\text{Aqueous acid}} \begin{matrix}PB-CH_2-C_6H_4-\overset{O}{\overset{\|}{C}}-BP\\ \text{or}\\ PB-\overset{O}{\overset{\|}{C}}-C_6H_4-\overset{O}{\overset{\|}{C}}-BP\end{matrix} \qquad (6)$$

The product from reaction (6) may now be used for grafting as in reaction (2), but with no danger of premature loss of the active site. This product would also fulfill the requirement for the backbone because it would be of well-defined length with one or two attachment sites at the center. The nitrile reactions, therefore, were selected for study.

Substitution of a benzyl halide by a lithium reagent is well known.[2,3] The feasibility of this scheme, therefore, would depend upon the ability of a lithium reagent to add to a nitrile. Fortunately, the reactions of interest have been clearly demonstrated by Vaulx et al.,[9] who added a substituted benzyllithium to benzonitrile and hydrolyzed to the ketone. It remained to duplicate the small molecule reactions with polymer anions.

As a first test, polystyryllithium was terminated by reaction with benzonitrile. The reaction appeared to proceed smoothly, with the rapid but gradual disappearance of anion color. The product was hydrolyzed with aqueous acid, and several attempts were made to demonstrate the presence of the carbonyl group. None of the methods proved to be sufficiently sensitive. For example, infrared absorption at 5.8 μ could not be detected. Reaction with 2,4-dinitrophenylhydrazine did not give a colored product, nor could any unusual ultraviolet-visible absorption be detected as compared to a blank. Presumably a single ketone group in a high polymer chain (molecular weight of 10^4 or higher) could not be detected by these methods. A more sensitive test, however, would be reaction of the ketone-containing polymer with a living polymer. The addition reaction would give a product of higher molecular weight than either component. The molecular weight increase was demonstrated easily by viscosity measurements, so the reactions of polystyryllithium with nitriles and ketones were shown to be feasible. The next step was to prepare a graft polymer according to the reaction sequence (4), (5), (6), (2).

The experiments proceeded, for the most part, in accord with the plan. The major practical difficulty encountered was the low yield of the desired product. This probably reflected poor efficiency of the hydrolysis, reaction (6), or of the coupling step, reaction (2). These results will now be discussed in more detail.

The backbone preparation appeared fairly straightforward. Styrene was polymerized anionically, a small sample was taken, and the remaining solution of living polymer was divided into two equal portions. One portion was capped by adding a small amount of 1,1-diphenylethylene or α-methylstyrene as in reaction (4) while the other portion was used without further treatment. To each of these living polymers was added a solution of nitrile coupling agent as in reaction (5), and the reaction was allowed to proceed as shown in Table I. The polymers were recovered and subjected to acid hydrolysis to form the backbone, reaction (6). They were then fractionated to isolate virtually monodisperse polystyrene for subsequent grafting. Solutions of these backbones were then added to living polystyrene or living poly-2-vinylpyridine to form the grafts as in reaction (2).

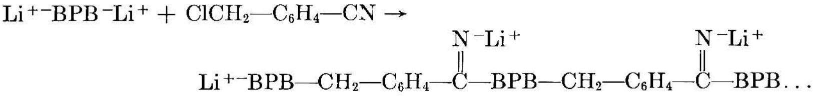
The graft polymers were recovered by column methods. In the case of polystyrene backbones and polystyrene side chains, a fractionation[5] was carried out. For the polystyrene backbone–poly-2-vinylpyridine side chains, the column was eluted successively with methanol (to remove only the ungrafted side chains), then cyclohexane (to remove only ungrafted backbone), then with benzene to recover the residue which was the true graft.[3,4]

The yield of graft varied from approximately 20 to 40%. There are not enough data to assess the reaction conditions with confidence. Grafting appeared to be promoted, however, by higher temperature and retarded by increasing molecular weight (or lower concentration) of the side chain. The results do not show a striking advantage for the capping procedure so that reaction (3) was not a major factor in this work. It may yet be important, however, if means can be found to improve the yields of graft. At least there was no apparent hindrance to the coupling or grafting reactions due to α-methylstyryl endgroups.

There was still a possibility that diethyl carbonate could be useful for the backbone preparation according to reaction (1). This could come about if, for example, the rate of replacement of the ester groups was much more rapid than the addition to the carbonyl. The reaction of living polystyrene and diethyl carbonate yielded almost an equivalent amount of polymer which contained two and three chains. This reaction product was analyzed by fractionation and the desired backbone isolated. As shown in Table II, however, very little graft was produced from this backbone or from one prepared with sodium ethyl carbonate. Adiponitrile was also ineffective as a coupling agent, perhaps due to acidic hydrogens α to the nitrile, similar to reaction (3).

Despite the somewhat disappointing yields, this work has attained two major goals. First, a series of reactions has been shown to be feasible for the preparation of backbones with specifically placed attachment sites. Second, hitherto unknown graft polymers have been prepared which have two equal length branches and one or two branches of another length or composition. Inasmuch as all of the polymers have been synthesized by using anionic initiation, the products were very well defined.

The products synthesized in this work are considered to be of interest in themselves. But they also serve as models for a general synthetic scheme for comb type branched polymers. The next step would be to extend this work to synthesize grafts with more than one branch point. This would follow simply by using dianions in place of monoanions in the backbone coupling reaction, that is, by using $\mathrm{Li^{+}BPB^{-}Li^{+}}$ or $\mathrm{Li^{+-}P^{-}Li^{+}}$ in place of $\mathrm{PB^{-}Li^{+}}$ in reaction (5):



$$\mathrm{Li^{+-}BPB^{-}Li^{+} + ClCH_2\text{—}C_6H_4\text{—}CN} \rightarrow$$
$$\mathrm{Li^{+-}BPB\text{—}CH_2\text{—}C_6H_4\text{—}}\overset{\mathrm{N^{-}Li^{+}}}{\overset{\|}{\mathrm{C}}}\mathrm{\text{—}BPB\text{—}CH_2\text{—}C_6H_4\text{—}}\overset{\mathrm{N^{-}Li^{+}}}{\overset{\|}{\mathrm{C}}}\mathrm{\text{—}BPB}\ldots \tag{7}$$

By this means, as many attachment sites as desired could be placed in the backbone, the exact number being controlled by the mole ratio of anions to coupling agent. This would provide a backbone with attachment positions at precisely spaced intervals along the chain because all of the BPB units are of identical length. The subsequent reactions of hydrolysis to the ketone, fractionation to isolate essentially monodisperse backbones, and addition of the side chains would all follow exactly as above for the single side chain preparation. It would be very desirable to improve the yield of graft as an aid in isolating the final graft sample. Presumably, this means improving the hydrolysis efficiency, because the carbonyl addition appears to proceed smoothly as shown by the work of Vaulx et al.[9] It is quite possible, however, that even the conditions examined in this work would suffice to produce a backbone with rigorously spaced carbonyl sites. If this can be accomplished, it would provide comb type branched polymers with completely controlled structure. That is, the length of the backbone and side chains and the spacing between the side chains would all be clearly defined.

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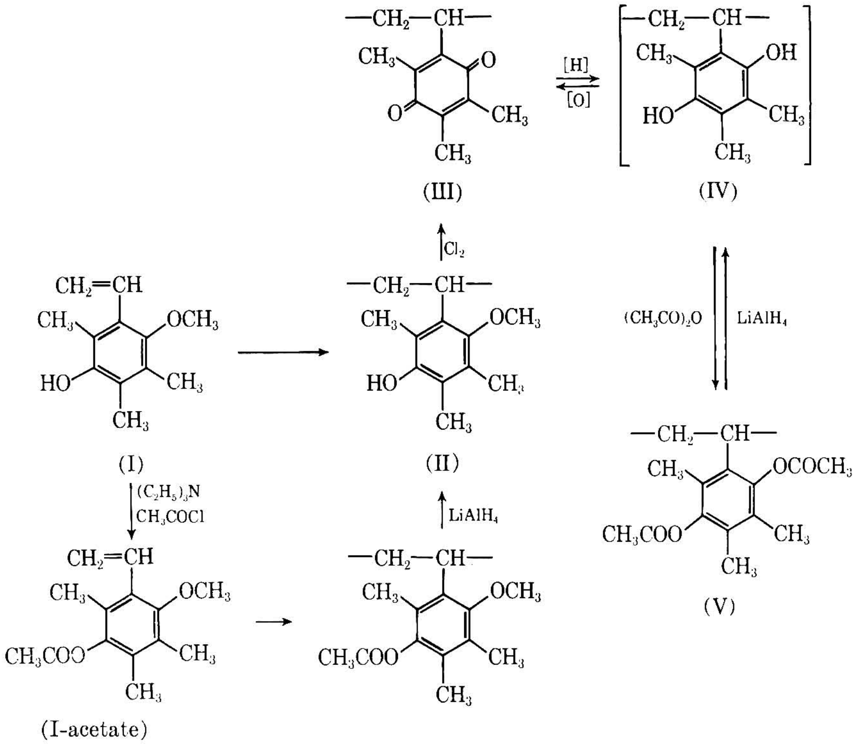
Electron-Transfer Polymers. XXX. Preparation of Poly(1-vinyl-3,4,6-trimethyl-2,5-benzoquinone)

NOBUO NAKABAYASHI, GERHARD WEGNER, and
HAROLD G. CASSIDY,
Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06520

Synopsis

1-Vinyl-3,4,6-trimethyl-2-methoxy-5-hydroxy-benzene (I) was prepared in good yield by the Wittig reaction from the corresponding chloromethyl compound. It could be polymerized cationically to low molecular weight material. The polymer could be oxidized to poly(1-vinyl-3,4,6-trimethyl-2,5-benzoquinone) (III) and could be reduced to the corresponding hydroquinone. Compound (I) was acetylated at the phenolic hydroxyl group and polymerized. The acetyl group was quantitatively reduced with lithium aluminum hydride, and the resulting polymer could be oxidized quantitatively to (III). Its molecular weight was a little higher than that prepared directly from (I).

Polyvinylhydroquinone electron-transfer polymers (redox polymers) are prepared by polymerizing the corresponding vinyl monomers in which the two hydroquinone hydroxyls are protected. The protecting groups are subsequently removed.[1] As protecting groups, ether,[2] acetate,[3] benzoate,[3] and acetal[4] have been studied. Each has its limitations.[1] In this paper we investigate a new approach. A monoether is employed instead of the diether, and after polymerization the ether group is cleaved by oxidation. That the still phenolic monoether may polymerize is understandable, because vinyl phenols polymerize.[5,6] That the monoether can be successfully oxidized without crosslinking[7] rests on the fact that in this polymer all positions on the hydroquinone ring are substituted. It was found that the phenolic hydroxyl present in the monoether adversely affects cationic polymerization. The monomer was therefore further protected by forming the acetate. This was then polymerized. The acetate group could be removed from the polymer by reduction with lithium aluminum hydride. Then the resulting polymer could be oxidized. We report a method of preparing the monomer 1-vinyl-3,4,6-trimethyl-2-methoxy-5-hydroxybenzene (I) by means of the Wittig reaction,[8] for its polymerization. The resulting polymer (II) may be oxidized and yellow poly(1-vinyl-3,4,6-trimethyl-2,5-benzoquinone) (III) isolated. This can be reductively acetylated to the hydroquinone diacetate form (V). We also report the synthesis of 1-vinyl-3,4,6-trimethyl-2-methoxy-5-acetoxy-benzene (I-acetate), its polymerization, and its reduction with lithium aluminum hydride to (II).



EXPERIMENTAL

Preparation of Monomer (I)

A mixture of 53.1 g. (0.24 mole) of 1-chloromethyl-5-hydroxy-2-methoxy 3,4,6-trimethyl benzene,[9] 65.6 g. (0.25 mole) of triphenyl phosphine, and 250 ml. of toluene was refluxed for 3 hr. The precipitated triphenyl(3-hydroxy-6-methoxy-2,4,5-trimethyl)benzylphosphonium chloride was washed with toluene and dried. The yield was 113.2 g. (95.4%). To 16.0 g. (0.034 mole) of this material in 150 ml. of commercial-grade tetrahydrofuran (THF) was added 22.7 ml. (0.037 mole) of *n*-butyllithium reagent (15.18% in *n*-hexane, Foote Mineral Co.) with cooling in an ice bath (see note f to Table I). The initially dark-red solution became yellowish white after 1 hr. To this was added in one portion 10.0 g. of trioxane in 50 ml. of THF, and the mixture was brought to reflux and kept refluxing for 1 hr. The solvent was removed under reduced pressure and the residue extracted with ether. Removal of the ether gave a brown oil, which distilled at 105 to 120°C. and 1 mm. Recrystallization from *n*-heptane yielded very pale yellow crystals; mp. 67–68°C.

ANAL. Calcd. for $C_{12}H_{16}O_2$(%); C, 74.96; H, 8.39. Found (%): C, 74.90; H, 8.45.

TABLE I

Preparation of 1-Vinyl-3,4,6-trimethyl-2-methoxy-5-hydroxybenzene[a]

	Phosphonium chloride, g. (moles)	Base,[b] ml. or g. (moles)	Solvent, ml.	Time,[c] hr.	CH_2O,[d] g. per solvent, ml.	Temp., °C.	Time, hr.	Yield,[e] g. (%)
1	16.0 (0.0334)	A 51.6 (0.083)	THF,[f] 150	1	10.0, THF,[f] 50	reflux	1	5.8 (90.5)
2	47.8 (0.100)	A 155 (0.25)	THF,[f] 500	0.5	30.0, THF,[f] 100	reflux	1.5	16.3 (84.9)
3	16.0 (0.0334)	A 20.8 (0.034)	THF,[f] 150	1	10.0, THF,[f] 30	reflux	1	5.0 (78.0)
4	16.0 (0.0334)	A 20.8 (0.034)	Ether,[f] 200	0.85	10.0, Ether,[f] 50	room reflux	0.4 1.25	 1.8 (28.1)
5	16.0 (0.0334)	A 22.7 (0.037)	THF, 150	1	10.0, THF, 50	reflux	1	6.8 (100)
6	90.0 (0.190)	A 145 (0.27)	THF, 500	1.5	55.0, —	reflux	1.5	31.6 (86.6)
7	4.78 (0.010)	B 1.2 (0.03)	H_2O, 50	0.33	3.7, H_2O, 10	room	2.5	0
8	4.78 (0.010)	B 1.2 (0.03)	H_2O, 50 C_2H_5OH, 50	1 (80°C.)	3.7, H_2O, 10	80	3	0.39 (20)
9	4.78 (0.010)	C 0.30 (0.13)	C_2H_5OH, 50	1 (60°C.)	20,—	60	1.5	1.15 (60.0)

[a] With a ratio of base to phosphonium chloride of 1:1 a good yield of final product is obtained from THF (runs 1, 2, 3, 5) but not from ether. It is thought that formation of phenoxide (itself a base) is an alternative, temporarily competing, pathway in the reaction. The low yield in ether may reflect poor solubility of lithium phenoxide in this solvent, or perhaps increased competition along this pathway, or perhaps both.

[b] A, *n*-butyllithium, ml.; B, sodium hydroxide, g.; C, sodium, g.

[c] The reaction temperatures are room temperatures except as mentioned.

[d] Trioxane is used in Nos. 1–6 and 9; 37% formaldehyde is used in Nos. 7, 8.

[e] Amount of distillate.

[f] Anhydrous.

TABLE II

Polymerization of (I) and I-Acetate

	Monomer, g.	Solvent, ml.	Catalyst, amt.	Temp., °C.	Time, hr.	Yield, g. (%)
Monomer (I):						
1	1.00	—	AIBN[a] 0.05 g.	70	24	trace
2	0.50	—	BPO[b] 0.05 g.	70	65	trace
3	0.50	CH_2Cl_2 2.0	BF_3[c] 0.20 ml.	−10	16.5	0.42 (84)
4	0.50	CH_2Cl_2 2.0	BF_3 0.02 ml.	−10	24	0.30 (60)
5	0.50	CH_2Cl_2 4.0	BF_3 0.02 ml.	−78	24	0.09 (18)
6	3.84	CH_2Cl_2 15.0	BF_3 0.10 ml.	−10	24	2.34 (61)
7	0.50	CCl_4 4.2	$SnCl_4$ 0.02 ml.	25	24	0.41 (82)
8	3.84	CCl_4 31.0	$SnCl_4$ 0.10 ml.	30	4	2.01 (52%)[d]
Monomer (I-acetate):						
9	0.50	—	BPO 0.01 g.	70	24	0.10 (20)[e]
10	3.0	—	BPO 0.04 g.	70	87	0.46 (15)
11	0.50	CH_2Cl_2 2.0	BF_3 0.02 ml.	−10	42	0.18 (36)[f]

[a] AIBN, α,α'-azobisisobutyronitrile.

[b] BPO, benzoyl peroxide.

[c] BF_3, boron trifluoride etherate.

[d] Number-average mol. wt. 610, $\eta_{sp}/c = 0.03$ in acetonitrile at 30.0°C.

[e] Number-average mol. wt. 1.15×10^3.

[f] Crosslinked polymer.

Compound (I) showed hydroxyl in the infrared spectrum at 3420 cm.$^{-1}$; vinyl, at 3020, 1630, 968, and 911 cm.$^{-1}$; ether at 1258, 1240, and 1078 cm.$^{-1}$. The NMR spectrum showed ring methyl at 7.82 (6) and 7.88 τ (3), methoxy methyl at 6.41 τ (3), hydroxyl at 5.34 τ (1), and vinyl hydrogens at 4.26, 4.61, and 3.17 τ (1 each). A compilation of data for a number of runs for the preparation of monomer (I) is given in Table I.

Polymerization of Monoether (I)

Monomer (I) and solvent were introduced into a polymerization ampule under nitrogen; the catalyst was added and the tube sealed. After the scheduled time at the designated temperature (Table II), the tube was opened and a small amount of methanol was added to destroy the remaining catalyst. The polymer solution was concentrated under reduced pressure and poured into petroleum ether. Three reprecipitations of the polymer from methanol or acetone, accomplished by pouring the solution into petroleum ether, yielded dark-brown material soluble in most organic solvents except petroleum ether. This was poly(1-vinyl-3,4,6-trimethyl-2-methoxy-5-hydroxybenzene) (II), in impure form, since some oxidized form was always present. The analysis seemed reasonable.

ANAL. Calcd. for $(C_{12}H_{16}O_2)_n$ (%): C, 74.96; H, 8.39. Found (%): C, 74.70; H, 8.41.

Oxidation of Polymer (II)

A slow stream of chlorine was passed into a stirred solution of 1.53 g. of (II) in 100 ml. of acetonitrile for 45 min. at room temperature. The resulting yellow solution was poured into water, to precipitate the oxidized polymer. This was collected, washed with water, and dried *in vacuo.* The yield was 1.34 g. This polymer, poly(1-vinyl-3,4,6-trimethyl-2,5-benzoquinone) (III), did not give satisfactory analytical data, probably because it is difficult to burn it. However, its nature was confirmed in other ways and by analysis of polymer (V). The bright-yellow quinoid polymer is soluble in THF, acetone, and glacial acetic acid and sparingly soluble in methanol. The oxidation could also be achieved readily with ceric ammonium nitrate.

Reduction of Polymer (III)

Reduction of the quinoid polymer (III) to the hydroquinone form was attempted without success by using palladium charcoal in acetic acid. Zinc powder in acetic acid and sodium borohydride in methanol changed the color of the polymer from yellow to colorless. However, the reduced polymer is extremely unstable to oxygen and has not been isolated. Upon reduction with borohydride the polymer (IV) shows a maximum in the ultraviolet spectrum at 289 mμ. As the polymer is oxidized by exposing the solution to the air, this peak is gradually obscured by the intense quinoid absorption at 264 mμ, which immediately begins to develop and increases in intensity (Duroquinone absorbs at 259 and 267 mμ). The rate of oxidation could be followed by observing the increase in intensity of the absorption at 264 mμ. Since it was evident that polymer (IV) would be extremely difficult to isolate and handle, it was decided to characterize the polymer in the hydroquinone diacetate form.

Reductive Acetylation of Polymer (III)

A mixture of 0.25 g. of yellow quinoid polymer (III) and 0.85 g. of zinc powder in 20 ml. of acetic acid containing 5.0 ml. of acetic anhydride was refluxed for 2.5 hr. When the colorless solution was poured into water, a white polymer precipitated, weighing 0.20 g. This is poly(1-vinyl-3,4,6-trimethyl-2,5-diacetoxybenzene) (V), which was characterized by its analysis and by its stability to air.

ANAL. Calcd. for $(C_{15}H_{18}O_4)n$ (%): C, 64.7; H, 6.9. Found (%): C, 64.5; H, 6.9.

Polymer (V) is soluble in ether, methanol, acetone, acetonitrile, acetic acid, THF, carbon tetrachloride, and benzene. The presence of acetoxy groups was shown by bands at 1760, 1200, and 1080 cm.$^{-1}$ in the infrared spectrum.

Preparation of 1-Vinyl-3,4,6-trimethyl-2-methoxy-5-acetoxy-benzene: (I-Acetate)

To a stirred solution of 22.4 g. (0.117 mole) of (I) and 12.9 g. (0.129 mole) of triethylamine in 400 ml. of absolute ether was added dropwise, with ice bath cooling, 100 ml. of an ether solution containing 10.1 g. of acetyl chloride. After the completion of the addition stirring was continued for 15 min. at this temperature and for 0.5 hr. more after removal of the ice bath. Triethylamine hydrochloride was removed by filtration, and the ether was removed from the filtrate by evaporation. The slightly yellow, oily residue distilled at 100–111°C. at 0.4 mm. The colorless liquid so obtained was recrystallized at low temperature from petroleum ether to yield 24.6 g. (89.9%) of white crystals; m.p. 38–39°C.

ANAL. Calcd. for $C_{14}H_{18}O_3$ (%): C, 71.75; H, 7.74; Found (%): C, 71.90; H, 7.79.

The (I-acetate) showed vinyl bands at 3080, 1640, 975, and 910 cm.$^{-1}$, ester at 1770 and 1215 cm.$^{-1}$, and ether at 1258 and 1085 cm.$^{-1}$ in the infrared spectrum. The NMR spectrum showed ring and acetyl methyl at 7.84, 7.90, 8.03, and 8.07 τ, methoxy methyl at 6.48 τ, and vinyl bands at 3.26, 4.42, and 4.63 τ.

This monomer, on reduction with lithium aluminum hydride in THF, gave (I) in 84.0% yield; the product melted at the same temperature as (I) (67–68°) and gave no depression in admixture with (I). It could be polymerized by the same technique as (I).

Reduction of Poly(I-Acetate)

To a stirred solution of 0.43 g. of poly(I-acetate) in 30 ml. of THF was added 0.40 g. of lithium aluminum hydride powder, a little at a time. The mixture was refluxed 3 hr., and the remaining hydride was destroyed by careful addition of water to the cooled solution. The mixture was acidified with glacial acetic acid and mixed with saturated aqueous ammonium chloride. The THF solution of the polymer was separated, it was dried over magnesium sulfate, and the solvent was evaporated. The resulting viscous solution, poured into petroleum ether, precipitated polymer, which was collected, dissolved in THF, and reprecipitated several times. A yield of 0.29 g. (83%) was obtained. The polymer gave the same infrared spectrum as polymer (II) prepared from monomer (I).

Reduction of Polymer (V)

As a further test of the reduction process for removing acetoxy protecting groups, polymer (V), 0.19 g., was reduced with 0.5 g. of lithium aluminum hydride as described above, but for 2 hr. at reflux temperature. The polymer was recovered and purified as before. During this process it became oxidized. It was dissolved in glacial acetic acid and freeze-dried. The yield was 0.11 g. (86%) of polymer with the infrared spectrum of (III).

DISCUSSION

The preparation of poly(1-vinyl-3,4,6-trimethyl-2,5-hydroquinone) has been investigated previously,[2,10] little success being achieved. The reasons for interest in it are twofold. Since durohydroquinone (the tetramethyl-substituted hydroquinone) possesses the lowest potential among methylated hydroquinones,[11] the polymer should have an equally low midpoint potential (of the order of 0.5 v.). Further, because all the ring hydrogens of hydroquinone are substituted in the polymer (as in duroquinone), the molecule should be stable to oxidation or reduction over a very wide range of pH, and the presence of free radical, which is to be expected at basic pH, should be readily recognized because of this stability.

Difficulties were experienced in making monomer, because the hydroxyl groups had to be protected. Acetal protecting groups[4] are too bulky and contribute to too high a molecular weight, as shown by difficulties in distilling such monomers. The diether is readily made; however, removal of the ether groups has proved to be difficult and incomplete.[2] As a compromise it was decided to use the monoether (I), since it was known[1] that monoethers of hydroquinone could be readily oxidized to the quinones. With hydroquinones that have one or more ring hydrogens open dimerization (crosslinking) can occur; however, here this was not possible. When the polymer (II) was oxidized to (III) three peaks (6.45, 7.70, and 7.83 τ) disappeared from the NMR spectrum, and a new peak at 8.20 τ appeared. This peak is the only one present in duroquinone. Moreover, polymer (II) showed, in the infrared spectrum, ether bands at 1250 and 1080 cm.$^{-1}$ and no carbonyl, whereas the oxidized polymer (III) showed no ether bands and a carbonyl band at 1650 cm.$^{-1}$.

We are glad to acknowledge the technical assistance of Miss Irmlind Ungar in this work and that the work was supported by PHS research grant GM 10864, National Institute of Arthritis and Metabolic Diseases, Public Health Service.

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Thermosetting Polyimides*

G. M. BOWER, J. H. FREEMAN, E. J. TRAYNOR,
L. W. FROST, H. A. BURGMAN, and C. R. RUFFING,
*Westinghouse Research & Development Center,
Pittsburgh, Pennsylvania 15235*

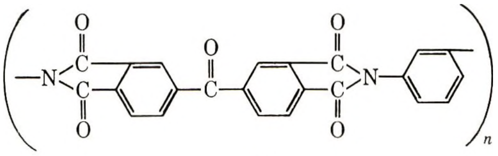
Synopsis

Linear polyimides prepared from *m*-phenylene diamine (MPD) and 3,4,3′,4′-benzophenonetetracarboxylic dianhydride (BTDA) were modified so as to be thermosetting. This was done by replacing a portion of the MPD with either 2,4-diaminoacetanilide or *p*-(2,4-diaminophenoxy) acetanilide and 3,5-diaminobenzoic acid; it is thought that during final processing of the laminates the carboxyl group and the acetamido group react, forming amide crosslinks. Alternatively, excess anhydride was incorporated into the polymer to react with some of the attached acetamido groups; these would give imide crosslinks. A series of resins and glass-reinforced laminates incorporating these resins was prepared. The laminates were aged and tested at 315°C. Flexural strength at 315°C. versus hours aged at 315°C. is presented. Flexural strength after 100 hr. at 315°C. for two of the better laminates from modified polymers was about 48,000 psi, compared to 24,000 psi for the straight linear polymer. The flexural strength of the modified polymers decreased more rapidly, however, and after 1000 hr. of aging at 315°C. the flexural strength of the best laminates, including the linear polymer, was 12,000 psi.

INTRODUCTION

Previous papers[1,2] have described the preparation of glass-reinforced polyimide laminates. The flexural strength of these materials at high temperatures before aging is quite good. Westinghouse I-8, for example, has a flexural strength of 39,000 to 40,000 psi at 315°C. The same laminates when tested at room temperature had a flexural strength 10–50% greater.

I-8 is prepared from *m*-phenylene diamine (MPD) and benzophenone tetracarboxylic dianhydride (BTDA). The structure in cured form is given as (I).



(I)

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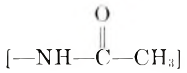
*To be published in SPE Transactions.

This polymer is linear and somewhat thermoplastic. By observing the electrical dissipation factor as a function of temperature we have found the T_g to be 365°C. From film samples provided by us, Cooper et al.,[3] using a modulus–temperature curve, reported the T_g to be about 290°C. Tobolsky's results indicate that crosslinking is needed for greater high-temperature strength. This paper describes a procedure for introducing crosslinks into polyimides, the incorporation of these resins into laminates, and the properties of the laminates.

DISCUSSION

The basic resin in all cases was I-8. It was modified by the replacement of a portion of the MPD with other aromatic diamines containing acetamide groups,

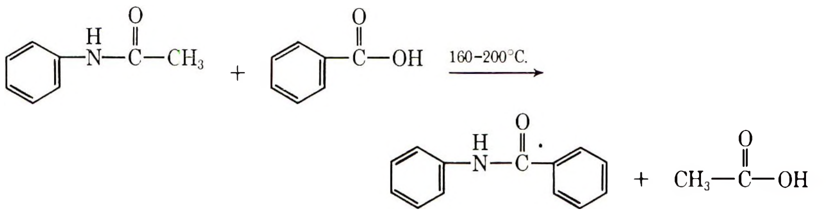


$$[\text{—NH—}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{—CH}_3]$$

and carboxylic acid groups,

$$[\text{—CO}_2\text{H}]$$

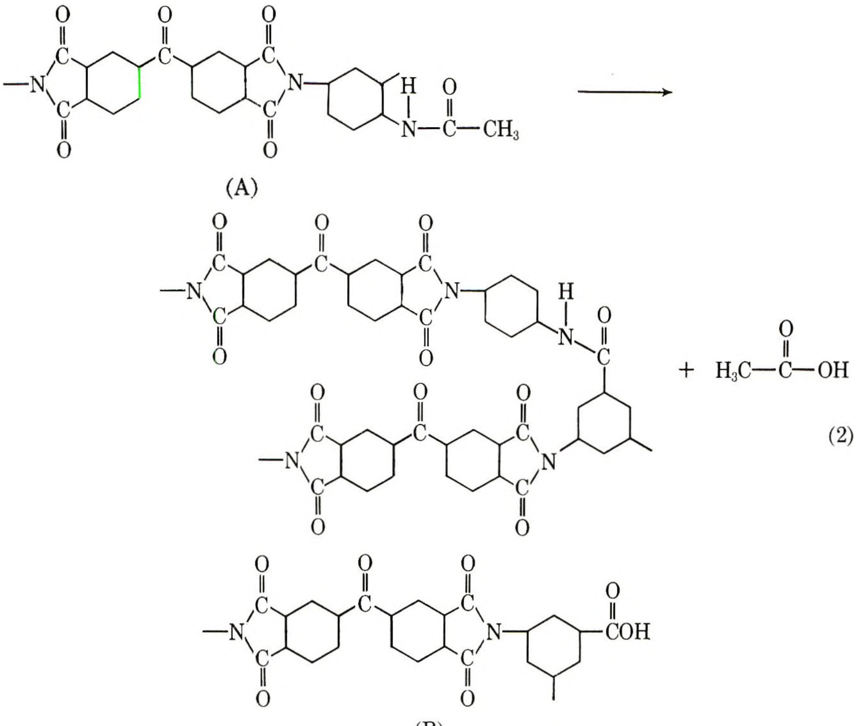
In a preliminary experiment acetanilide and benzoic acid were fused together and found to give a moderate yield of benzanilide. Acetic acid also is a product of this reaction, as shown in eq. (1).



(1)

Substituting 2,4-diaminoacetanilide (DAA) for a portion of the MPD in the basic I-8 resin produces a molecular segment such as (A) in eq. 2. When 3,5-diaminobenzoic acid is substituted for MPD, a segment such as (B) is obtained. When the acetamido and carboxylic acid groups are in favorable position relative to one another, they can react to form a crosslinked infusible polymer. The crosslink is shown as the principal product of eq. 2.

The DAA shown in eq. (2) has been prepared from 2,4-dinitroaniline in two steps. Acetylation by acetic anhydride with a few drops of sulfuric acid proceeds smoothly in good yield. The nitro groups are catalytically hydrogenated to give DAA. Later some crude material, purchased from Gallard-Schlesinger Chemical Manufacturing Corporation, was recrystallized from water to give a compound with a melting point of 161–163°C. (Heilbron: 158–159°C.).



(A)

(B)

(2)

A new compound, *p*-(2,4-diaminophenoxy) acetanilide (DAPA), was used as an alternative diaminoacetamido compound. It was obtained by the condensation of sodium 4-acetamidophenolate with 2,4-dinitrochlorobenzene, which gave *p*-(2,4-dinitrophenoxy) acetanilide, and this compound was catalytically hydrogenated, giving DAPA; m.p., 144–145°C.

Free carboxylic acid groups were obtained from 3,5-diaminobenzoic acid; m.p., 240–242°. This compound was prepared by catalytic hydrogenation of 3,5-dinitrobenzoic acid.

I-43, I-58, I-89, I-90, and I-91 are examples of resins containing equal amounts of attached acetamido and carboxylic acid groups. They were all prepared by first dissolving the diamines in either DMAC or NMP and then, while they were cooling, adding solid BTDA in several portions over a period of about 2 hr.

Table I gives the composition of the resins studied and some of the more important processing conditions used in the fabrication of the laminates. The glass cloth was coated continuously, being passed first through a trough containing the resins and then through two heated towers, by which means most of the solvent was removed and a partial cure effected. The maximum temperature to which the treated glass cloth was subjected in the tower is given in Table I. As noted in the table, some samples of cloth were given a further cure before being laminated. This was necessary in the case of I-91, I-91B, and I-90A, because the first laminates prepared from

TABLE I
Composition and Processing of Laminates with Amide Crosslinks

	I-43 (MPD_{50}, DAA_{25}, DAB_{25}, $BTDA_{100}$)[a]						I-89 (MPD_{50}, $DAPA_{25}$, DAB_{25}, $BTDA_{100}$)[a]		I-58 (MPD_{60}, DAB_{20}, $DAPA_{20}$, $BTDA_{96}$, PA_8)[a]			I-91 (MPD_{60}, DAB_{20}, $DAPA_{20}$, $BTDA_{100}$)[a]		I-90 (MPD_{60}, DAB_{20}, DAA_{20}, $BTDA_{100}$)[a]
Laminate number:	A	B	C	D	E	F	A	B	A	B	C	A	B	A
Max. treating-tower temp., °C.	205	205	185	185	185	190	195	195	200	200	200	185	185	165
Further precure	No	15 min., 285°C.	No	No	No	No	No	No	No	No	No	15 min., 190°C.	15 min., 190°C.	15 min., 190°C.
Resin, prepreg, %	41.0	34.3	34.8	35.5	36.0	34.5	36.0	36.4	37.0	36.8	37.5	33.5	33.0	36.8
Laminating temp., °C.	370	370	330	300	270	240	240	300	360	370	370	300	330	270
Time at pressure and temp., min.	30	30	30	30	30	90	80	60	30	30	30	60	60	60
Postcure[b]	No	No	Yes	Yes	Yes	Yes	Yes	Yes	No	No	Yes	Yes	Yes	Yes
Resin, laminate, %	38.8	33.5	32.5	33.8	35.3	30.6	33.5	33.8	34.0	34.3	34.8	31.0	30.0	34.2

[a] Composition (subscripts indicate molar ratios): MPD = *m*-phenylenediamine, DAA = 2,4-diaminoacetanilide, DAPA = *p*(2,4-diaminophenoxy) acetanilide, DAB = 3,5-diaminobenzoic acid, BTDA = 3,4,3′,4′-benzophenonetetracarboxylic dianhydride, PA = phthalic anhydride.

[b] During postcure temperature was raised from 150–315°C. at a rate of 5°C./hr.

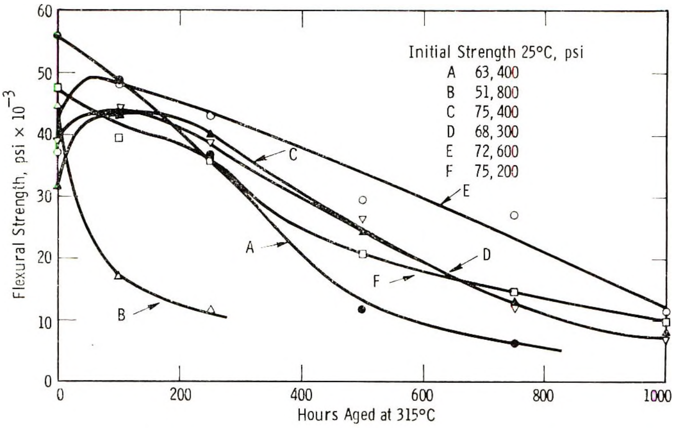


Fig. 1. I-43 laminates aged and tested at 315°C.

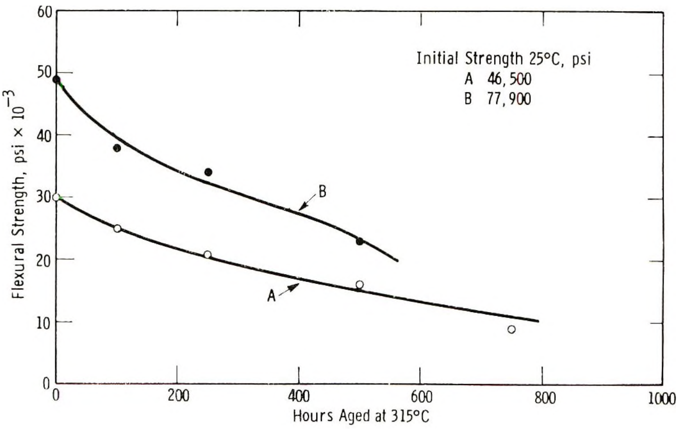


Fig. 2. I-89 laminates aged and tested at 315°C.

cloth that had not received this added treatment blistered badly on postcuring. Postcuring was carried out on the full 14 × 14 in. laminate, and if too much volatile material was entrapped, blistering occurred in spite of the careful postcure schedule.

After final processing the laminates, approximately 1/8 in. thick, were cut into 1 × 4 in. sections and aged at 315°C. Figures 1–4 show the flexural strength at 315°C. of these laminates as a function of time at temperature.

The curves for I-43 in Figure 1 indicate several things. First they indicate that the curing temperature of the prepreg is critical. I-43A and I-43B, which were cured at 205°C. (I-43B getting an extra precure at 285°C.), are definitely inferior to the I-43C to I-43F, which were cured 15–20° lower. On the other hand, they show that the pressing temperature is not as critical, since latter four, which were pressed at 330, 300, 250, and 240°C., respectively, all declined in strength at about the same rate for the

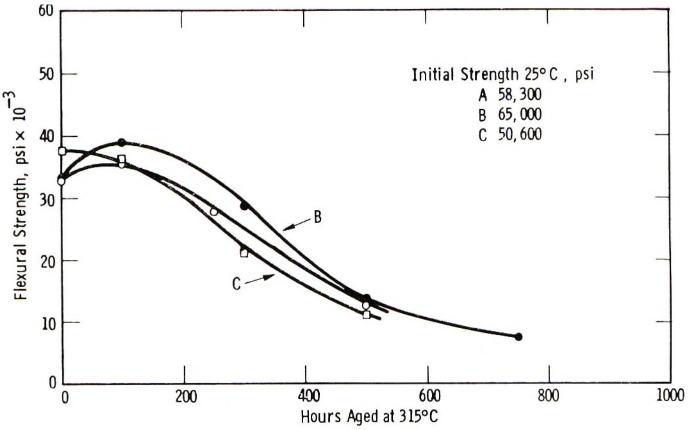


Fig. 3. I-58 laminates aged and tested at 315°C.

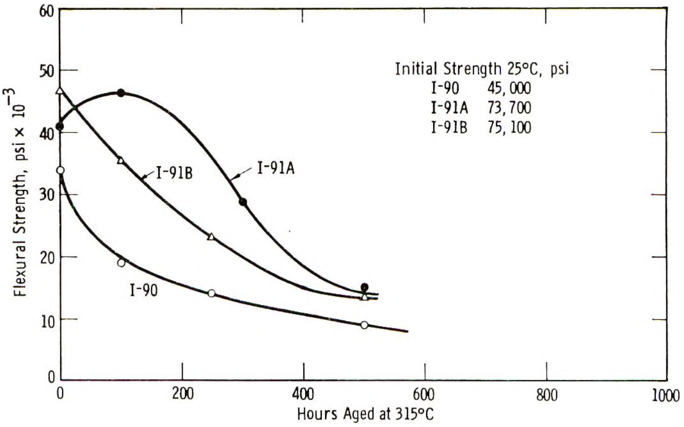


Fig. 4. I-90 and I-91 laminates aged and tested at 315°C.

first 500 hr. I-43E, when compared with I-8 in Figure 9, has a somewhat lower initial flexural strength at temperature but, upon aging at 315°C. it increases in flexural strength, while I-8 drops off rapidly, and at 100 hr. I-43E is much stronger than I-8. After 100 hr. I-43E declines in strength much faster than I-8, and at the end of about 1000 hr. they are of equal strength.

The flexural strength versus time aged at 315°C. for I-89 is given in Figure 2. This resin differs from I-43 in that DAPA replaces DAA. The laminate pressed at 300°C. is considerably better than the one pressed at 240°C. Neither are as good as the best I-43 laminates.

I-58, I-90, and I-91 contain fewer acetamido and carboxyl groups than I-43 and I-89. I-58 also is end-blocked with phthalic anhydride. DAPA provides the acetamido groups for I-58 and I-90; DAA, for I-91. The flexural strength versus time at 315°C. for these resins is given in Figures 3 and 4. I-90, the only laminate in this series containing DAA, has some-

TABLE II

Composition and Processing of Laminates with Amide and Imide Crosslinks[a]

	I-64 (MPD_{84}, $DAPA_{16}$, $BTDA_{108}$)			I-75 (MPD_{40}, $DAPA_{35}$, DAB_{25}, $BTDA_{1005}$)		I-76 (MPD_{60}, DAA_{30}, DAB_{10}, $BTDA_{110}$)	I-77 (MPD_{70}, DAA_{20}, DAB_{10}, $BTDA_{105}$)	I-83, (MPD_{50}, $DAPA_{40}$ DAB_{10}, $BTDA_{115}$)		I-85 (MPD_{50}, $DAPA_{35}$ DAB_{15}, $BTDA_{110}$)		I-86 (MPD_{60}, $DAPA_{30}$, DAB_{10}, $BTDA_{110}$)		
Laminate number:	A	B	C	A	B	A	A	A	B	A		A	B	C
Max. treating-tower temp., °C.	170	170	170	150	150	150	150	155	155	170		150	150	150
Precure	No	No	No	No	No	No	No	No	2 hr., 125°C.	30 min., 175°C.		No	No	No
Resin prepreg	48.3	50.0	52.0	39.3	43.7	32.4	34.3	39.3	37.2	38.0		31.5	32.4	32.7
Laminating temp., °C.	370	370	370	360	315	320	340	350	330	240		320	240	210
Time at pressure and temp., min.	30	30	30	30	60	30	30	30	30	90		30	90	120
Postcure	No	No	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes		Yes	Yes	Yes
Resin, laminate, %	36.3	32.4	34.2	34.3	37.7	29.5	31.0	30.4	32.0	36	32.0	24.5	28.3	27.3

[a] See notes Table I.

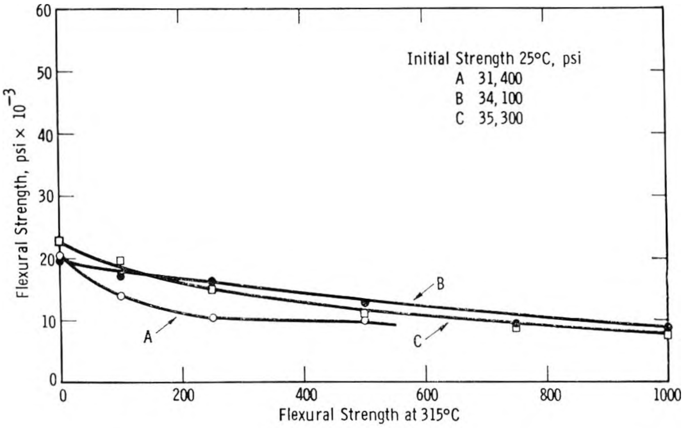


Fig. 5. I-64 laminates aged and tested at 315°C.

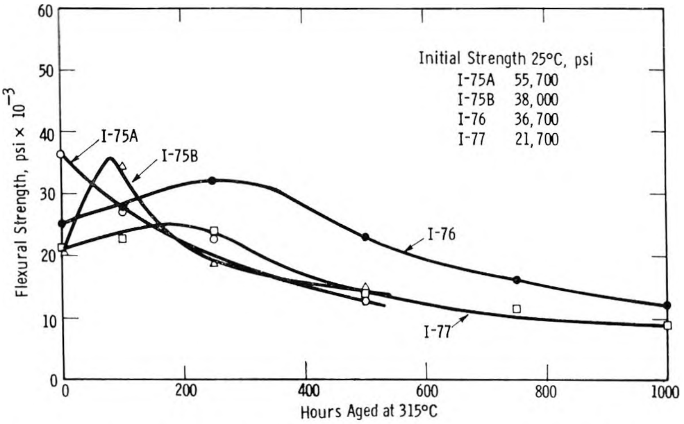


Fig. 6. I-75, I-76, and I-77 laminates aged and tested at 315°C.

what lower flexural-strength values than the others, but this may be due partly to the laminating temperature. End-blocking gives somewhat lower values initially, but after 500 hr. of aging there is little to choose between the laminates.

Table II contains the composition and processing details of laminates containing both imide crosslinks and amide crosslinks.

Three laminates were prepared from I-64 resin, which contains acetamido groups and excess anhydride. They were prepared under almost identical conditions. Their flexural strength as a function of aging at 315°C. is given in Figure 5. The curves are characteristic of a noncrosslinked resin, with low initial values that drop off only slowly on aging.

It was very difficult to prepare laminates containing a large excess of anhydride. Because of their low molecular weight the temperature in the treating towers had to be kept low, or the resin tended to flake off. This low treating temperature left more solvent than could easily be removed

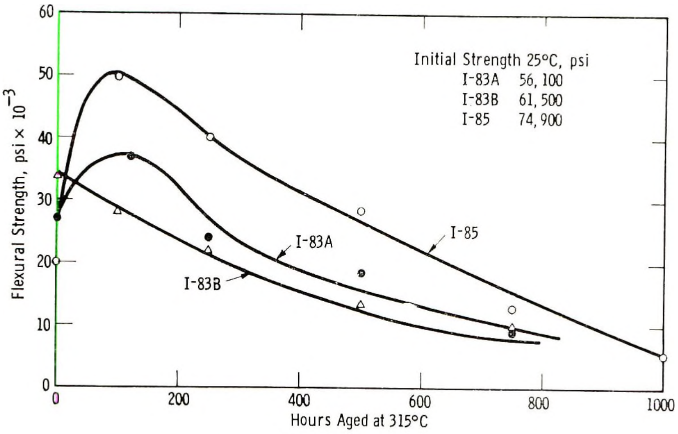


Fig. 7. I-83 and I-85 laminates aged and tested at 315°C.

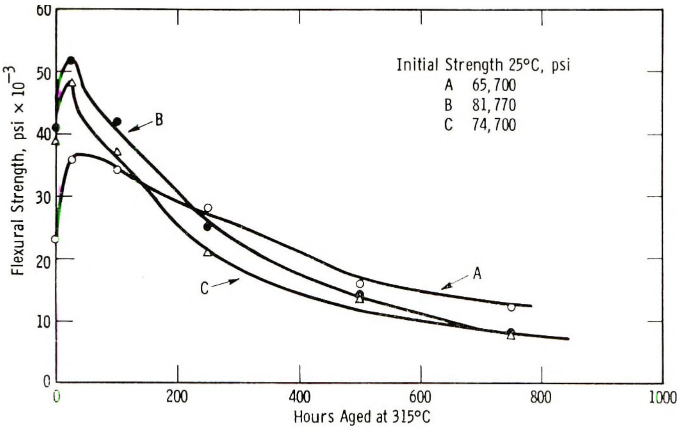


Fig. 8. I-86 laminates aged and tested at 315°C.

during the laminating operation. The result was "hot spots" and blistering. The hot spots are dark areas in the laminate, where degradation has apparently occurred. To help the solvent escape during laminating, the pressure was kept very low until temperature was obtained, and then was increased gradually to 200 psi over a period of about 5 min. A momentary release of pressure after the laminating temperature was reached ("bumping") was tried, but this did not result in an improvement.

Almost all of the laminates whose flexural strength versus time at 315°C. are given in Figures 6–8 had a hot spot or some blistering.

The retention of flexural strength of these laminates with time, compared with that of I-8 or I-43, is poor, with the exception of I-76 and I-85. I-85 gives high initial values and then drops off, whereas I-76 gives lower initial values but after 1,000 hr. still retains a flexural strength of 12,000 psi, which is comparable to the best values given by I-8 and I-43 laminates.

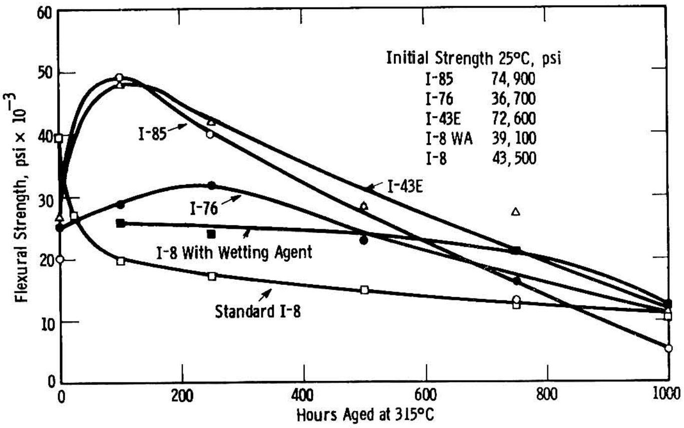


Fig. 9. Laminates from crosslinked polyimides compared with I-8.

Figure 9 compares the retention of flexural strength with time at 315°C. of I-43E, I-76, and I-85 with two types of I-8 resin. Thus from Figure 9 it may be seen that I-43E and I-85 have flexural strengths of about 50,000 psi, compared to values of 20,000 and 26,000 psi for two I-8 samples. After 1000 hr. the flexural strength of I-43E and the two I-8 samples had dropped to 12,000 psi, while the flexural strength of the I-85 sample had dropped to 6000 psi. I-76 had a flexural strength after 100 hr. of about 30,000 psi, which after 1000 hr. dropped to 12,000 psi. This all indicates that the modified resins with higher initial flexural strength declined in strength at a more rapid rate than the unmodified resin.

The flexural-modulus values for I-43E, I-85, and a standard I-8 laminate are given in Table III. These are nearly equivalent at all stages of aging,

TABLE III
Flexural Modulus at 315°C. after Aging at 315°C.

Aging time, hr.	Modulus, psi ($\times 10^{-6}$)		
	I-43F	I-85	I-8
0 RT[a]	2.8	3.3	2.5
0.5	1.9	1.2	2.2
100	2.7	2.7	2.1
250	2.7	2.4	2.7
500	2.4	2.3	2.4
750	2.5	2.1	2.2
1000	2.2	1.4	2.2

[a] Measured at room temperature.

contrary to what one would expect when comparing a crosslinked resin with a linear resin. Thus, there is no specific evidence that crosslinking actually has taken place in these modified resins.

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Polycondensation Rate of Poly(ethylene Terephthalate). I. Polycondensation Catalyzed by Antimony Trioxide in Presence of Reverse Reaction*

R. W. STEVENSON and H. R. NETTLETON, *Mobil Chemical Company, Research and Development Division, Edison, New Jersey 08817*

Synopsis

The technique of G. Challa was employed for following the reaction of oligomeric poly(ethylene terephthalate) in the presence of antimony trioxide. This technique is based on determining the changes in glycol and bishydroxyethyl terephthalate concentrations with time at a given temperature. The linear trimer of ethylene terephthalate, prepared from terephthaloyl chloride and bishydroxyethyl terephthalate, was employed as starting material. Rate constants were not corrected for catalyst concentrations. The reaction was studied over the temperature range 221–251°C. The equilibrium constant k_p/k' for the polycondensation reaction

$$2\text{\textasciitilde}COOCH_2CH_2OH \underset{k'}{\overset{k_p}{\rightleftharpoons}} \text{\textasciitilde}COOCH_2CH_2OOC\text{\textasciitilde} + HOCH_2CH_2OH$$

was found to be 0.36. Observed reaction rates were low but faster than in the uncatalyzed reaction studied by Challa. At 231°C. the values of the rate constants found in the presence of 0.025% by weight antimony trioxide were $k_p = 0.15$ l. mole^{-1} hr.$^{-1}$ and $k' = 0.33$ l./mole-hr., and the redistribution rate constant was $k_R = 0.11$ l./mole-hr. From data at four temperatures the estimated activation energies were $E_p = 29$ kcal. and $E_R = 24$ kcal. The polycondensation rates were low compared with rates calculated from literature data. A mechanism to explain the difference requires that bishydroxyethyl terephthalate endgroups compete successfully with oligomer endgroups for antimony trioxide catalyst and that the bishydroxyethyl terephthalate catalyst product is unreactive in polymerization.

INTRODUCTION

Processes for the preparation of high molecular weight poly(ethylene terephthalate) may be described as having essentially two parts. In the first part dimethyl terephthalate or terephthalic acid is converted to prepolymer, i.e. a low molecular weight poly(ethylene terephthalate). (Substantial amounts of bishydroxyethyl terephthalate are often present in such prepolymers and, in fact, some low molecular weight oligomeric mixtures have been loosely referred to as bishydroxyethyl terephthalate;

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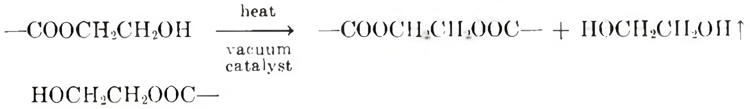
in this paper the term bishydroxyethyl terephthalate will refer only to the specific compound $HOCH_2CH_2OOCC_6H_4COOCH_2CH_2OH$.) In the second part the prepolymer is converted to high molecular weight poly(ethylene terephthalate), e.g. with $M_n = 18{,}000$, by elimination of glycol between the hydroxyethyl ester endgroups:



$$\begin{array}{l}\text{—COOCH}_2\text{CH}_2\text{OH} \xrightarrow[\text{vacuum catalyst}]{\text{heat}} \text{—COOCH}_2\text{CH}_2\text{OOC— + HOCH}_2\text{CH}_2\text{OH}\uparrow \\ \text{HOCH}_2\text{CH}_2\text{OOC—}\end{array}$$

This report is concerned with the rate of the second reaction, with its reverse (glycolysis reaction), and the redistribution reaction, which is the reaction of the endgroup of one polymer molecule with an internal diester group of another polymer molecule, producing two new polymer molecules of different sizes. Challa has studied the forward, reverse, and redistribution rates in the absence of catalyst.[1-3] The technique he employed was unique in taking full account of the effect of the reverse reaction on the observed forward rate. The purpose of the present study was to study the forward, reverse, and redistribution rates in the presence of antimony trioxide. Antimony trioxide was chosen as catalyst, since it is less likely to facilitate degradation reactions than some other well-known catalysts of poly(ethylene terephthalate) polycondensation.[4]

Relationships derived by Challa,[1-3] which assume that the forward, or polycondensation, reaction is second-order in endgroups, are used in this work to derive estimates of the antimony trioxide catalyzed rate. In the kinetic analysis employed in the present study the contribution of catalyst concentration to rate is not explicitly treated and the rate constants determined are to be understood as including the effect of catalyst concentration. In the kinetic analysis an equilibrium defined in terms of K,

$$K = k_p/k' = (4[\sim\text{COOCH}_2\text{CH}_2\text{OOC}\sim][\text{HOCH}_2\text{CH}_2\text{OH}])/[\sim\text{COOCH}_2\text{CH}_2\text{OH}]^2 \quad (1)$$

is assumed, wherein k_p is the rate constant for polycondensation and k' that for the glycolysis, or reverse, reaction:

$$2\sim\text{COOCH}_2\text{CH}_2\text{OH} \underset{k'}{\overset{k_p}{\rightleftharpoons}} \sim\text{COOCH}_2\text{CH}_2\text{OOC}\sim + \text{HOCH}_2\text{CH}_2\text{OH}$$

The rate constants are expressed in terms of the reaction of a single functional group with one other functional group. The relationship for the forward rate is, according to Challa[2]

$$k_pt = (K/4B)(V/U_0)\ln\{(p_0 - p_e)[(1 - K)(p - p_e) + B]/ (p - p_e)[(1 - K)(p_0 - p_e) + B]\} \equiv \tau \quad (2)$$

where K = equilibrium constant, V = volume in liters, U_0 = moles of repeating units $\text{—CH}_2\text{OOCC}_6\text{H}_4\text{COOCH}_2\text{—}$, p_e = extent of reaction at equilibrium, p_0 = extent of reaction at $t = 0$, p = extent of reaction at time t, $B = [(2K + q - p_0)^2 - 4K(K - 1)]^{1/2}$, and q = ratio of initial glycol concentration to U_0.

The relationship for the redistribution reaction, i.e. the reaction between the endgroup of one molecule and an internal ester link of another molecule, has been expressed by Challa[3] as follows:

$$k_r t = (V/4U_0) \ln (1 - f_0/1 - f) - 2k' \int_0^t (q + p - p_0)/(1 - p)\, dt \equiv \tau_R \quad (3)$$

The reaction is followed by measuring the bishydroxyethyl terephthalate concentration as a function of time (it is necessary to have an abnormal bishydroxyethyl terephthalate concentration at the start). The deviation from normal bis-hydroxyethyl terephthalate concentration is designated by f, defined by

$$U_1 = fU_0(1 - p)^2 \quad (4)$$

where U_1 designates moles of bishydroxyethyl terephthalate. The term f is designated the "deviation factor." Thus, f_0 would be the deviation factor at time t_0.

The work reported in this paper covers the temperature range 221–251°C. Two levels of catalyst are considered: 0.01 and 0.025% by weight antimony trioxide. The starting material for the study was a synthetic linear ethylene terephthalate trimer, $HOCH_2CH_2(OOCC_6H_4COOCH_2CH_2)_3OH$. This oligomer was assumed to be of sufficient length for the theory of equal reactivities of like functional groups to be applicable in the initial phases of reaction. At the same time the oligomer is of sufficiently low molecular weight to provide measurable quantities of the reaction products glycol and bishydroxyethyl terephthalate as a function of time at temperature.

EXPERIMENTAL

Synthesis of Linear Ethylene Terephthalate Trimer

Two methods were employed for synthesizing linear ethylene terephthalate trimer.

In the first method excess bishydroxyethyl terephthalate reacted with terephthaloyl chloride as follows. First 210 g. of bishydroxyethyl terephthalate was heated to 120°C., and then 8.5 g. of recrystallized terephthaloyl chloride was added to the melt. Heating and stirring were continued for 30 min. The cooled reaction product was ground in a Waring Blendor and washed several times with warm acetone; filtration was carried out after each wash. The melting point (185–192°C.) and infrared spectrum of the material so prepared agreed with literature data on the trimer.[5]

In the second method excess terephthaloyl chloride reacted with bishydroxyethyl terephthalate and then with excess ethylene glycol in acetone, as follows. An excess of recrystallized terephthaloyl chloride (100 g.) was heated with 10 g. of bishydroxyethyl terephthalate at 90°C. with nitrogen sweep for about 60 min. The melt was poured into 2000 g. of a 50% by weight glycol–acetone solution, and heating to 60–70°C. followed. Heating was continued for 1 hr. with stirring and nitrogen sweep. The material was filtered and washed twice in a Waring Blendor with warm acetone. The yield of linear ethylene terephthalate trimer averaged about 16% for four preparations.

Procedure for Rate Studies in Presence of Reverse Reaction

A 1 g. amount of linear ethylene terephthalate trimer and an appropriate amount of antimony trioxide catalyst were placed in a glass tube, which was sealed. After the technique of Challa a glass dummy in the tube minimized the vapor space. Following reaction at the specified time and temperature in an aluminum block, the reaction mixture was recovered and fractionally distilled under vacuum. Appropriate conditions found for the fractionation were 57°C. at 1 mm. for glycol removal and 127°C. at 1 mm. for bishydroxyethyl terephthalate removal. At each temperature the reaction mixture was taken to constant weight for three or more successive weighings. The weight differences were taken as glycol or bishydroxyethyl terephthalate, respectively.

RESULTS

The relationship derived by Challa[1] for the equilibrium constant K (no glycol present initially) is

$$K = p_e(p_e - p_0)/(1 - p_e)^2$$

This equation was used for estimating the value of the equilibrium constant at each of the three temperatures 231, 241, and 251°C. for the reaction of linear ethylene terephthalate trimer in the presence of 0.025 wt.-% antimony trioxide. The results are given in Table I. These data do not permit the detection of any variation of K with temperature. The average value of K for this temperature range is, with standard deviation, 0.36 ± 0.11. This value of K differs from that obtained under the most nearly comparable conditions by Challa,[1] namely 0.86, by a factor of more than 2. Since experimental error can account for the difference, the average

TABLE I
Equilibrium Constant K for Reaction of Linear Ethylene Terephthalate Trimer between 231 and 251°C.[a]

Temp., °C.	p_e	K
231	0.719	0.473
241	0.700	0.257
251	0.710	0.363
	$p_0 = 0.667$	

[a] 0.025 wt.-% Sb_2O_3.

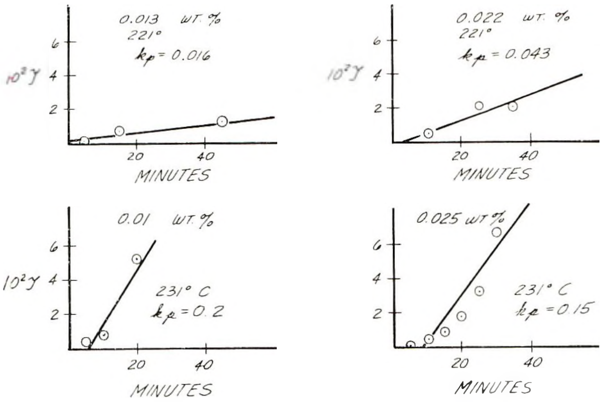


Fig. 1. Effect of catalyst concentration on polycondensation rate (l./mole-hr.).

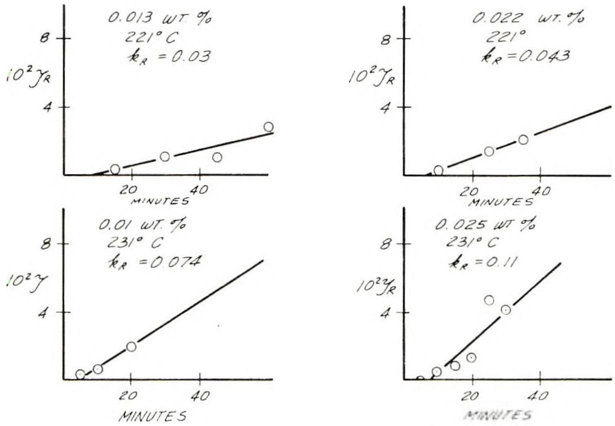


Fig. 2. Effect of catalyst concentration on redistribution rate (l./mole-hr.).

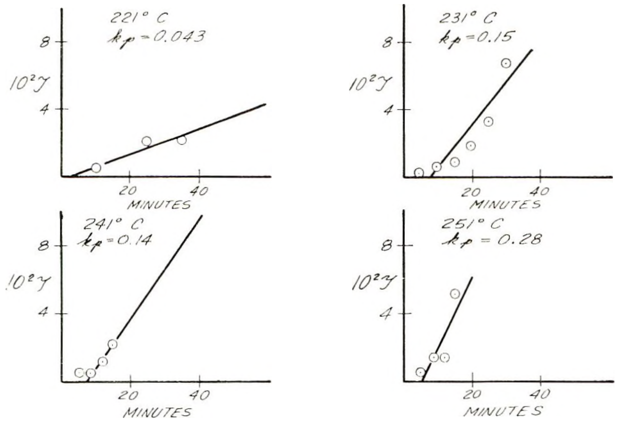


Fig. 3. Effect of temperature on polycondensation rate (l./mole-hr.).

equilibrium constant of 0.36 was arbitrarily chosen for treatment of the data of the catalyzed reaction. It can be shown by substitution of the two different values of K in eq. (2) that the polycondensation rate constant k_p is only moderately affected by a change in K of the magnitude indicated. The glycolysis, or reverse, rate constant, however, will be affected to the extent that K varies. Although the reverse rate constant k' appears in the expression for the redistribution rate constant, eq. (3), the second term in which k' appears, is in general smaller than the first term, which is based completely on the measurement of bishydroxyethyl terephthalate concentration with time. Consequently, the redistribution rate constant k_R also is only moderately affected by the discrepancy in the value determined for the equilibrium constant.

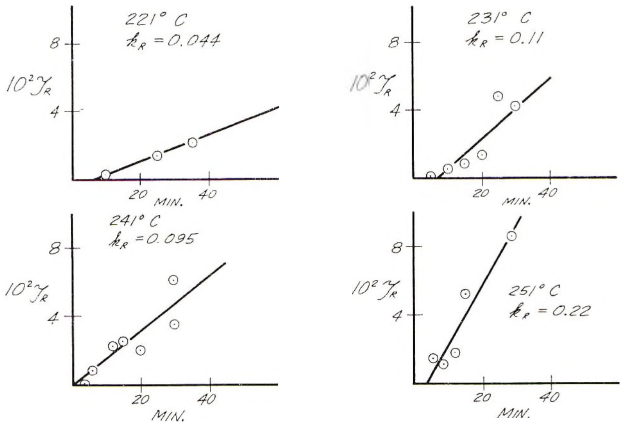


Fig. 4. Effect of temperature on redistribution rate (l./mole-hr.).

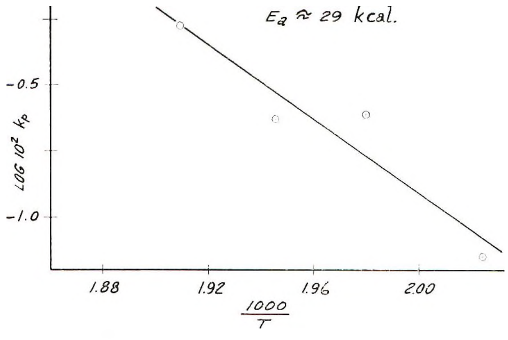


Fig. 5. Activation energy for polycondensation rate.

In Figures 1 and 2 rate plots for k_p and k_R at 221 and 231°C. are shown for different concentrations of antimony trioxide catalyst. With one exception for four comparisons the rates are seen to increase with increasing catalyst concentration.

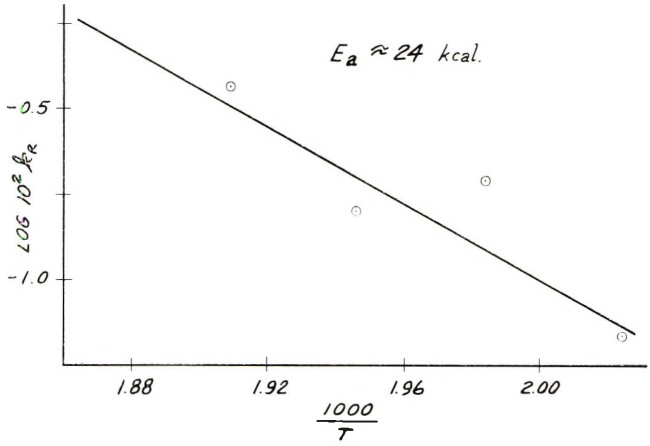


Fig. 6. Activation energy for redistribution rate.

NOTE: The exception is doubtless due in large part to the use of an insufficiently accurate balance for weighing the catalyst in one instance. The figure 0.01% could, conceivably, be as high as 0.02% because of this. This factor, together with ordinary experimental error in the determination of k_p, could readily account for the difference.

Figures 3 and 4 show rate plots for k_p and k_R from 221 to 251°C. The data are summarized in Table II. From the data of Figures 3 and 4 it was possible to obtain estimates of the activation energy for k_p and k_R. The derivation of these activation energies is shown in Figures 5 and 6, wherein k_p and k_R are expressed in units of liters per mole per minute. The results for the activation energy are as follows: for polycondensation, $E_a \approx 29$ kcal.; for redistribution, $E_a \approx 24$ kcal. Because of data scatter these estimates are not significantly different from Challa's estimates of 22–23 kcal. for the polycondensation activation energy[2] and 31 kcal. for the redistribution activation energy.[3]

A mixture of poly(ethylene terephthalate) oligomers was prepared by polycondensation of bishydroxyethyl terephthalate. This mixture, which

TABLE II

Catalyzed Polycondensation and Redistribution Rate Constants for Poly(ethylene Terephthalate), as Determined in the Presence of the Reverse Reaction

Temp., °C.	Concn. Sb_2O_3, wt.-%	k_p ($\times 10^{-2}$), l./mole-hr.	k_R ($\times 10^{-2}$, l./mole-hr.
221	0.013	1.61	3.04
221	0.022	4.26	4.36
231	0.01	20.3	7.47
231	0.025	14.52	11.48
241	0.025	14.28	9.49
251	0.025	28.2	22.2

$K = k_p/k' = 0.363$

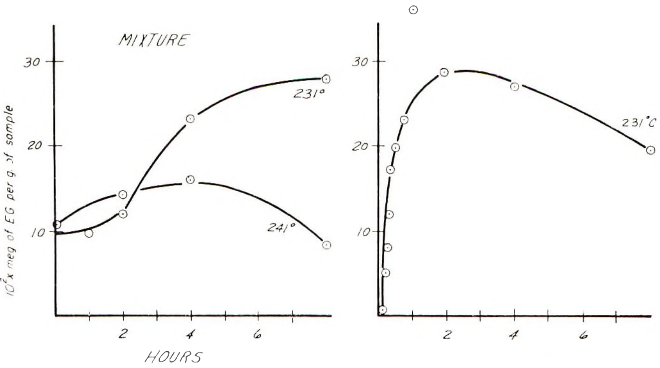


Fig. 7. Comparison of glycol evolution from synthetic trimer with that from a typical oligomer mixture.

contained an appreciable fraction of bishydroxyethyl terephthalate, behaved anomalously when reacting in sealed tubes in the presence of 0.025% by weight antimony trioxide. In Figure 7 glycol evolution versus time for the oligomer mixture is contrasted with that for the synthesized linear trimer. At 231°C. there appears to be no glycol evolution from the oligomer mixture; after this an apparent equilibrium is approached over an 8 hr. period. At 241°C. at least 4 hr. are required for reaching "equilibrium." The reason for the decline in glycol content after 4 hr. is not immediately apparent. It is certain, however, that initial conditions do not represent equilibrium conditions, and the time for reaching equilibrium is about ten times that required with the synthesized linear trimer of ethylene terephthalate.

DISCUSSION

If a reaction second-order in endgroups is assumed to describe the catalyzed polycondensation reaction, "rate constants" (which involve catalyst concentration) can be derived from polycondensation reactions in which glycol is removed. For this the endgroup concentration is estimated from data on the degree of polymerization or molecular weight. The reverse reaction is ignored. Intrinsic viscosity data are converted to molecular weight data by the relationship of Conix.[9] In Table III, a number of such "rate constants" estimated from literature and other laboratory data are given. In many of the citations of this table there is an unaccounted-for reverse reaction. Therefore, rate constants estimated for these citations must represent values less than the true forward rate. Some of the estimates are based on several data points; others, on two or three. It should be noted that the "rate constants" estimated are *not* those derived by the authors cited. Rather, their data were used for deriving "rate constants" on the basis of an assumed second-order reaction. Since the purpose of the tabulation is to show the extent to which attained polycondensation rates vary, the differences in temperature or type and

TABLE III
Poly(ethylene Terephthalate) Polycondensation Rate Constants, Estimated from Literature and Laboratory Data, for Reactions with Glycol Removal

Prepolymer[a]	Temp., °C.	Catalyst and concn., wt.-%	k_p, l./mole-hr.	Bibliog. ref. no.
BHT	280	None	1.1	Unpub.
M_n = 800 (from ethylene glycol and terephthalic acid)	280	Sb_2O_3, 0.025	2.5	Unpub.
BHT, 0.1 mil thick on stainless steel	275	$Mn(OAc)_2 \cdot 4H_2O$, 0.015 Sb_2O_3, 0.035	550	6
BHT 0.1 mil thick on aluminum	275	$Mn(OAc)_2 \cdot 4H_2O$, 0.025 Sb_2O_3, 0.035	270	6
BHT	242	LiO Al_2O_3	0.095	7
BHT	285	LiO Al_2O_3	0.33	7
Derived from ethylene glycol and dimethyl terephthalate	270 275 285	$Zn(OAc)_2 \cdot 2H_2O$ (?)	4.1 (mean)	8

[a] BHT = bishydroxyethyl terephthalate.

amount of catalyst are relatively unimportant. A range of difference of more than three orders of magnitude is observed for the derived rate constants. The highest rate derived is represented by k_p = 550 l./mole-hr. at 275°C.

By contrast, data derived from polycondensation in the presence of the reverse reaction yield a value of k_p of only 0.28 l./mole-hr. at 251°C. for an 0.025 wt.-% concentration of antimony trioxide. On the basis of the derived activation energy of 29 kcal. this corresponds to a rate of 1.28 l./mole-hr. at 280°C. Although this estimate is based on a procedure that takes full account of the reverse reaction, the value of 1.28 is only half that derived from 100 g. scale polymerizations (second line of Table III), in which glycol could be observed refluxing onto the melt.

Challa[1,2] has distinguished the reactivity of bishydroxyethyl terephthalate endgroups from the reactivity of bishydroxyethyl terephthalate endgroups with polymer endgroups; the latter in turn is different from that of polymer endgroups with polymer endgroups. The polycondensation of polymer endgroups is found by Challa to be 1.8 times as fast as the polycondensation of polymer with bishydroxyethyl terephthalate endgroups. The latter reaction is 1.8 times as fast as the polycondensation reaction of two bishydroxyethyl terephthalate endgroups. This difference cannot explain the observed reactivity difference, since for both 100 g. scale polymerizations under vacuum and equilibrium (sealed tube) polymerization an oligomer of degree of polymerization of at least 3 was employed.

Furthermore, the observed extremely low reactivity of an oligomer mixture (Fig. 7) versus the reactivity of synthetic linear ethylene terephthalate trimer should be explained. A suitable hypothesis consistent with the wide range of rates derived from literature and the observations of this paper may be developed. The hypothesis requires the reversible interaction of a vacuum volatile constituent of the reaction mixture with the catalyst, rendering it inactive. Removal of such a constituent would free the catalyst for participation in polycondensation. Among the volatile constituents of a reacting poly(ethylene terephthalate) mixture are glycol (which also participates in the reverse reaction), bishydroxyethyl terephthalate, and cyclic compounds such as cyclo trisethylene terephthalate.[8]

There are good reasons for supposing that bishydroxyethyl terephthalate can inactivate antimony trioxide catalyst. Thus, antimony trioxide has been observed not to catalyze effectively the initial polycondensation of bishydroxyethyl terephthalate. Therefore, the further development of the hypothesis will be in terms of the interaction of bishydroxyethyl terephthalate with catalyst, suppressing the rate. The following terminology will be used:

B:—CH_2OH (glycol) equivalent.

EB″: an equivalent of bishydroxyethyl terephthalate (E is —C_3H_2-$COOCH_2$—, the equivalent for half a repeating unit, and B″ is —CH_2OH in a bishydroxyethyl terephthalate molecule).

EB′: an equivalent of oligomer or polymer endgroup (E is =C_3H_2-$COOCH_2$— and B′ is —CH_2OH in an oligomer or polymer molecule.

C: catalyst equivalent).

On the basis of this terminology the hypothesis may be expressed in terms of the following equations.

$$EB'' + C \overset{K''}{\rightleftharpoons} EB''C, \qquad \text{fast equilibrium} \tag{5}$$

$$EB' + C \overset{K'}{\rightleftharpoons} EB'C, \qquad \text{fast equilibrium} \tag{6}$$

Forward reactions are:

$$3EB'' + EB''C \xrightarrow{k_1} 2B + 2E + 2EB' + C \tag{7}$$

$$EB'' + EB''C + EB' \xrightarrow{k_2} 2B + 2E + EB' + C \tag{8}$$

$$2EB'' + EB'C \xrightarrow{k_4} 2B + 2E + EB' + C \tag{9}$$

$$EB'C + EB' \xrightarrow{k_5} 2B + 2E + C \tag{10}$$

If with a given catalyst k_1 and k_2 are small relative to k_4 and k_5 and K'' is appreciable, the observed forward rate will be relatively slow. The amount of catalyst rendered inactive will depend on the number of equivalents of bishydroxyethyl terephthalate (—EB″) present. Bishydroxyethyl terephthalate results from glycolysis and redistribution reactions, written as follows:

$$EB''C + EB'' + (E - EB' - EB'') \xrightarrow{k_3} 2EB''\left(\frac{EB'}{E - EB' - EB''}\right) + 2EB'\left(1 - \frac{EB'}{E - EB' - EB''}\right) + (E - EB' - EB'') + C \tag{11}$$

$$\mathrm{EB'C} + \mathrm{EB'} + (\mathrm{E} - \mathrm{EB'} - \mathrm{EB''}) \xrightarrow{k_6} 2\mathrm{EB''}\left(\frac{\mathrm{EB'}}{\mathrm{E} - \mathrm{EB'} - \mathrm{EB''}}\right) + 2\mathrm{EB'}\left(1 - \frac{\mathrm{EB'}}{\mathrm{E} - \mathrm{EB'} - \mathrm{EB''}}\right) + (\mathrm{E} - \mathrm{EB'} - \mathrm{EB''}) + \mathrm{C} \qquad (12)$$

$$2\mathrm{B} + 2(\mathrm{E} - \mathrm{EB'} - \mathrm{EB''}) + \mathrm{C} \xrightarrow{k_7} 2\mathrm{EB''}\left(\frac{2\mathrm{EB'}}{\mathrm{E} - \mathrm{EB'} - \mathrm{EB''}}\right) + 2\mathrm{EB'}\left(1 - \frac{2\mathrm{EB'}}{\mathrm{E} - \mathrm{EB'} - \mathrm{EB''}}\right) \qquad (13)$$

The rate constant k_7 is identical with k' as defined earlier in this report. The reaction represented by eq. (13) contributes to the production of bishydroxyethyl terephthalate only to a minor extent. Equation (11) describes the disappearance of bishydroxyethyl terephthalate via redistribution, and eq. (12) describes its appearance. The value of k_R determined above, therefore, must be a function of k_3, k_6, and k_7. In the presence of antimony trioxide catalyst the found values for k_R were of about the same size as those of k_p. The observed low rates for both k_p and k_R are commensurate with the hypothesis of inactivation of the catalyst caused by bishydroxyethyl terephthalate.

The situation might be different if another catalyst were chosen, such that the species EB″C and EB′C were more nearly equal in reactivity. Unfortunately, many such potential catalysts could be undesirable in commercial processing because of their propensity ultimately to promote degradation side reactions.

CONCLUSION

The values found for k_p, the polycondensation rate constant for linear ethylene terephthalate trimer, are very low. This is surprising, since the technique employed took full account of the reverse reaction. The values found for k_R, the redistribution rate constant (reaction of a polymer end-group of one molecule with an ester group of another molecule, producing two new polymer molecules of different sizes) are similarly low. The data are consistent with a mechanism in which a normally volatile constituent of the reaction mixture, e.g. bishydroxyethyl terephthalate, interacts with the antimony trioxide in such a way as to inactivate it.

The authors wish to thank W. H. McCarty for the development of eqs. (5) through (13). Thanks are due H. U. Yourison for carrying out most of the experimental work.

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Kinetics of the Polymerization of Tetrahydrofuran in the Presence of Water*

M. KUČERA, E. HLADKÝ, and K. MAJEROVÁ,
Research Institute of Macromolecular Chemistry, Brno, Czechoslovakia

Summary

The polymerization of tetrahydrofuran was studied with regard to the presence of polar and nonpolar compounds, or well-solvating and poorly solvating compounds, respectively. Tetrahydrofuran is highly nucleophilic, with a high solvation ability. It is capable of activating the native initiator itself and can be polymerized without any added cocatalyst. The addition of water to the tetrahydrofuran–initiator system decreases the polymerization rate. However, the dependence of the polymerization rate on the concentration of water in the dilute tetrahydrofuran runs through a maximum. The reaction rate is a function of the position of an equilibrium established during the solvation of initiator. All components of the system take part in the establishment of equilibrium.

INTRODUCTION

This paper is part of a series showing the important part of solvation in initiating the cationic polymerizations of oxygenous heterocycles.[1–6] By adding a compound with great solvating ability to the monomer–initiator system the kinetics of the process is so much changed that it is possible to call this additive a cocatalyst.

In previous work we studied the effect of water on the polymerization of trioxane[1–4] and dioxolane.[5,6] To complete the information obtained it was necessary to study the behavior of tetrahydrofuran (THF), the most nucleophilic member of nonsubstituted five-membered and six-membered oxygenous heterocycles capable of being polymerized.

While the most electrophilic trioxane does not activate ion pairs of the native initiator by solvation (the curve of the dependence of reaction rate on concentration of a better solvating additive starts at the origin of the coordinates), the most nucleophilic dioxolane seems to take part in the activation of the initiator. Trioxane does not polymerize in a water-free medium (and in the absence of solvating compounds which are able to take the place of water); dioxolane polymerizes at an appreciable rate even at very low water contents. Dependences of the reaction rate on the amount of water present bear qualitatively the same character and run through

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*A part of this paper was referred at the meeting of the Czechoslovak Chemical Society in Prague, July 1966.

maxima in both cases. The strongly nucleophilic THF with a great solvation ability may be expected to take an intense part in solvation and also in the activation of the acid native initiator. In the following text we describe results of the measurements proving our assumptions.

EXPERIMENTAL

The course of the THF polymerization was followed dilatometrically by means of very simple equipment. The glass dilatometer (Fig. 1) has a bulb 5.5 ml. in volume and a capillary 1.5 mm. in diameter. Filling and handling of the dilatometer have been described previously.[7] The filled dilatometer was placed in a water thermostat. The contraction-conversion relation was calibrated gravimetrically.

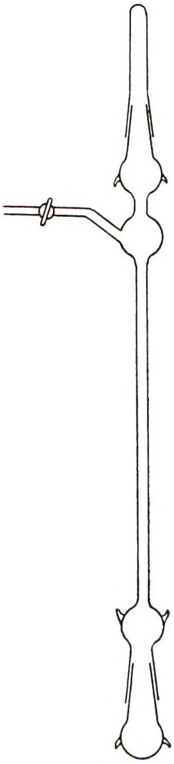

Fig. 1. The dilatometer.

Commercial THF was freed from peroxides by refluxing with $FeSO_4$, dried with solid KOH, and distilled. The distillation product was dried and rectified over sodium metal in a column with approximately 5 TP. A fraction boiling between 64 and 66°C. was taken off and stored over a molecular sieve.

Solvents

The following solvents were employed in the THF polymerizations: heptane and heptane–tetrachloroethane mixture of the same dielectric constant as that of THF at corresponding temperature.

Technical-grade heptane was stirred with concentrated sulfuric acid for 4 hr. The product was washed with water, dried by KOH, and distilled over sodium metal.

Commercial 1,1,2,2-tetrachloroethane was distilled twice. The refraction index was used as a check of purity.

The water content in the polymerization charge (without initiator) was measured by a coulometric modification of Fischer's method allowing determinations in parts per million.[8] The initiator used, the ion pair of the type $\sim\mathrm{Si}^{\oplus}\mathrm{ClO}_4^{\ominus}$, however, interfered with the water determination; therefore the actual concentration of water could not be measured during polymerization. Moist mixtures (with $H_2O > 100$ ppm) were mixed up from dry and wet monomers or their solutions.

Initiator

The initiator $\sim\mathrm{Si}^{\oplus}\mathrm{ClO}_4^{\ominus}$ was prepared by mixing $\mathrm{Me_2SiCl_2}$, $\mathrm{Me_3SiCl}$, and $\mathrm{HClO_4}$ (70%) in a stoichiometric ratio and gave $\mathrm{Me_3Si(OMe_2Si)_{2-5}OSi^{\oplus}ClO_4^{\ominus}}$ by hydrolysis. Volatile products of the hydrolysis (HCl, unreacted chlorsilanes) were pumped out. The concentration of the active component of the initiator $\sim\mathrm{Si}^{\oplus}\mathrm{ClO}_4^{\ominus}$ was determined by titration.

Antimony Pentachloride

Gaseous chlorine was dried with sulfuric acid and led into a tube containing solid antimony. The $\mathrm{SbCl_5}$ formed was trapped in a flask.

RESULTS

The conversion curves were obtained from the contraction–time dependence. One of these curves is plotted in Figure 2. As for the character, the

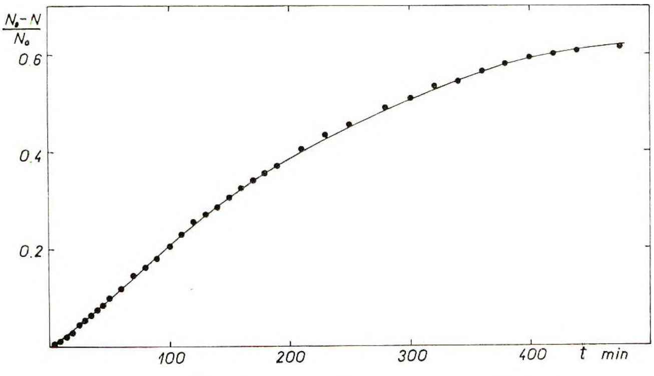

Fig. 2. Conversion curve of THF polymerization. Initial water concentration, $[H_2O]_0 = 9.3$ mmoles/kg.; initiator concentration, $[\sim\mathrm{Si}^{\oplus}\mathrm{ClO}_4^{\ominus}] = 250$ mmoles/kg.; T = 30°C.

curve does not differ from dependences of the conversion on time published recently.[9,10] The reaction rate (per cent per minute) was read off from the curve in the inflection point.

The presence of water in any concentration retards the polymerization of THF. Qualitatively there is no difference between the initiator $SbCl_5$

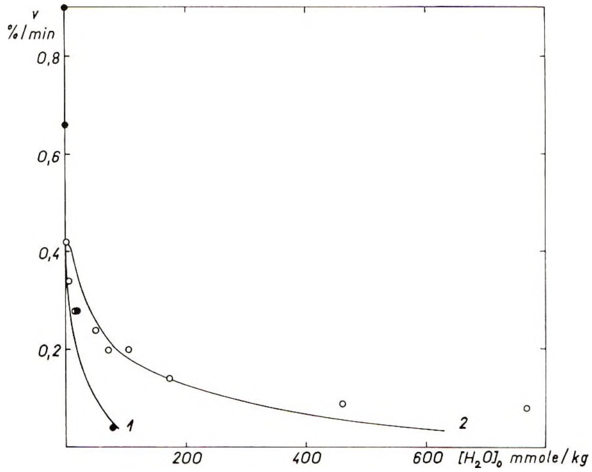

Fig. 3. Dependence of rate of bulk polymerization of THF on the amount of water present: (curve 1) initiator, $[SbCl_5] = 67$ mmoles/kg., $T = 30$°C.; (curve 2) initiator, $[\sim Si^{\oplus}ClO_4^{\ominus}] = 324$ mmoles/kg.; $T = 0$°C.

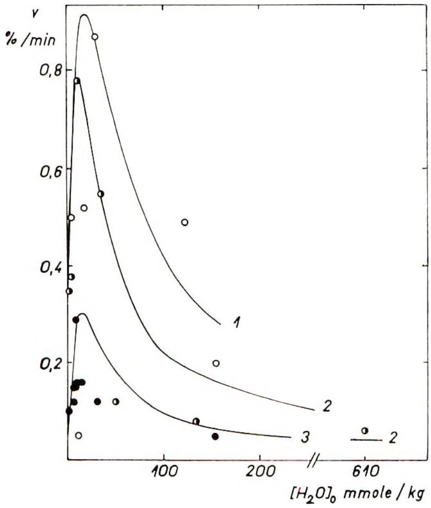

Fig. 4. Dependence of polymerization of THF in solution on water concentration: (curve 1) THF (8.0 moles/kg.) in heptane (4.3 moles/kg); initiator, $[\sim Si^{\oplus}ClO_4^{\ominus}] = 290$ mmoles/kg.; $T = 30$°C.; (curve 2) THF (8.6 moles/kg.) in mixture of heptane (0.09 moles/kg.) and tetrachloroethane (2.4 moles/kg.); initiator concentration, 270 mmoles/kg; $T = 0$°C.; (curve 3) THF (5.2 moles/kg.) in mixture of heptane (0.14 moles/kg.) and tetrachloroethane (3.9 moles/kg.); initiator concentration, 180 mmoles/kg.; $T = 0$°C.

and $\sim Si^{\oplus}ClO_4^{\ominus}$, as is shown in Figure 3. The reaction rate decreases with increasing concentration of water. If we dilute THF with a solvent, then a small amount of water increases the polymerization rate but, again, a higher concentration of water retards the reaction (Fig. 4). A paper about the polymerization of THF in solution with the same result appeared very recently.[11]

DISCUSSION

THF is shown to be able to activate the native initiator. Its polymerization both in bulk and in solution occurs without special cocatalysts. According to our conception described in previous papers,[1-6] THF itself is a cocatalyst. Since we must admit that more compounds take part in the solvation of the native initiator, it is more correct to include this fact in a scheme derived originally for one cocatalyst only:[2]

$$\mathrm{Ac}^{\oplus}\mathrm{B}^{\ominus} + \textstyle\sum_k n_k \mathrm{S}_k \xrightleftharpoons{K_{k1}} \mathrm{Ac}^{\oplus}\|\mathrm{B}^{\ominus} \tag{1}$$

$$\mathrm{Ac}^{\oplus}\|\mathrm{B}^{\ominus} + \textstyle\sum_k m_k \mathrm{S}_k \xrightleftharpoons{K_{k2}} \mathrm{A\text{-}P} + \mathrm{Ac}^{\oplus}\mathrm{SB}^{\ominus} \tag{2}$$

$$\mathrm{Ac}^{\oplus}\mathrm{SB}^{\ominus} \xrightleftharpoons{K_{k3}} \mathrm{Ac}^{\oplus}\|\mathrm{B}^{\ominus} + \textstyle\sum_k r_k \mathrm{S}_k \tag{3}$$

In these equations $Ac^{\oplus}B^{\ominus}$ is the native initiator which, in the form of an "intimated" ion pair, is not able to start the polymerization. After it has been "loosened" by n_k molecules of the solvating agent S_k, an active initiating or growth centrum $Ac^{\oplus}\|B^{\ominus}$ is formed. If there is an excess of solvating molecules in the system, the equilibrium is shifted in favor of the strongly solvated ion pairs $Ac^{\oplus}SB^{\ominus}$, which are virtually inactive during the initiation and growth. Strongly solvated $Ac^{\oplus}SB^{\ominus}$, either themselves or in cooperation with the monomer, can again become active centers; a certain number r_k of solvating molecules S_k is liberated at the same time. In the equations A-P is an inactive species, (e.g., A may be initiating or growth chain, P may be an OH group), and K_{k1}, K_{k2}, and K_{k3} are the equilibrium constants.

If the equilibria in these equations are established fast enough, the equation for the initial reaction rate may be obtained by solving the following equation (derived by Kučera and Hladký[2]).

$$v_{\text{initial}} = k[\mathrm{Ac}][\mathrm{M}] \tag{4}$$

where $[\mathrm{Ac}] = [\mathrm{Ac}^{\oplus}\|\mathrm{B}^{\ominus}] = q[\text{initiator}]$:

$$q = \textstyle\sum_k K_{k1}\mathrm{S}_k^{n_k}/[1 + \sum_k K_{k1}\mathrm{S}_k^{n_k} + (\sum_k [\mathrm{S}_k]^{r_k}/\sum_k K_{k3})\sum_k K_{k1}[\mathrm{S}_k]_k^{n_k} \tag{5}$$

During the bulk polymerization of THF (Fig. 3), the native initiator could be solvated only by THF and by water. For this pair eq. (5) can be arranged as follows:

$$q = (K_{11}[\mathrm{H_2O}]^{n_{\mathrm{H_2O}}} + K_{12}[\mathrm{THF}]^{n_{\mathrm{THF}}}) \Big/ \Big(1 + K_{11}[\mathrm{H_2O}]^{n_{\mathrm{H_2O}}}\{1 + [1/(K_{31} + K_{32})][\mathrm{THF}]^{r_{\mathrm{THF}}}\} + K_{12}[\mathrm{THF}]^{n_{\mathrm{THF}}}\{1 + [1/(K_{31} + K_{32})][\mathrm{H_2O}]^{r_{\mathrm{H_2O}}}\} + \{(K_{11}[\mathrm{H_2O}]^{n_{\mathrm{H_2O}}+r_{\mathrm{H_2O}}} + K_{12}[\mathrm{THF}]^{n_{\mathrm{THF}}+r_{\mathrm{THF}}})/(K_{31} + K_{32})\}\Big) \quad (6)$$

The relations among some constants in eq. (6) can be estimated with great probability. For example, it is hardly possible that the monomer would be able to "oversolvate" active centers. In such case it is to be expected that the highest rate would be connected with the greatest solvation. Therefore it is not necessary to take eq. (3) into account, or $K_{3,\mathrm{THF}} = K_{32} = 0$; $[\mathrm{THF}]^{r_{\mathrm{THF}}} = 0$. We can also admit that $K_{11} \gg K_{31}$ and $K_{11} \gg K_{12}$ (this is supported by measurements in the dioxolane polymerization).[6] When polymerizing trioxane and dioxolane it was found that $n_{\mathrm{H_2O}} = r_{\mathrm{H_2O}} = 1$. If we use the same values of $n_{\mathrm{H_2O}}$ and $r_{\mathrm{H_2O}}$ also for the case described, it is possible to rewrite eq. (6) in a more simple, approximate form:

$$q \doteq (K_{11}[\mathrm{H_2O}] + K_{12}[\mathrm{THF}]^{n_{\mathrm{THF}}})/\{1 + K_{11}[\mathrm{H_2O}] + K_{12}(1 + [\mathrm{H_2O}]/K_{31})[\mathrm{THF}]^{n_{\mathrm{THF}}} + (K_{11}/K_{31})[\mathrm{H_2O}]^2\} \quad (7)$$

It follows from eq. (7) that at lower THF concentrations it is necessary to increase the water concentration to reach the maximum value of q (supposing that the initiator is not activated by a solvent).

By lowering the concentration of THF, unfortunately, the affinity of the medium to water changes. Water has also a considerable influence on q and, hence, on the reaction rate (we shall try to analyze this factor in our next communication). Both effects cannot be separated. Therefore, we are afraid that it will not be possible to give an explicit, direct proof of the validity of eq. (7); only a comparison between calculated and measured rates is available at present.

Equation (7) is in a good agreement with the experimental data. In Figures 3 and 4 the lines represent computed values, and the experimental

TABLE I
Values of Constants for Computing Dependence of Polymerization Rate of Tetrahydrofuran on Water Content[a]

THF concn., moles/kg.	Polymzn. conditions, Fig. no. and curve no.		k	K_{11}	K_{12} ($\times 10^{-4}$)	K_{31} ($\times 10^{-2}$)
13.8	3	1	7.2	60	0.6	0.04
13.8	3	2	0.5	5	0.85	1.00
8.6	4	2	8.0	5	0.3	0.12
5.2	4	3	8.6	5	0.3	0.12
8.0	4	1	4.7	6	0.8	0.43

[a] Here, $n_{\mathrm{THF}} = 3$ and $n_{\mathrm{H_2O}} = r_{\mathrm{H_2O}} = 1$.

points represent experimental values. The constants used for calculation are summarized in Table I.

CONCLUSION

THF itself cocatalyzes the native initiator. The kinetics of the process are shown to be determined not only by the concentration of the proper cocatalyst (i.e., by a compound with the highest solvation ability), but by the equilibrium, the establishment of which is influenced by all components present in the system.

The reaction rate is a function of the state of this equilibrium.

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Polymerization of Styrene with VCl_4–Aluminum Alkyls

L. C. ANAND, S. S. DIXIT, and S. L. KAPUR, *National Chemical Laboratory, Poona, India*

Synopsis

Polymerization of styrene has been carried out with VCl_4–$AlEt_3$ and VCl_4–Al(i-Bu)$_3$ catalyst systems. These two systems have been found to behave in a similar manner but their behavior is different from those systems where $VOCl_3$ had been used instead of VCl_4. Reaction is first order with respect to monomer concentration for both the systems and first order with respect to catalyst in the case of VCl_4–$AlEt_3$. In the case of VCl_4–Al(i-Bu)$_3$, the rate of polymerization is independent of catalyst concentration but intrinsic viscosities increase with increasing catalyst concentration. The average valence of vanadium in the catalyst complexes has been discussed in relation to nature of catalyst sites. Activation energy and effect of diethyl zinc support the anionic mechanism for the two systems.

The use of $VOCl_3$–aluminum alkyl catalyst systems in the polymerization of styrene[1] gave poor stereospecificity and high rates of polymerization. It was indicated that the presence of oxygen in the $VOCl_3$ molecule is somehow responsible for the poor stereospecificity as well as higher rates than those obtained with conventional Ziegler catalyst, i.e., $TiCl_4$–aluminum alkyl. To verify this, the polymerization of styrene with VCl_4–aluminum alkyls has been studied at 40°C. It was observed that though these results are in great contrast with those obtained from $VOCl_3$-aluminum alkyls, they are quite parallel to those obtained with $TiCl_4$–aluminum alkyls catalyst systems. Also an attempt has been made to relate the valence of vanadium in the catalyst with its activity. The catalyst systems formed by reaction of VCl_4 with different alkyls[2–9] have been used earlier for the polymerization of several hydrocarbon monomers including dienes, but no detailed kinetic study for styrene polymerization with the above catalyst systems has appeared.

EXPERIMENTAL

Materials

VCl_4 was obtained as a sample from Ethyl Corporation, U.S.A. It was distilled under inert conditions before use and a stock solution (0.5*M*) in *n*-hexane was prepared. A fresh solution was made after every 4–5 days from freshly distilled VCl_4, because a dark-brown solid started depositing on the walls of the container after that time.

$AlEt_3$ and $Al(i\text{-}Bu)_3$ (Ethyl Corporation, U.S.A.) were distilled under reduced pressure in an atmosphere of nitrogen before use. Stock solutions of $AlEt_3$ ($2M$) and $Al(i\text{-}Bu)_3$ ($1M$) in *n*-hexane were prepared.

Styrene (Dow Chemicals, U.S.A.) was treated with alkali, washed with water and dried over anhydrous Na_2CO_3. It was distilled under reduced pressure in an atmosphere of dry nitrogen and kept over activated silica gel.

n-Hexane was treated with concentrated H_2SO_4(C.P.) till it gave no color to the acid layer; it was then washed with water and dried over anhydrous $CaCl_2$. It was distilled and stored over sodium wire. It was refluxed over sodium under nitrogen for 12 hr. and redistilled before use.

Polymerization

All the experiments were carried out inside a dry glove box, which was maintained anhydrous under an oxygen-free nitrogen atmosphere. All the reagents were added with all-glass hypodermic syringes, fitted with stainless steel needles.

In an Erlenmeyer flask (50 ml.) fitted with B-19 cone joint, the reagents were added in the following order: solvent, VCl_4 solution, aluminum alkyl solution. The catalyst complex formed was aged for a given time and then monomer was introduced into the system. The flask was closed with a well greased B-19 socket joint and held in a thermostat maintained at constant temperature. The reaction mixture was stirred vigorously with a specially fabricated magnetic stirrer.[10] After the specified time of reaction, the polymer was precipitated with an excess of methanol containing 5% HCl and left overnight to settle down well. It was washed thoroughly with methanol in a weighed crucible provided with a sintered disk and dried to constant weight.

The polymer obtained was dissolved in hot chlorobenzene, reprecipitated, separated over a sintered disk, dried, and redissolved for determination of intrinsic viscosity. Viscosities were determined in chlorobenzene at 25°C. since it was reported[11] that isotactic polystyrene is completely soluble in it.

Potentiometric Titration for the Determination of Vanadium Valence

To get an insight into the type of catalytic species responsible for polymerization, the valence distribution of vanadium in the catalytic complexes at various Al/V ratios was studied potentiometrically. Redox titrations of an acid solution of the complex were carried out with the use of saturated calomel and platinum indicator electrodes at 80°C., $0.1N$ $KMnO_4$ solution being used as oxidant.

RESULTS AND DISCUSSION

A dark-brown precipitate was formed instantly on mixing the solution of alkyl with VCl_4 solution, irrespective of their concentrations. On addition of the monomer to this complex, its color became lighter. This behavior was observed in the case of both catalyst systems. In the case of the VCl_4–$AlEt_3$ catalyst system, the rate of polymerization increased with increasing aging time up to 20 min. The reaction carried out at a 24-hr. aging time, however gave a lower rate of polymerization as well as a lower intrinsic viscosity of the polymer (see Table I). In the case of the VCl_4–$Al(i\text{-}Bu)_3$ catalyst system, the rate of polymerization decreased rather slowly with aging time up to 24 hr. but there was no significant change in intrinsic viscosity (Table II). For all further experiments, an aging time of 20 min. was decided upon for both catalyst systems.

TABLE I
Effect of Aging Time on VCl_4–$AlEt_3$ System[a]

Aging time, min.	Conversion, %	[η], dl./g.
10	1.26	0.412
20	1.63	0.505
30	1.42	0.410
60	1.56	0.447
1440	1.36	0.353

[a] [VCl_4] = 0.02 mole/l.; [$AlEt_3$] = 0.04 mole/l.; Al/V = 2; [styrene] = 3.48 mole/l.; reaction time = 60 min.; temperature = 40°C.

TABLE II
Effect of Aging Time on VCl_4–$Al(i\text{-}Bu)_3$ System[a]

Aging time, min.	Conversion, %	[η], dl./g.
10	3.89	0.2289
20	2.02	0.2278
30	1.81	0.2989
60	1.84	0.1896
1440	1.10	0.3036

[a] [VCl_4] = 0.02 mole/l.; Al/V = 3; reaction time = 60 min.; [$Al(i\text{-}Bu)_3$] = 0.06 mole/l.; [styrene] = 3.48 mole/l.; temperature = 40°C.

The ratio of the catalyst components is known to have a profound effect[12,13] on the nature of the catalyst sites. In the two systems under investigation, the rate of polymerization was found to decrease with increase in Al/V ratio (Figs. 1 and 2). In the case of the VCl_4–$AlEt_3$ system (Fig. 1), the rate of polymerization decreased sharply between Al/V ratios of 1 and 2, and a further increase in ratio had no effect on the rate of polymerization. There was a sharp increase in intrinsic viscosity of polymer above an Al/V ratio of 1.5, and it reached a maximum at an Al/V

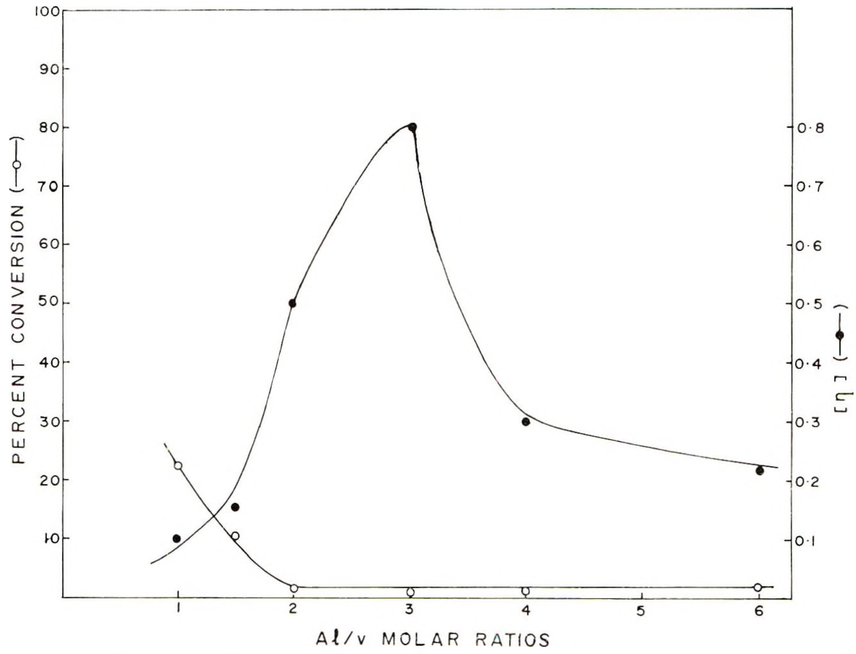

Fig. 1. Effect of Al/V ratio on VCl$_4$–AlEt$_3$ catalyst system: (○) conversion vs. Al/V; (●) Al/V vs. [η]. [VCl$_4$] = 0.02 mole/l.; [styrene] = 3.48 mole/l.; total volume = 25 ml.; aging time = 20 min.; reaction time = 60 min.; temperature = 40°C.

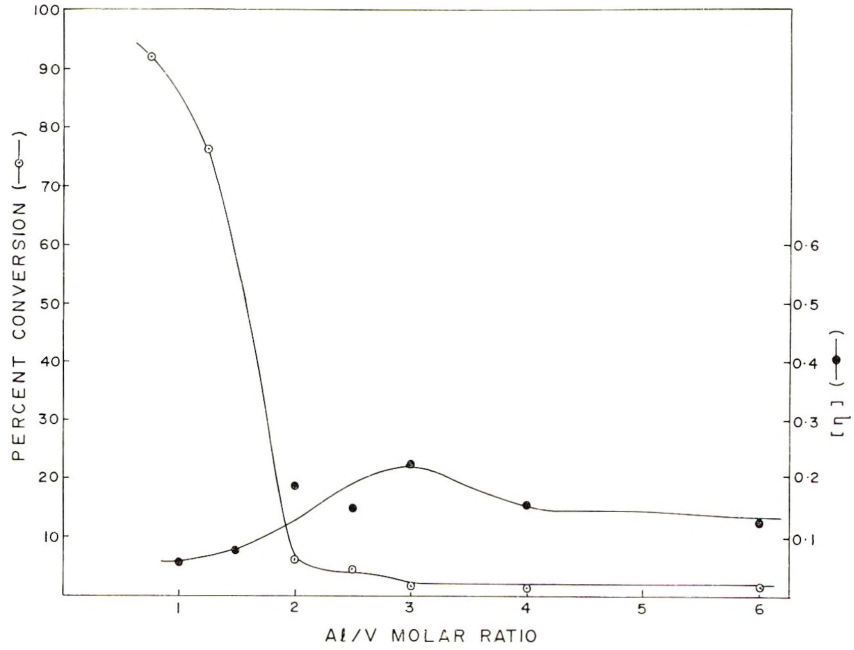

Fig. 2. Effect of Al/V ratio on VCl$_4$–Al(i-Bu)$_3$ system: (⊙) conversion vs. Al/V; (●) Al/V vs. [η]. [VCl$_4$] = 0.02 mole/l.; [styrene] = 3.48 mole/l.; total volume = 25 ml.; aging time = 20 min.; reaction time = 60 min.; temperature = 40°C.

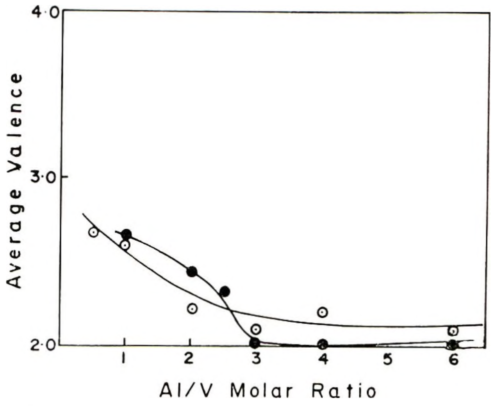

Fig. 3. Effect of Al/V ratio on the valence of vanadium in (⊙) VCl_4–$AlEt_3$ and (●) VCl_4–$Al(i\text{-}Bu)_3$ catalyst systems.

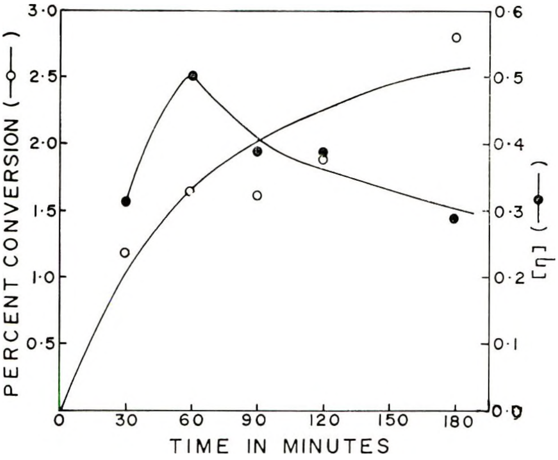

Fig. 4. Effect of time on VCl_4–$AlEt_3$ system: (O) conversion vs. time; (●) [η] vs. time. $[VCl_4]$ = 0.02 mole/l.; Al/V = 2; [styrene] = 3.48 mole/l.; aging time = 20 min.; temperature = 40°C.

ratio of 3. A further increase in Al/V ratio gave a polymer with lower intrinsic viscosity, probably due to the chain transfer action of the excess $AlEt_3$. In the case of the VCl_4–$Al(i\text{-}Bu)_3$ catalyst system (Fig. 2), there was also a decrease in the rate of polymerization as the Al/V ratio was increased, but in this catalyst system, a stable state was obtained after an Al/V ratio of 3. The intrinsic viscosity of the polymer was also maximum at an Al/V ratio of 3. The lower intrinsic viscosity at higher Al/V ratio was probably due to chain transfer action of an excess of metal alkyl. The low values of intrinsic viscosities at low Al/V ratios in both the systems are attributable to the fact that the reaction between the catalyst components is incomplete at these ratios thereby giving rise to species which presumably act by cationic mechanisms, thus lowering the intrinsic

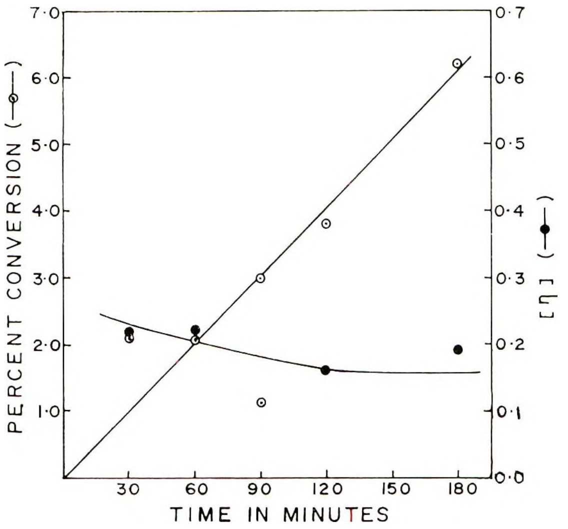

Fig. 5. Effect of time on VCl_4–Al(i-Bu)$_3$ system: (O) conversion vs. time; (●) [η] vs. time. [VCl_4] = 0.02 mole/l.; Al/V = 3; [styrene] = 3.48 mole/l.; aging time = 20 min.; temperature = 40°C.

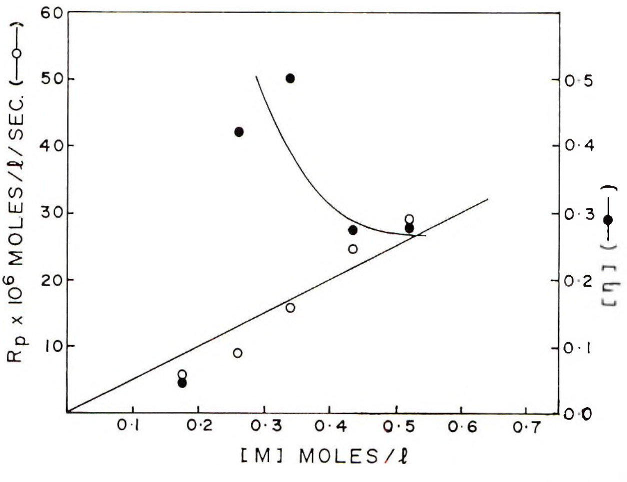

Fig. 6. Effect of monomer concentration on VCl_4–$AlEt_3$ system: (O) R_p vs. [M]; (●) [M] vs. [η]. [VCl_4] = 0.02 mole/l.; Al/V = 2; aging time = 20 min.; reaction time = 60 min.; temperature = 40°C.

viscosity and giving higher rates of polymerization at these lower ratios. The same conclusions can be drawn from the plots of Al/V ratios versus average valence of vanadium (Fig. 3) in the catalytic complex. It can be seen that average valence of vanadium decreases up to a ratio of Al/V of about 2 in the case of the VCl_4–$AlEt_3$ system and up to a ratio of Al/V of about 3 in the case of the VCl_4–Al(i-Bu)$_3$ system. In both catalyst systems a further increase in Al/V ratios has no effect on the average valence of vanadium. A similar dependence of rate of polymerization on the Al/V ratios was previously observed for the $VOCl_3$–$AlEt_3$ and $VOCl_3$–$Al(i\text{-}Bu)_3$ catalyst systems.[1] Since the reaction between the components of the VCl_4–$AlEt_3$ catalyst system is complete at an Al/V ratio of 2, a detailed

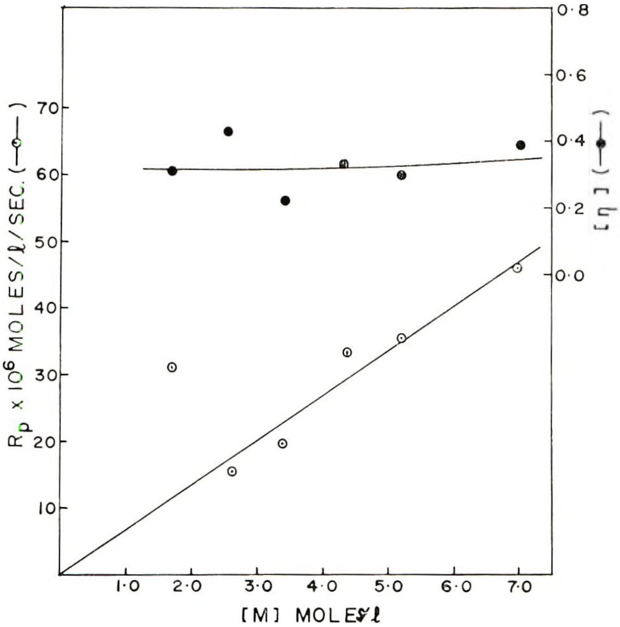

Fig. 7. Effect of monomer concentration on VCl_4–$Al(i\text{-}Bu)_3$ system: (⊙) R_p vs. [M]; (●) [M] vs. [η]. [VCl_4] = 0.02 mole/l.; Al/V = 3; aging time = 20 min.; reaction time = 60 min.; temperature = 40°C.

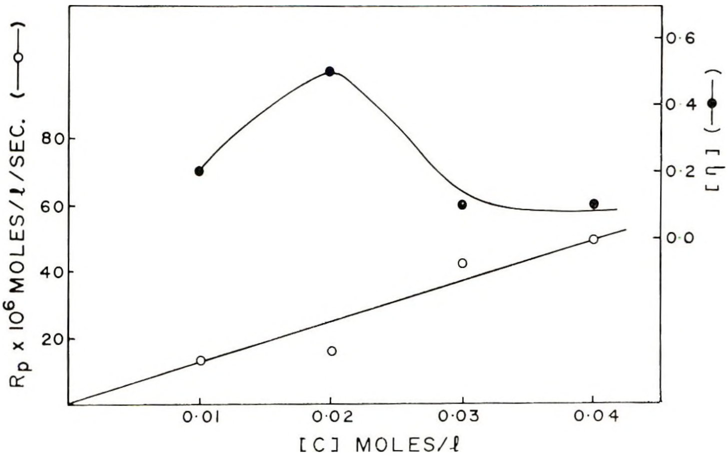

Fig. 8. Effect of catalyst concentration on VCl_4–$AlEt_3$ system: (○) R_p vs. [C]; (●) [C] vs. [η]. Al/V = 2; [styrene] = 3.48 mole/l.; aging time = 20 min.; reaction time = 60 min.; temperature = 40°C.

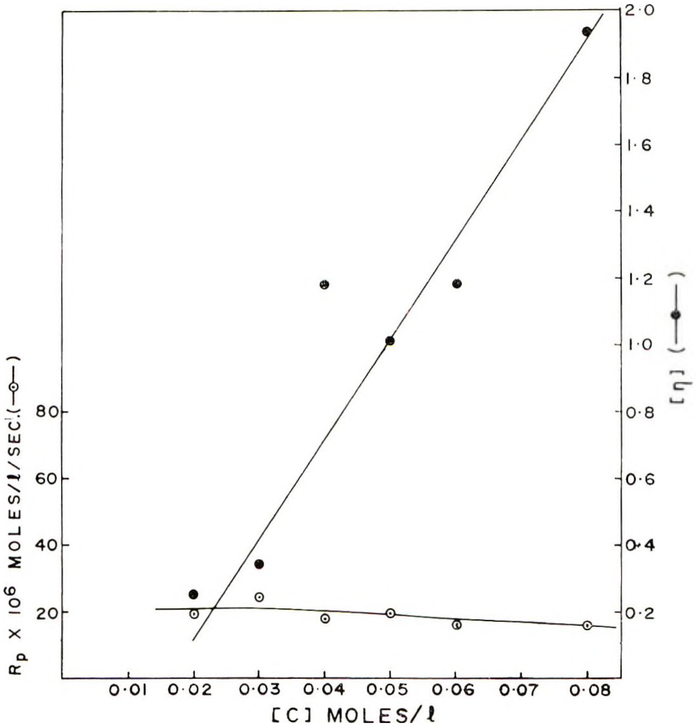

Fig. 9. Effect of catalyst concentration on VCl_4–$Al(i\text{-}Bu)_3$ system: (⊙) R_p vs. [C]; (●) [C] vs. [η]. Al/V = 3; [styrene] = 3.48 mole/l.; aging time = 20 min.; reaction time = 60 min.; temperature = 40°C.

kinetic study was carried out at this ratio only, even though the value of intrinsic viscosity was highest at Al/V ratio of 3 (Figs. 1 and 3).

The kinetic study with the VCl_4–$Al(i\text{-}Bu)_3$ system was carried out at an Al/V ratio of 3, since the reaction between the catalyst components is complete at the ratio of 3 (Figs. 2 and 3).

In the case of VCl_4–$AlEt_3$, the rate of polymerization was steady only during the first 60 min. (Fig. 4), after which it decreased probably due to the covering of catalyst sites with the precipitated polymer in hexane. A similar covering of catalyst sites has been established for the system $TiCl_3$–$AlEt_2Cl$ for the polymerization of ethylene.[14] There was a slight decrease in the value of intrinsic viscosity with reaction time. In the case of the VCl_4–$Al(i\text{-}Bu)_3$ system (Fig. 5) the rate of polymerization was steady up to 3 hr. reaction time, and also there was very little variation in the value of intrinsic viscosity with reaction time. A reaction time of 1 hr. was decided upon for all further studies with both the catalyst systems.

Polymerization was found to be first order with respect to monomer concentrations (Figs. 6 and 7) in both the catalyst systems, and rates of polymerization as well as rate constants for the two systems are of the same order [$K = 2.69 \times 10^{-8}$ l./mole/sec. for the VCl_4–$AlEt_3$ system and

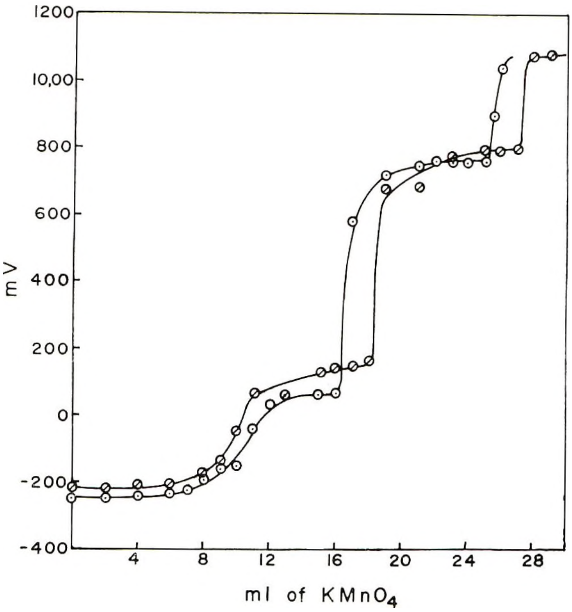

Fig. 10. Distribution of valence of vanadium (⊙) in VCl_4–$AlEt_3$ system at Al/V = 2; (⦶) in VCl_4–$Al(i\text{-}Bu)_3$ system at Al/V = 3.

$K = 3.5 \times 10^{-8}$ l./mole/sec. for the VCl_4–$Al(i\text{-}Bu)_3$ system]. When $VOCl_3$ is used as transition metal compound in combination with $AlEt_3$ and $Al(i\text{-}Bu)_3$ there is a very large difference in the rates of polymerization as well as in the rate constants in the two systems, whereas VCl_4 with these two metal alkyls gives catalyst systems which behave similarly. The activity of the catalyst systems under investigation is comparable to that of $TiCl_4$–Al alkyls for the polymerization of styrene.

The reaction is first order with respect to catalyst concentration (Fig. 8) in the case of VCl_4–$AlEt_3$ catalyst system ($K = 3.9 \times 10^{-8}$ l./mole/sec.) and there is no change in intrinsic viscosity with catalyst concentration. In the case of the VCl_4–$Al(i\text{-}Bu)_3$ catalyst system, however (Fig. 9), there is no increase in rate of polymerization with the increase in catalyst concentration, and the reaction is zero order with respect to catalyst concentration. However, there is a sharp increase in intrinsic viscosity with catalyst concentration (Fig. 9). The absence of increase in rate of polymerization with increase in catalyst concentration may be explained by the fact that as the concentration of catalyst is increased, there is more coagulation of catalyst resulting in no increase in the catalyst surface and thus no increase in the rate.

Most of vanadium in the catalyst complex is in the divalent form in the case of both catalyst systems (Fig. 10). This is in contrast with earlier observations[1–16] that trivalent vanadium is more effective for stereospecific polymerization. The catalyst systems under investigation, though almost completely in divalent form, give better stereospecificities (more than

40% isotactic). Another reason for the better performance of the catalysts under investigation may be the less complicated reactions of the catalyst components (compared to $VOCl_3$–Al alkyl systems), giving rise to lesser number of catalytic species.

All the above observations indicate a coordinated anionic type of mechanism similar to that observed with the $TiCl_4$–$AlEt_3$ system.

Further support to the above mechanism is obtained from the studies of activation energy and effect of diethylzinc on polymerization. The activation energy calculated from the plots of log R_p versus $1/T$ was 5.53 kcal./mole for the VCl_4–$AlEt_3$ system and 5.34 kcal./mole for the VCl_4–$Al(i\text{-}Bu)_3$ system; these values are in the range of the values usually obtained (5–12 kcal./mole) for most Ziegler-type catalyst systems like $TiCl_4$–$AlEt_3$ and $TiCl_3$–$AlEt_3$.[17,18] Also diethylzinc was found to act as a chain transfer agent, which is similar to its behavior with classical Ziegler catalyst, $TiCl_4$–$AlEt_3$.[19]

Thus, these studies show that the oxygen atom in the transition metal halide can change the behavior of catalyst systems greatly.

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Study of Ziegler-Natta Catalysts. Part I. Valence State and Polymerization Activity

L. KOLLÁR, A. SIMON, and J. OSVÁTH, *Research Institute for the Plastics Industry, Budapest, Hungary*

Synopsis

Polymerization at temperatures lower than the temperature of catalyst formation induces no change in the solid phase of the catalyst formed by $Al(C_2H_5)_3 + TiCl_4$. In polymerizations with catalysts of this class, maximum activity is observed when the titanium component of the catalyst is trivalent. Any different behavior indicates the presence of aluminum alkyl chlorides in the liquid phase of the catalyst.

INTRODUCTION

The various parameters—such as temperature, concentration, molar proportion of the catalysts, aging, etc.—which influence the formation of polymerization catalysts from $AlEt_3$ and $TiCl_4$ determine two essential factors with a decisive influence on the polymerization process, namely the concentration of trivalent titanium in the catalyst and the type of aluminum alkyls in solution formed during or after the reaction of the two components.

The experiments were devised in such a way as to show as clearly and separately as possible the role of both factors. Thus catalysts of different valences were on the one hand determined by the temperature of catalyst formation, and polymerization with these catalysts was carried out under conditions when it was safe to assume no further change in the catalyst. On the other hand experiments were carried out in which polymerization was performed (*a*) at various temperatures with catalysts which presumably were not further affected by the polymerization conditions and (*b*) with catalysts which were modified by the addition of aluminum alkyls.

The present work attempts to clarify the role of the valence state of the titanium in active catalysts. Conclusions are drawn on the polymerization process by comparing the effect of the valence state of titanium in the catalyst and polymerization rate.

EXPERIMENTAL

Determination of the Valence of Titanium

$AlEt_3$ was reacted with $TiCl_4$ in a flask provided with stirrer in an oxygen-free heptane medium at various temperatures. To determine the reduced titanium the catalyst was decomposed with sulfuric acid, a 50% $FeCl_3$ solution was added, and the reduced iron was titrated with $KMnO_4$. Details of the method have been described earlier.[1–4]

Polymerization Apparatus

A sketch of the apparatus is shown in Figure 1. From the flask *e*, ethylene passes into a copper helix *f*; the pressure of the gas is registered by the manometer *g*. The pressure is adjusted with the reductor *h*, to a definite value (0.4 atm.) and the gas is led through the valve *i* and a pressure regulator into the polymerization reactor, *a*. The rate of stirring was 1300 rpm. The volume of the reactor was 500 ml. and the total quantity of the (*n*-heptane) solvent was 220 ml.

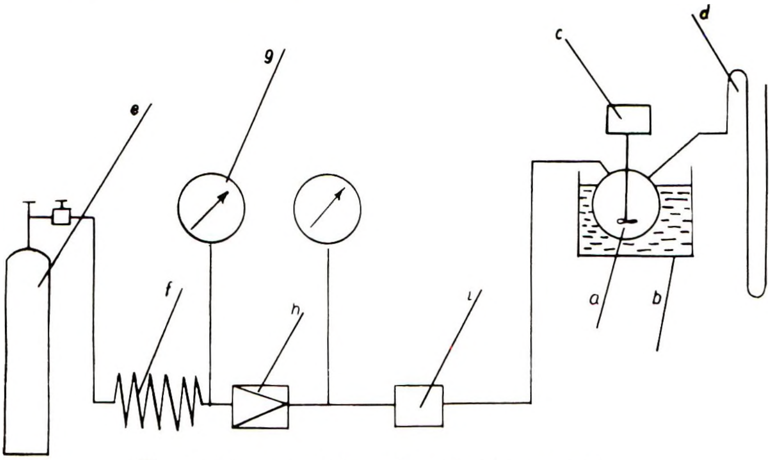

Fig. 1. Diagram of the polymerization apparatus.

Polymerization

After flushing with argon, first the titanium tetrachloride and then the triethylaluminum, in the form of a 0.796 mole/l. *n*-heptane solution, were

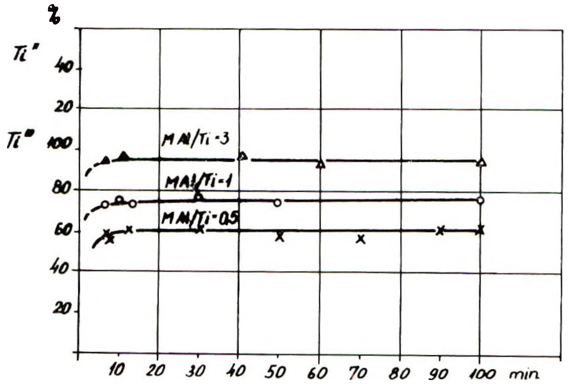

Fig. 2. Changes in the valence of titanium in the reaction $AlEt_3 + TiCl_4$ vs. the molar ratio of the components. $[TiCl_4] = 9.25 \times 10^{-3}$ mole/l. *n*-heptane; 0°C.

added. The components were allowed to react for 30 min. at which time the pressure was reduced to 100 mm. Hg and ethylene was introduced; polymerization proceeded at a constant pressure of 660 mm. Hg. Polymerization was observed by the pressure drop (in milliliters) per minute.

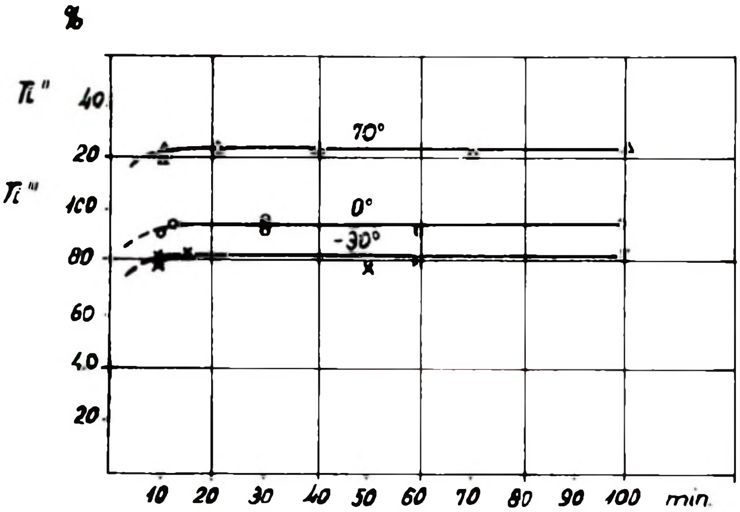

Fig. 3. Changes in the valence of titanium in the reaction $AlEt_3 + TiCl_4$ vs. temperature. $[TiCl_4] = 9.25 \times 10^{-3}$ mole/l. n-heptane; $AlEt_3/TiCl_4 = 3$.

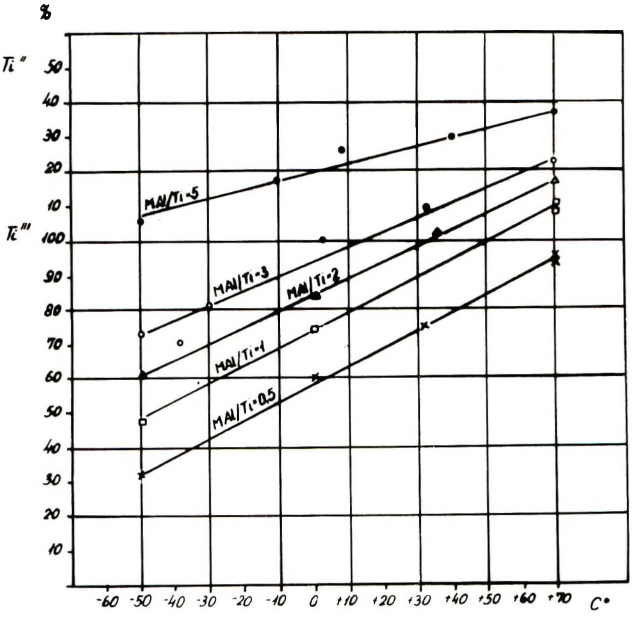

Fig. 4. Changes in the valence of titanium vs. reaction temperature at different Al/Ti molar ratios. Reaction time 30 min.; $[TiCl_4] = 9.25 \times 10^{-3}$ mole/l. n-heptane.

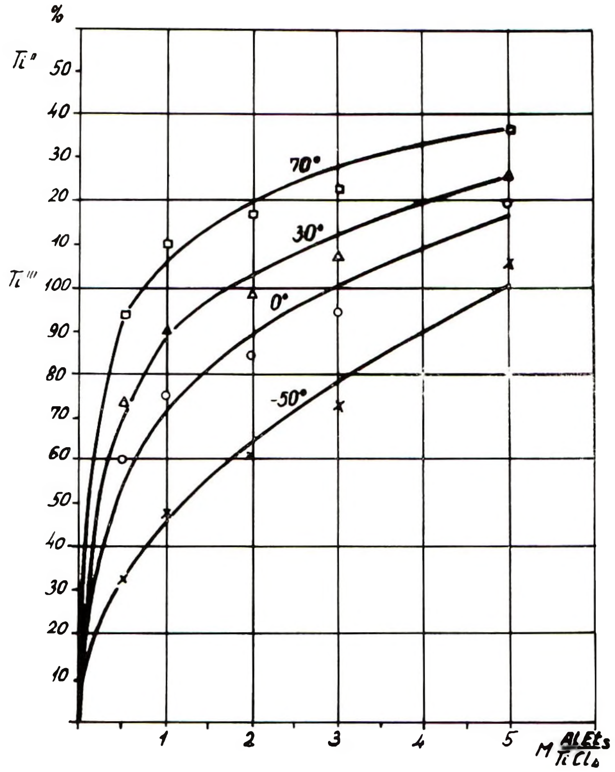

Fig. 5. Changes in the valence of titanium vs. the molar ratio $AlEt_3/TiCl_4$ at different temperatures. Reaction time 30 min.; $[TiCl_4] = 9.25 \times 10^{-3}$ mole/l. *n*-heptane.

The smallest ethylene consumption which could be read off was 0.1 ml. The rate curves were reproducible.

For the kinetic curves, the polymerization rate was plotted versus ethylene consumption in 1 hr. and for a 1-liter volume of the polymerizing mixture.

The average valence of titanium is known to decrease very rapidly under these conditions, and it soon reaches a practically constant value[3] (Figs. 2 and 3). It is difficult to reproduce the rapid section of the reduction process, so that the values measured after 30 min. reaction are plotted as characteristic of the valence state of titanium.

The data furnished by the reduction curves indicate that the degree of reduction of titanium is proportional to the temperature (Fig. 4). It can be seen that the observations of other authors[3,5,6] are manifest here too, namely that reduction progresses also with increasing Al/Ti molar ratio. The valence state of titanium in the temperature interval between −50 and + 70°C. and for Al/Ti molar ratios of 0.5–5 can be read off Figure 4. For the same molar ratio the valence changes linearly with the temperature.

The decrease in the slope of the curves with increasing Al/Ti molar ratios indicates a lesser dependence of the reduction on the temperature at higher molar ratios; thus the isotherm dependence of the reduction on the molar ratio is not linear (Fig. 5).

Ethylene was polymerized at −30°C. with catalysts formed at different temperatures. After the 30 min. allowed for the formation of the catalyst

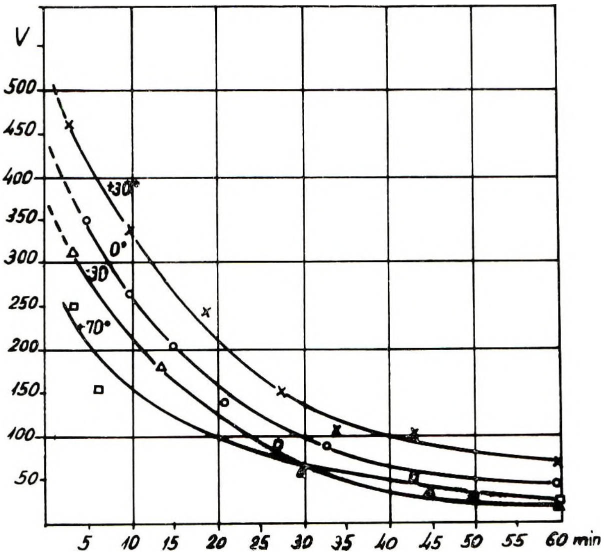

Fig. 6. Polymerization rate of ethylene vs. temperature of catalyst formation. $[TiCl_4] = 9.25 \times 10^{-3}$ mole/l. *n*-heptane; $AlEt_3/TiCl_4 = 2$. V = in units of grams ethylene per liter solvent per hour per atm..

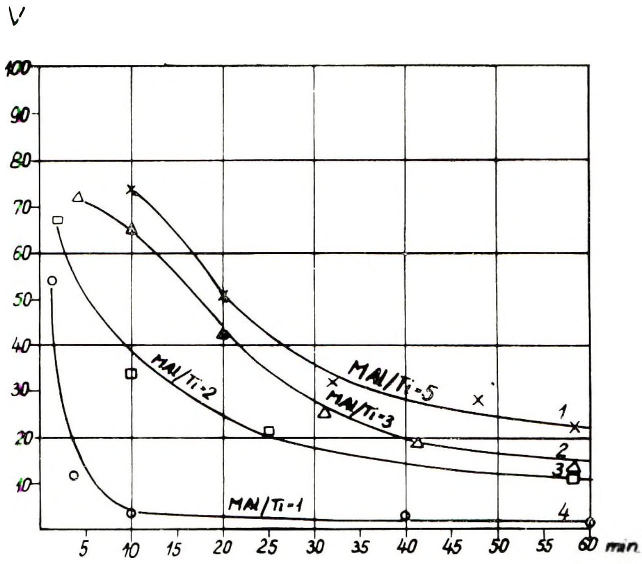

Fig. 7. Polymerization rate of ethylene vs. the molar ratio of Al/Ti. $[TiCl_4] = 3.7 \times 10^{-3}$ mole/l. *n*-heptane.

the system was kept for another 30 min. at −30°C. The molar ratio of the components was Al/Ti = 2. Figure 6 shows that the polymerization activities of catalysts formed between −30 and +30°C. increase with the temperature at which they were formed, but the polymerization rate with the catalyst formed at 70°C. is lower than the highest rate obtained at lower temperatures.

Figure 7 shows rate curves for catalysts which were formed at 0°C. and used for polymerization at the same temperature. The molar ratio of the catalyst components varied between 1 and 5. It seems that polymerization rate increases with increasing Al/Ti molar ratio.

DISCUSSION

It appears from Figure 4 that the valence state of the titanium in the catalyst is well defined by the temperature and the molar ratio of the components. In the experiments illustrated in Figure 6, the experimental conditions ensured the slightest possible change in the valence state of the catalyst during the polymerization process, as polymerization temperature (−30°C.) was lower than the temperature used in the formation of the catalyst. The maximum polymerization rate occurred at the maximum concentration of trivalent titanium, corresponding at 30°C. to Al/Ti = 2, (Fig. 6, curve *1*), with a Ti (III) concentration of about 98% (Fig. 4). At 70°C. the activity of the catalyst with the same molar ratio is considerably lower (Fig. 6, curve *4*). Corresponding to Figure 4 this contains already about 20% Ti (II). These observations are illustrated by Figure 8, which compares the polymerization rates after 25 min. (in Fig. 6) with the corresponding valence values read off Figure 4.

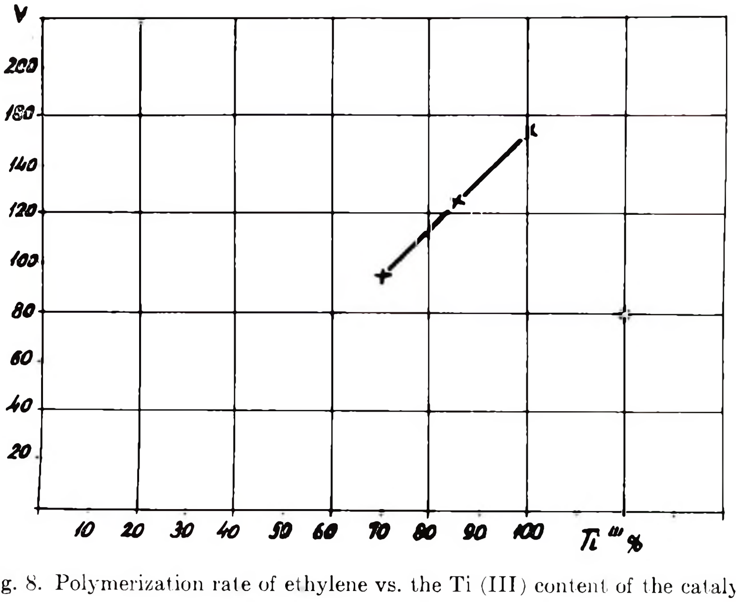

Fig. 8. Polymerization rate of ethylene vs. the Ti (III) content of the catalyst.

The constancy of the catalysts prepared according to the above principles is demonstrated for the catalyst prepared at 70°C. with a molar ratio of Al/Ti = 1 [90% Ti (III), 10% Ti (II)]. With this catalyst for polymerizations at 0, 30, and 70°C., rate curves of rather similar profiles were obtained (Fig. 9). The rate differences change according to the Arrhenius equation, that is to say, changes in polymerization rate may be attributed to temperature changes alone. The value of the overall activation energy is 5.8×10^3 kcal./mole + 2.7×10^3 cal./mole solution heat.

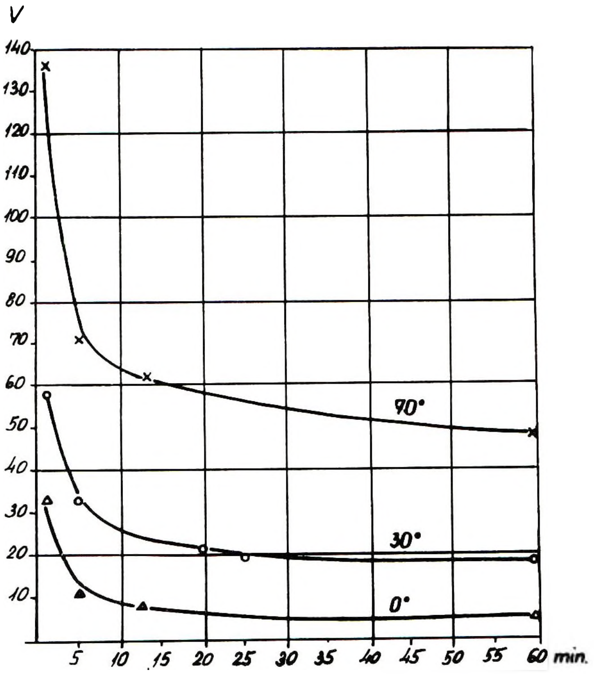

Fig. 9. Polymerization rate of ethylene vs. temperature. [$TiCl_4$] = 1.85×10^{-2} mole/l. *n*-heptane; $AlEt_3/TiCl_4$ = 1; temperature of catalyst production 70°C.; aging of catalyst 30 min.

In some cases, however, phenomena were observed which appeared to be anomalous. The polymerization rates in Figure 7 increase with the increasing Al/Ti molar ratio of the catalyst. In agreement with the other observations a molar ratio Al/Ti = 3 should correspond to the maximum Ti (III) concentration (at Al/Ti = 5, 20% Ti (II) is already formed. Nevertheless, the polymerization rate is higher at Al/Ti = 5 than Al/Ti = 3.

We believe that the reason for this behavior might be sought in the quality and quantity of aluminum alkyl remaining in solution, which may even reverse the order of polymerization rate determined by the concentration of trivalent titanium. These phenomena shall be dealt with in detail in a following communication.[8]

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Study of Ziegler-Natta Catalysts. Part II. The Liquid Phase and Polymerization Activity of the Catalyst

L. KOLLÁR, A. SIMON, and J. OSVÁTH,
Research Institute for the Plastics Industry, Budapest, Hungary

Synopsis

The polymerization activity of the Ziegler-Natta catalysts is significantly affected by the aluminum alkyls in the liquid phase. These may be studied provided the solid phase of the catalyst remains unchanged. Part of these aluminum alkyls is adsorbed on the surface of the solid phase. It is possible to displace one type of alkyls by another one or to elute it from the adsorbed layer. This last affects the polymerization rate.

INTRODUCTION

Several authors have studied the liquid phase of the catalysts formed from aluminum alkyl and titanium tetrachloride, some by analysis of the dissolved substances[1–3] or by the kinetics of polymerization[4] and partly by theoretical considerations.[5–7] They arrived, in general, at the conclusion that from the point of view of the polymerization process the liquid phase represents not only a reservoir of monomer, but is also one of the essential participants in the catalytic process. The results obtained with different systems and by different methods of course yielded often different results. In the work presented here we have attempted to clarify the role which the aluminum alkyls dissolved in the liquid phase or adsorbed on the surface of the solid catalyst play in the polymerization process.

In our previous work[8] we pointed out that, in addition to the unchanged solid phase of the Ziegler-Natta catalyst, the aluminum alkyl layer adsorbed on this solid phase has also a significant influence on the course of polymerization. In this work we shall present further proofs of sorption and will discuss some interesting cases when this adsorbed layer is changed. A presumably stable catalyst system was used in all experiments.[8] The solid phase of this catalyst was freed as far as possible from any adsorbed aluminum alkyl and from the liquid phase; the adsorption layer was varied by the addition of different aluminum alkyls. It was relatively easy to exchange the adsorption layers whose effect on the polymerization rate greatly varied.

EXPERIMENTAL

Materials and Methods

The conditions under which the catalysts were prepared, as well as the method and equipment used in the polymerization experiments were described in detail in our previous paper.[8]

Preparation of the Solid Phase of the Catalyst

Equimolar solutions of $AlEt_3$ and $TiCl_4$ in *n*-heptane (0.796 mole/l.) were mixed and allowed to react for 30 min. at 30°C., centrifuged to achieve sedimentation, repeatedly made up with *n*-heptane, and decanted until the supernatant liquor contained no more aluminum alkyl. The precipitate obtained was dried at 40°C. under vacuum and stored in sealed glass ampules. Analysis showed a composition with Cl/Ti = 3. The crystalline Debye-Scherrer diagram of the preparation is shown in Figure 1.

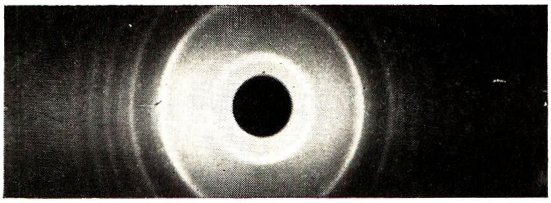

Fig. 1. Debye-Scherrer diagram of α-$TiCl_3$.

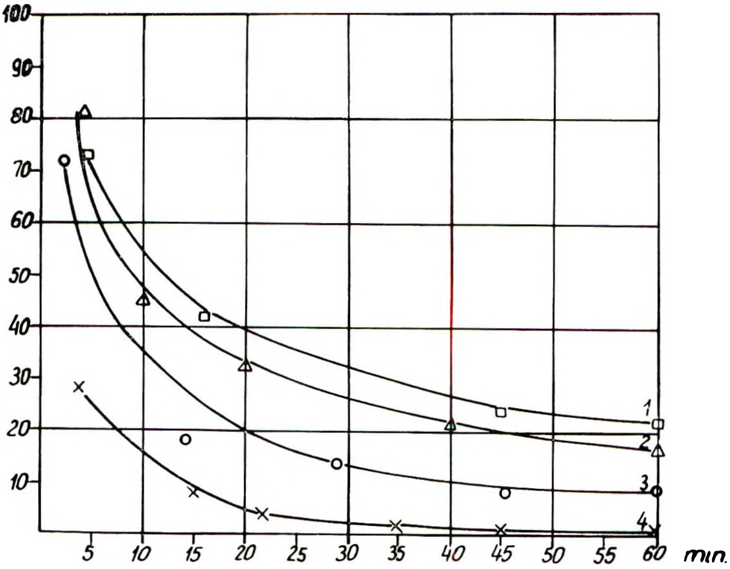

Fig. 2. Polymerization rate of ethylene under the influence of subsequently added $AlEt_3$: (*1*) 4 mole/mole $TiCl_4$; (*2*) 2 mole/mole $TiCl_4$; (*3*) 1 mole/mole $TiCl_4$; (*4*) 0 mole/mole $TiCl_4$. V in units of grams ethylene/l. solvent per hour at atmospheric pressure. $[TiCl_4] = 3.7 \times 10^{-3}$ mole/l. *n*-heptane.

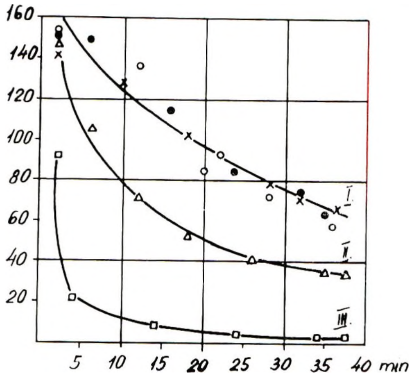

Fig. 3. Polymerization rate of ethylene vs. the washing of the solid catalyst: (×) initial catalyst; (○) catalyst obtained by the removal of the liquid phase; (△) washed three times with 12 ml. n-heptane; (□) = Washed ten times with 12 ml. n-heptane; (●) after mixing of the solid catalyst with the liquid phase and the superatant liquid.

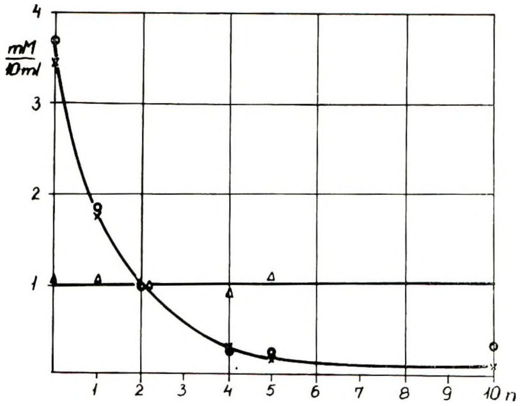

Fig. 4. Composition of the supernatant liquid of the solid catalyst after n washing cycles at 22°C.: (×) = Al; (○) Cl; (△) = Cl/Al.

Catalysts which produced polymerization rate curves corresponding to those in Figure 2 were prepared at a mole ratio Al/Ti = 1 at 70°C. The system was subsequently cooled to 0°C. and varying quantities of $AlEt_3$ (1–4) mole $AlEt_3$/mole titanium) were added. Polymerization proceeded at 0°C. The rate increased proportionally to the concentration of the subsequently added aluminum alkyl.

From the 0.796 mole/l. n-heptane solutions of $AlEt_3$ and $TiCl_4$, 10 ml. portions of each were mixed at 30°C. and made up to a total volume of 220 ml. with n-heptane; this catalyst was used for the polymerization of ethylene at atmospheric pressure. The polymerization rate curve was plotted from the measurement of the ethylene consumed by the reaction; this curve was considered in the following as the basic curve (Fig. 3, curve 1).

The experiments were then repeated with the modification that after the formation of the catalyst the solid precipitate was sedimented by centrifuging, the liquid phase was decanted, and made up with *n*-heptane again to 220 ml. The polymerization rate curve obtained with this catalyst was practically the same as the previous one (Fig. 3, curve 1).

In another experiment, after decanting the liquid phase the precipitate was washed by repeated addition of 12 ml. of *n*-heptane, mixing, centrifuging, and decanting. (The preparation obtained by this method is

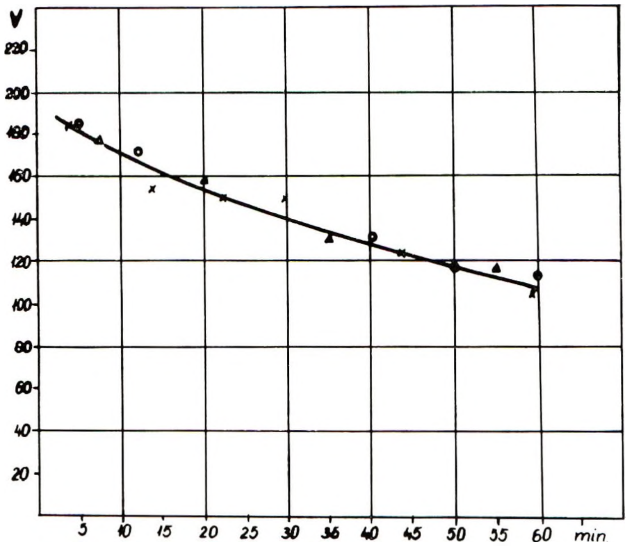

Fig. 5. Effect of $AlEt_3$ subsequently added to the solid phase of the catalyst on the polymerization rate of ethylene: (○) 5 mole $AlEt_3$/mole Ti; (△) 2 mole $AlEt_3$/mole Ti; (×) 1 mole $AlEt_3$/mole Ti. [Ti] = 1.05 g./l. *n*-heptane.

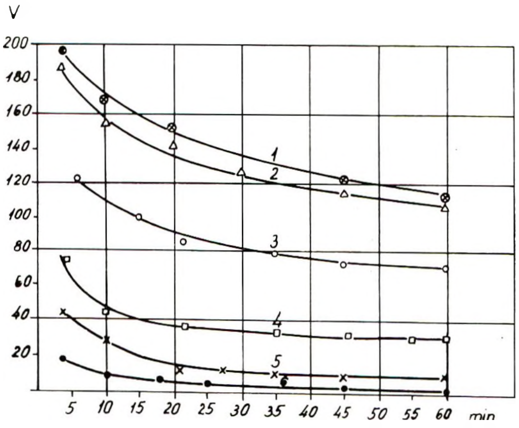

Fig. 6. Effect on the polymerization rate of ethylene of the addition of constant quantities of $AlEtCl_2$ and varying quantities of $AlEt_3$ to the prepared catalyst: (*1*) 2 mole $AlEtCl_2$, 5 mole $AlEt_3$/mole Ti; (*2*) 2 mole $AlEtCl_2$, 4 mole $AlEt_3$/mole Ti; (*3*) 2 mole $AlEtCl_2$, 3 mole $AlEt_3$/mole Ti; (*4*) 2 mole $AlEtCl_2$, 2 mole $AlEt_3$/mole Ti; (*5*) 2 mole $AlEtCl_2$, 1 mole $AlEt_3$/mole Ti; (*6*) 2 mole $AlEtCl_2$, 0 mole $AlEt_3$/mole Ti. [Ti] = 1.05 g./l. *n*-heptane.

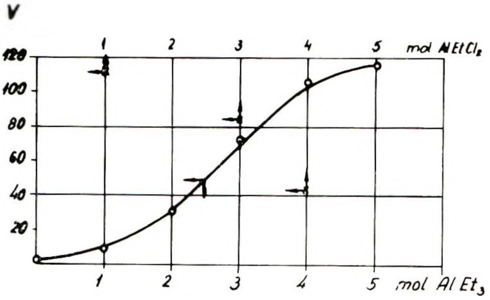

Fig. 7. Effect of the addition of $AlEtCl_2$ and $AlEt_3$ to the prepared catalyst on the polymerization rate of ethylene at 60 min. of polymerization: (O) values pertaining to Fig. 6; (×) values pertaining to Fig. 8.

Fig. 8. Effect on the polymerization rate of ethylene of the addition of constant quantities of $AlEt_3$ and varying quantities of $AlEtCl_2$: (*1*) 5 mole $AlEt_3$, 1 mole $AlEtCl_2$/mole Ti; (*2*) 5 mole $AlEt_3$, 3 mole $AlEtCl_2$/mole Ti; (*3*) 5 mole $AlEt_3$, 4 mole $AlEtCl_2$/mole Ti. [Ti] = 1.05 g./l. *n*-heptane.

generally known as β-$TiCl_3$.) After making up to 220 ml. it was found that when the catalyst is used for the polymerization of ethylene the rate of polymerization decreases gradually with the repetition of the washing cycle. Curves *2* and *3* in Figure 3 are curves obtained with catalysts which had been subjected to three and ten washing cycles, respectively. Figure 4 shows the composition of the decanted supernatant liquids.

When the supernatant liquid is returned to the solid phase the polymerization activity of the latter is practically restored (Fig. 3, curve 1).

The solid phase obtained from equimolar quantities of $AlEt_3$ and $TiCl_4$ by the method described in the experimental part was washed free of aluminum alkyl and $AlEt_3$, 1–4 mole/mole titanium, was added. Ethylene was polymerized with this catalyst at 30°C. The polymerization rate was practically the same in all cases (Fig. 5).

To a preparation washed and prepared in the same way as above enough $AlEtCl_2$ was added to raise the Al/Ti ratio to 2. Various quantities of

$AlEt_3$ were added to the preparation obtained in this way, and the polymerization of ethylene was then carried out under the usual conditions. Figure 6 shows that the rate of polymerization increases with increasing quantities of added $AlEt_3$, i.e., with decreasing concentration of $AlEtCl_2$ relative to the overall aluminum alkyl concentration. Figure 7 shows the polymerization rates after 60 min. of polymerization versus the $AlEt_3$ concentration.

Figure 8 shows a similar correlation for experiments in which first $AlEt_3$ and then $AlEtCl_2$ are added to the solid catalyst.

DISCUSSION

As pointed out earlier in the discussion of the role of the liquid phase of the catalyst, the adsorbed layer on the solid phase is included also in the considerations; this layer might be removed by washing and consists practically entirely of aluminum alkyl compounds.

It was important to decide to what extent the solid phase of the catalyst remained stable in our experiments, in other words, how much of the kinetic changes observed can be attributed to the effect of the liquid phase alone.

We wish to recall here those experiments in which we determined the conditions under which the solid phase of the catalyst can be considered constant.[8] Such a catalyst is obtained, e.g., if the catalyst is prepared at 70°C. from equimolar quantities of the components (about 10% Ti (II) content) and cooled to 0°C. If at this temperature 0–4 mole of $AlEt_3$/mole titanium is added and this composition is used in the polymerization of ethylene, the subsequently added $AlEt_3$ has no effect on the valence of the titanium in the catalyst, and thus the increase in the polymerization rate with increasing $AlEt_3$ concentration might be attributed to the effect of free aluminum alkyl (Fig. 2).

There are certain indications that at least part of the aluminum alkyl is adsorbed on the surface of the solid catalyst, thereby affecting indirectly the polymerization process.[5] Ingberman et al. calculated from the polymer yield with adsorption isotherms of diethylaluminum chloride.[9] We believe that these phenomena provide experimental evidence for the hypothesis.

It may be considered fortunate from the point of view of our studies that there is practically no change at least in the catalytic activity of the solid phase after repeated washing cycles. Curve *1* in Figure 3 shows that if the supernatant liquid is added to a precipitate washed ten times the polymerization curve is the same as that obtained with an unwashed catalyst.

It seems evident, therefore, that there is an adsorbed layer on the surface of the solid phase which plays an important role in the polymerization process. The sedimented residual solid catalyst retains this layer adsorbed on its surface even after careful decanting of the liquid phase; when it is made up to its initial volume with *n*-heptane its polymerization activity

TABLE I

Washing	Removed aluminum alkyl, %
First	39.80
Second	22.42
Third	13.02
Fourth	8.25
Fifth	3.85
Sixth	2.58
7th + 8th + 9th + 10th	5.08
Total	95.00

is equal to the initial activity (Fig. 3, curve *1*). This adsorbed aluminum alkyl can, however, be removed from the surface by repeated washing with *n*-heptane, as shown in Figure 4. The quantities of aluminum alkyl removed from the initial aluminum alkyl introduced into the system by washing with portions of *n*-heptane are shown by the data (calculated from analyses for Al content) given in Table I.

Parallel to the removal of the adsorbed aluminum alkyl there is a decrease in the polymerization activity of the catalyst (Fig. 3), indicating the importance of the adsorbed layer in the polymerization process.

There is a similar correlation between the decrease in polymerization rate with the increasing number of washing cycles (Fig. 3) rates pertaining to 30 min., and the quantity of aluminum alkyl still present in the catalyst after the various washing cycles. This latter was calculated from the aluminum contents of the decanted liquid phases (Fig. 9).

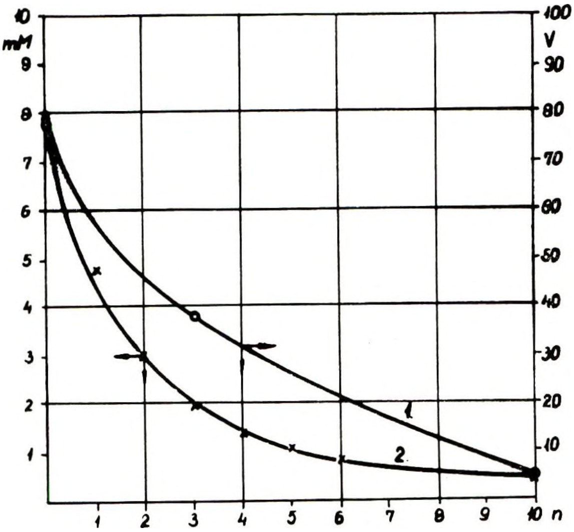

Fig. 9. Plots of (*1*) polymerization rate of ethylene and (*2*) the aluminum alkyl content of the washed catalyst vs. the number of washing cycles *n*.

The catalysts formed from $AlEt_3$ and $TiCl_4$ may contain adsorbed aluminum alkyls with varying halogen contents.[7] The type of adsorbed aluminum alkyl is an important factor. (The polymerization activity of aluminum alkyls decreases with the chlorine content in the order: $AlEt_3 > AlEt_2Cl > AlEtCl_2$). The $AlEtCl_2$ added to the prepared precipitate is displaced from the surface by the subsequently added $AlEt_3$ which causes an increase in the polymerization rate (Fig. 6), indicating not only that $AlEt_3$ is a more active catalyst than $AlEtCl_2$, but also that the quantities of the various aluminum alkyl types adsorbed on the surface of the catalyst are controlled by concentration-dependent equilibrium.

Essentially the same correlation was found in the experiments with nonprepared catalysts (Fig. 2).

The adsorption of the aluminum alkyls leads to a true equilibrium, indicating that the reverse process (when first $AlEt_3$ and then $AlEtCl_2$ is added to the precipitate) also takes place with a similar change in the reaction rate (Fig. 8).

Figure 7 shows the polymerization rate at 60 min. in both series of experiments; this type of curve is characteristic of the adsorption equilibirium.

Finally, it should be mentioned that the amount of a single type of aluminum alkyl has no significant effect on the polymerization rate. The addition of various quantities of $AlEt_3$ to the prepared solid catalyst resulted in the same polymerization at all concentrations (Fig. 5), obviously above a certain minimum concentration which is sufficient to cover the entire surface. This may explain that frequent contradiction found in the literature; some authors found a polymerization rate independent of the aluminum alkyl concentration,[10,11] while others found the polymerization rate to be concentration-dependent.[4,12,13]

It is an interesting but yet open question whether the adsorbed aluminum alkyl has an appreciable influence on the structure of the polymer, in addition to its effect on the polymerization rate. There is some information in the literature on other polymers and on the titanium trichloride–aluminum alkyl catalyst system.[14]

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Study of Ziegler-Natta Catalysts. Part III. Effect of the Structure of Titanium Trichloride on the Polymerization of Propylene

L. KOLLÁR, A. SIMON, and A. KALLÓ, *Research Institute for the Plastics Industry, Budapest, Hungary*

Synopsis

In addition to differences among the various modifications of $TiCl_3$ there may be certain structural differences even among α-$TiCl_3$ samples prepared by different methods. Electron microscopic examination of two samples has revealed widely different free surfaces, in spite of the fact that both the specific surfaces (measured by adsorption) and the polymerization activities were identical. This might be explained by the finding that the surfaces of the free lateral planes and the quantities of the free edges are the same. This explanation is in agreement with the assumption of Rodriguez and his co-workers that the active centers of polymerization are situated on the lateral planes and edges of the $TiCl_3$ crystals.

INTRODUCTION

In recent years much work has been devoted to the study of the structure of one of the components of stereospecific catalysts, namely, to the transitory metal salt, as to the nature of the factor which determines the structure of the catalyst and thus its essential polymerization properties. In practice the most important catalyst is $TiCl_3$, i.e., the titanium salts which have been described in detail in the literature.[1–7]

Today the view is predominantly accepted that polymerization is restricted to certain distinct sites—the so-called active centers—of the catalyst which are essentially characterized by a metal–carbon, probably Ti—C bond.[2–7] It is further required that these bonds should be related to the given characteristics of $TiCl_3$, e.g., should be formed in the proximity of a crystal defect.[4] According to Rodriguez et al.[2] the active centers are contained on the lateral planes of the α- or β-$TiCl_3$, as the not completely coordinated titanium atoms which are the most liable to the formation of the metal–carbon bond are situated on those planes where the titanium atoms are accessible without steric hindrance. On the other hand the 001 main plane which forms 95% of the surface of the α-$TiCl_3$ crystal may be considered passive from the point of view of the polymerization process.

We reported in an earlier work[8] the significant structural differences observed on the electron micrographs of two α-$TiCl_3$ samples of different origins. Though the crystal structures of the samples were the same, there was a considerable difference between the ratio of free surfaces of the 001 and lateral planes. Comparison of the catalytic behavior of these two samples promised therefore to yield some interesting results.

EXPERIMENTAL

Electron micrographs of α-$TiCl_3$ samples of different origins were compared. Evaluation of the results is complicated by the fact that the conditions of preparation of the titanium trichlorides are not always fully known. It is, however, quite certain that there is a significant

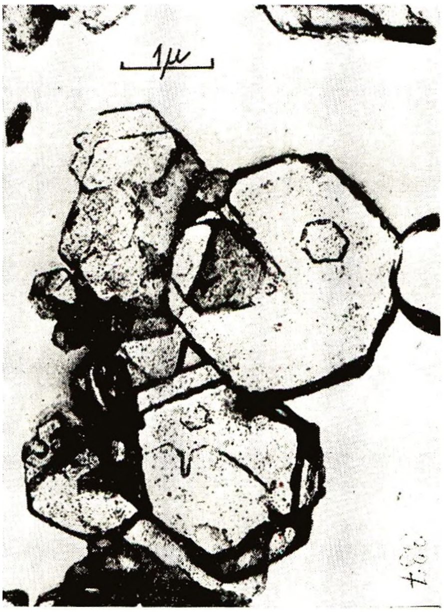

Fig. 1. Electron micrograph of α-$TiCl_3$ sample A.

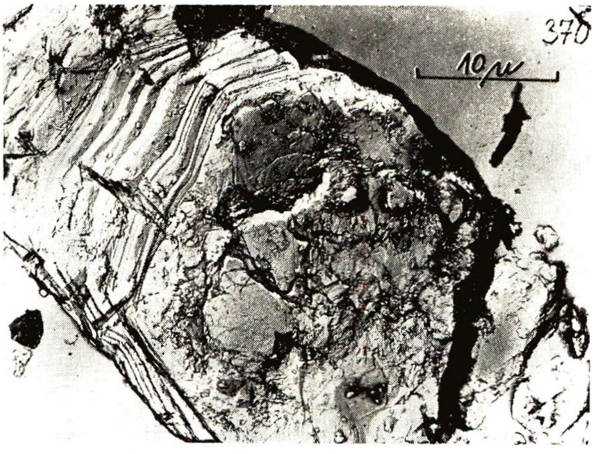

Fig. 2. Electron micrograph of α-$TiCl_3$ sample B.

difference between the structures of the various samples. One type is represented by the titanium trichloride prepared by us through reduction of $TiCl_4$ with hydrogen at 1000–1100°C. An electron micrograph of this sample is shown in Figure 1. This sample (A) is a system consisting of more or less regular hexagonal single crystals. The other type is represented by the $TiCl_3$ manufactured by Schuchardt which to the best of our knowledge was also prepared by reduction with hydrogen. Sample B, of which an electron micrograph is shown in Figure 2, shows again a hexagonal structure with the important difference that it consists of less regular laminar crystal agglomerations in which the 001 planes greatly overlap while the lateral planes are free.

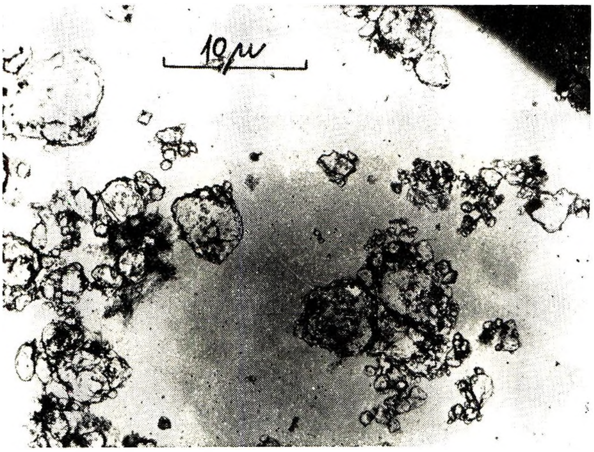

Fig. 3. Electron micrograph of ground α-$TiCl_3$ sample A.

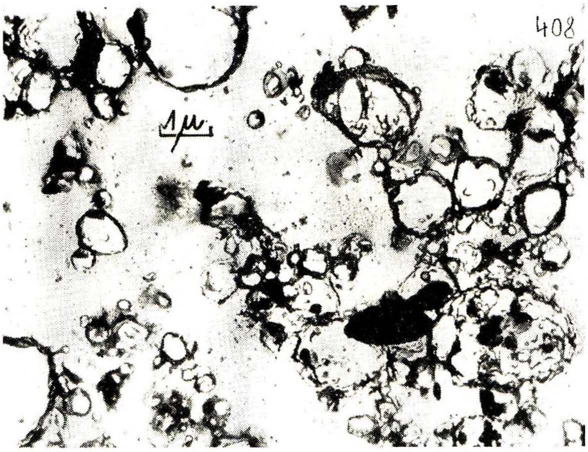

Fig. 4. Electron micrograph of ground α-$TiCl_3$ sample B.

α-$TiCl_3$ samples A and B were ground and the electron micrographs of the ground samples showed a similar character; both contained separated, crushed crystal debris (Figs. 3 and 4). The specific surfaces of the two samples were about the same (20–25 m.^{2}/g.).

To investigate whether there is any difference between the catalytic properties of the two α-$TiCl_3$ samples which have different microstructures, prior to polymerization both samples were ground in the same way in a one-liter vibration mill in an argon atmosphere. The frequency of the mill was 1400 per min., its amplitude 4 mm. The volume ratio of balls to $TiCl_3$ was 4. The specific surfaces of the $TiCl_3$ samples ground for different periods of time were determined by the BET method. The samples were used for the preparation of stereospecific catalysts with the addition of varying quantities of triethylaluminum. The polymerization activities of the catalysts were compared by measuring the polymerization rate of propylene.

Polymerization was carried out at constant pressure (660 mm. Hg) and constant temperature (60 ± 0.5°C.) in *n*-heptane. The apparatus used was the same as described in Part I.[9] The polymerization rate was followed by measuring the quantity of propylene consumed per minute. In the kinetic curve the polymerization rate is plotted versus the quantity of propylene consumed by one liter of polymerization mixture per hour.

RESULTS

Changes in the Specific Surface Due to Grinding

Measuring of the polymerization rate confirmed the findings of other researchers, namely that the polymerization activity of the catalyst increases with increasing surface of $TiCl_3$. This trend is independent of the quality of the α-$TiCl_3$, but varies in degree (Figs. 5 and 6). The specific surfaces of the two samples changed on grinding in different ways.

The specific surface of sample A reached a maximum after about 20 hr. grinding, after which it decreased; after about 70 hr. the specific surface was the same as that of the unground sample (Fig. 7).

Under identical conditions α-$TiCl_3$ sample B reached a maximum specific surface of about the same value after 150 hr. grinding, after which a very slow decrease of the surface was observed (Fig. 7). The maximum surfaces obtained under different conditions were in all cases practically identical (25–27 m.^{2}/g.).

Polymerization Rates with Titanium Trichlorides of Different Structures

Figure 5 shows the polymerization rate of propylene when catalyzed with sample A as a function of the surface of the catalyst. It seems that at low polymerization rates (i.e., in the case of low specific surfaces) the curve has no steeply rising section. It may be significant that the samples corresponding to the ascendent branch of the specific surface versus grinding time curve (Fig. 5) induce higher polymerization rates than samples with the same specific surfaces on the descending branch. Thus curves *4* and *5*

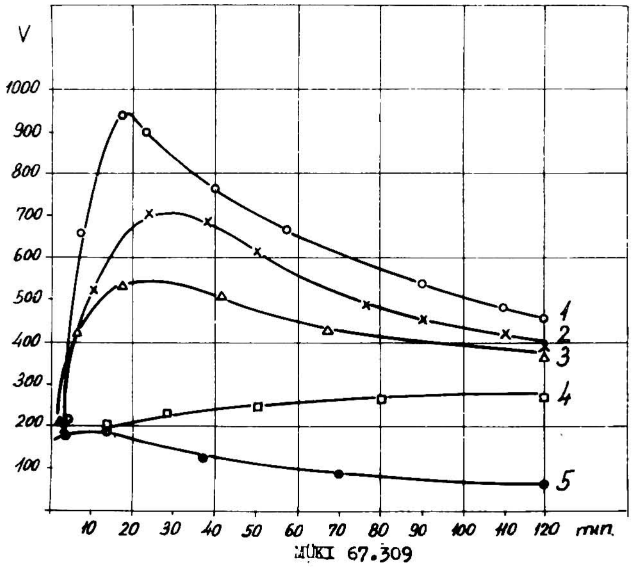

Fig. 5. Changes in the polymerization rate of propylene V with the dry grinding of α-$TiCl_3$ sample A: (*1*) grinding time 18 hr., specific surface 25 m.^{2}/g.; (*2*) 8.5 hr., 17 m.^{2}/g.; (*3*) 28 hr., 11 m.^{2}/g.; (*4*) 67 hr., 6 m.^{2}/g.; (*5*) 0 hr., 6 m.^{2}/g. Polymerization temperature 60°C.; polymerization pressure 660 mm. Hg; $[TiCl_3]$ = 3.7 g./l. *n*-heptane; $AlEt_3/TiCl_3$ = 5. V is in units of grams of monomer per liter solvent per hour per gram $TiCl_3$.

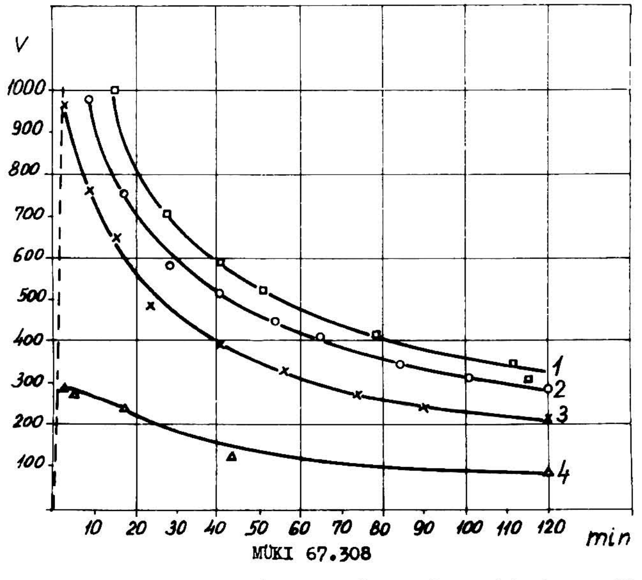

Fig. 6. Changes in the polymerization rate of propylene with the specific surface of α-$TiCl_3$ sample B: (*1*) specific surface 27 m.^{2}/g.; (*2*) 25 m.^{2}/g.; (*3*) 17 m.^{2}/g.; (*4*) 4 m.^{2}/g. Polymerization temperature 60°C.; polymerization pressure 660 mm. Hg; $[TiCl_3]$ = 3.7 g./l. *n*-heptane; $AlEt_3/TiCl_3$ = 5.

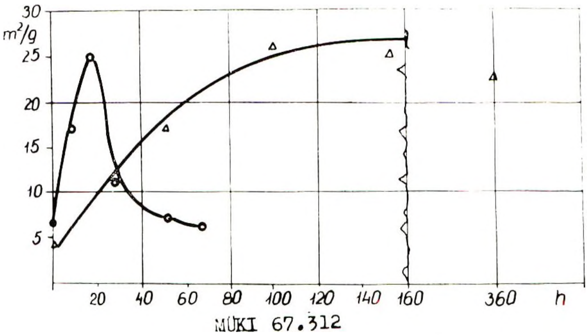

Fig. 7. Specific surface of α-$TiCl_3$ vs. grinding time: (○) sample A; (△) sample B.

in Figure 5 both correspond to samples with specific surfaces of about 6 m.^{2}/g., but curve *5* is the polymerization rate with unground $TiCl_3$ and curve *4* with $TiCl_3$ ground for 50 hr. After 120 min. polymerization the rates on curve *4* are about eight times the rates of curve *5*.

Under identical conditions polymerization with sample B proceeds at higher initial and lower end rates.

DISCUSSION

According to the electron micrographs, there is a marked difference between the structures of samples A and B (Figs. 1 and 2). This difference is reflected in the differences in behavior of the samples on mechanical grinding. Sample B is far more resistant to grinding than sample A: more than five times the grinding time is required to achieve the maximum specific surface of B than of sample A.

If the catalytic effect is related to the free surface which can be estimated from the electron micrographs of samples A and B, a significant difference between the behaviors of the unground samples might be expected, but, in fact, the catalytic activities of the unground titanium trichlorides A and B are practically the same (Fig. 5, curve *5*, and Fig. 6, curve *4*). Contrary to the unground samples, there is no characteristic difference between the electron micrographs of the ground samples, and accordingly there is a fair agreement between the kinetic curves. Though the initial polymerization rates are higher and the final polymerization rates lower with sample B (the ascending branch is so steep that it cannot be measured), this changes neither the maximum nor the character of the curves in any appreciable way.

The concept which ascribes the catalytic activity of crystalline α-$TiCl_3$ to the lateral planes[2] throws a new light on the identical polymerization behavior of the unground samples of A and B. No great difference can exist between the surfaces of the lateral planes of the two samples, as the lateral planes not only of sample A, but also of sample B form free surfaces; moreover it seems that not even the edges are covered.

The identical polymerization rates pertaining to the ground samples are, because of the similarity of the structures, in no need of further explanation.

The surfaces measured by adsorption were so far neglected in the discussion of the different structures and of visible surface differences of titanium trichlorides A and B, though the measured specific surfaces of the two samples were almost identical (that of sample A was 6 m.^{2}/g. of $TiCl_3$, that of sample B, 4 m.^{2}/g.).

The question now arises whether there is a correlation between the identical specific surfaces of the two unground samples and the identical polymerization rates achieved with them. In our opinion it would not be justified to suggest that a great difference exists between their adsorptive properties which parallels the marked polymerization activity differences assumed between the various geometrical elements of the titanium trichloride crystals. Though the adsorption power of the lateral planes and mainly of the edges is beyond all doubt greater than of the 001 plane, adsorption nevertheless also occurs quite certainly on the 001 plane, and because of the about twenty times greater surface adsorption it must be quite considerable here.

It is not yet clear why the surface decreases on continued grinding after reaching a maximum. Electron microscopic studies in this respect will perhaps throw light not only on the agglomeration following the maximum of the grinding effect, but also on the cause of the significant difference between the polymerization activities of the titanium trichloride samples ground for different periods of time.

We wish to thank our colleague András Gröbler for having kindly carried out the measurements of the specific surfaces of the $TiCl_3$ samples.

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Solid-State Initiation of Polymerization of *N*-Vinylcarbazole by Gases

R. A. MEYERS and E. M. CHRISTMAN, *Chemistry and Chemical Engineering Department, TRW Systems, Redondo Beach, California 90278*

Synopsis

Chlorine gas has been shown by previous investigators to initiate the polymerization of solid *N*-vinylcarbazole at room temperature, giving a maximum yield of 66% polymer after 18 hr. This initiation of polymerization of *N*-vinylcarbazole without the application of heat, by a gas, is the only solid-state initiation other than those that are radiation-induced known to us. This study was undertaken in order to determine both the scope and the mechanism of the room-temperature solid-state initiation of vinyl polymerization of *N*-vinylcarbazole by gases. The gases (HCl, Cl_2, and N_2O_4) were absorbed by solid *N*-vinylcarbazole, giving very rapid exothermic polymerization: HCl, 37% polymer yield, $\bar{M}_n$ 2500; Cl_2, 50% polymer yield, $\bar{M}_n$ 4703; N_2O_4, 91% polymer yield, $\bar{M}_n$ 7073. The gases NOCl, BF_3, and HBr were not absorbed by *N*-vinylcarbazole and did not initiate polymerization. The N_2O_4-initiated polymerization, which gave a high yield of polymer, was complete within 5 min. after introduction of gas. This polymerization method and the resulting polymer compared favorably with conventional peroxide-initiated melt polymerization and the polymer obtained therefrom. The mechanism of gas-initiated polymerization, which was studied with introduction of inhibitors, appears to be classically cationic in nature.

INTRODUCTION

N-vinylcarbazole is easily polymerized by a variety of methods: free-radical,[1] cationic,[2] Ziegler-type,[3] and charge-transfer[4] for solution or melt and high-energy radiation[5] for the solid state. In addition, it is known to be sensitive to thermal polymerization.[5] Recently Tsuji et al.[6] reported that its solid-state polymerization is initiated by the gases chlorine and sulfur dioxide. The reported initiation by chlorine gave a maximum polymer yield of 66% without application of heat over a period of 18 hr., and that by sulfur dioxide, which required heating, gave a maximum yield of 88%. This initiation of the polymerization of solid *N*-vinylcarbazole by gases is the only solid-state initiation other than those that are radiation-induced known to us. Because of the near uniqueness of the process it was decided to study both the scope and the mechanism of the gaseous initiation of solid *N*-vinylcarbazole. Since thermal polymerization of the monomer has been established, the polymerizations in this study were carried out at room temperature (22°C.).

EXPERIMENTAL

Materials

N-vinylcarbazole (B.A.S.F.) was recrystallized twice from cyclohexane and dried to a constant weight under high vacuum. Poly(*N*-vinylcarbazole) was synthesized by the standard peroxide-initiated melt polymerization with 0.1% di-*t*-butyl peroxide at 130°C. for 24 hr. All gases were obtained from The Matheson Co., Inc. Boron trifluoride (99%), chlorine (99.9%), and hydrogen chloride (99.0%) were passed through concentrated sulfuric acid. Hydrogen bromide (99.8%) was passed through both concentrated sulfuric acid and copper turnings. Nitrosyl chloride (93%) was passed through tetrachlorodifluorethane so as to remove dinitrogen tetroxide. Dinitrogen tetroxide (99.5%) was used without further purification. *m*-Dinitrobenzene (Eastman White Label) and triethylamine (Eastman White Label) were used without further purification.

Apparatus

The gases were introduced to the crystalline monomer in a flame-dried glass apparatus fitted with a fritted-glass entrance tube and a Drierite-protected exit. In runs in which wet *N*-vinylcarbazole was used no precautions against moisture were taken.

Thermogravimetric analyses were run on an American Instrument Co. apparatus at 3°C./min. under nitrogen flow (300 cm.^{3}/min.).

Differential scanning calorimetry was run on a Perkin-Elmer DSC-1 Differential Scanning Calorimeter (10°C./min.) with tin calibration under nitrogen atmosphere.

Methods

The gases were introduced at a rate of 85 ml./min. to 4 g. of the sample (22°C.). At the onset of initiation (initiation time, Table I) the white monomer formed a yellow melt at the point of initial entrance of the gas. The appearance of the melt and concomitant polymerization proceeded from the initial point of entrance to the opposite end of the sample, giving a brown, hard, fused mass. The polymerizations were complete within 4 min. after initiation. The products were weighed for gas uptake and then extracted with equal amounts of benzene so as to dissolve poly(*N*-vinylcarbazole), leaving all but a trace of the carbazole side-product behind. The insoluble solid was filtered out, analyzed by thin-layer chromatography, and found to contain only carbazole. The weight of filtrate, together with a correction for solubility of carbazole in benzene (0.5 g. per 100 ml. at 22°C.) was reported as per cent carbazole. The benzene solution was analyzed by thin-layer chromatography and found to contain only the expected poly(*N*-vinylcarbazole) and *N*-vinylcarbazole and small amounts of carbazole. The benzene solution was stripped under vacuum and the solid, washed with methanol, was reported as per cent polymer. Thin-layer chromatography was performed on silica gel G plates with 1:1 cyclohexane–benzene eluant. Development was accomplished with sulfuric acid–sodium nitrate reagent.

Number-average molecular weights $\bar{M}_n$ (vapor-pressure osmometry) were obtained from the Elek Microanalytical Laboratories. The polymer products were dissolved in benzene and recoagulated by addition of an equal volume of methanol. The resulting products were reported as yield of high molecular weight polymer based on amount of polymer taken for recoagulation.

RESULTS

Six purified Lewis acid gases were evaluated as initiators for polymerization of both dry and wet solid *N*-vinylcarbazole. The results are presented in Table I.

TABLE I
Initiation of Polymerization of Dry and Wet Solid *N*-Vinylcarbazole with Gases

Initiator gas	Gas absorbed, wt.-%	Initiation time, min.	Polymer yield, %	Carbazole yield, %
HCl	1	0.5	33	52
HCl[a]	1	0.5	37	44
Cl_2	1	15	50	19
Cl_2[a]	1.5	6	50	29
N_2O_4	1.5	1	91	7
N_2O_4[a]	1.5	3	91	7
BF_3, BF_3[a]	0	30[a]	—	—
NOCl, NOCl[a]	0	30[a]	—	—
HBr, HBr[a]	0	30[a]	—	—

[a] 0.44% by weight water absorbed on the *N*-vinylcarbazole by equilibration with water vapor.

[b] Gas flow for 30 min. gave no measureable gas absorption and no polymerization. By contrast, the unpurified gases boron trifluoride, nitrosyl chloride, and hydrogen bromide did initiate polymerization of both wet and dry *N*-vinyl carbazole. The unpurified hydrogen bromide initiated polymerization because of bromine and hydrochloric acid impurities, while the nitrosyl chloride contained dinitrogen tetroxide as an impurity; Boron trifluoride initiated polymerization possibly because of the sulphur dioxide or silicon tetrachloride impurities present.

A free-radical polymerization inhibitor, dinitrobenzene, does not inhibit the polymerizations induced by hydrogen chloride, chlorine, or dinitrogen tetroxide, whereas triethylamine, a cationic polymerization inhibitor, is an effective inhibitor of polymerization induced by all three gases.

The polymeric products obtained from the three purified gases that were found to initiate polymerization were recoagulated from benzene-methanol. The amount and number-average molecular weight of the polymers obtained are compared in Table II with the product obtained by conventional free-radical melt polymerization.

TABLE II
Yield of High Molecular Weight Poly(*N*-vinylcarbazole)

Initiator	Recoagulated polymer Yield, %	$\bar{M}_n$
HCl	5	2500
Cl_2	26	4703
N_2O_4	58	7073
Di-*t*-butyl peroxide	70	9956

As the polymerization initiated by dinitrogen tetroxide gave the highest yield of polymer with the highest molecular weight, this material was further analyzed and compared with conventional poly(*N*-vinylcarbazole). The infrared spectra (KBr pellet) were identical, and the thermogravimetric analyses were similar. The polymer initiated by dinitrogen tetroxide was 50% volatilized at 445°C., whereas that initiated by peroxide was 50% volatilized at 410°C.

Differential scan calorimetry gave a heat of fusion of *N*-vinylcarbazole of 3.5 kcal./mole.

DISCUSSION

Tsuji et al.[6] reported that chlorine-initiated polymerization of solid *N*-vinylcarbazole gives a maximum, after 18 hr., of 66% polymer without the application of heat and that sulfur dioxide gives 88% polymer if the reaction mixture is heated at 50°C. for 24 hr. The amounts of carbazole and molecular weights of the polymers obtained were not determined. This study is concerned only with the initiation of polymerization at room temperature; thus, the sulfur dioxide initiation at elevated temperatures reported by Tsuji et al.[6] was not reinvestigated. Table I shows that, besides chlorine, gaseous hydrogen chloride and dinitrogen tetroxide initiate solid-state polymerization of both dry and wet *N*-vinylcarbazole at room temperature, whereas the three gases boron trifluoride, nitrosyl chloride, and hydrogen bromide are not absorbed by *N*-vinylcarbazole over a period of 30 min. and thus do not initiate polymerization. The absence of addition by the latter three gases is puzzling. It is significant to note that hydrochloric acid and chlorine give relatively low yields of polymer and significant amounts of carbazole side-product. However, dinitrogen tetroxide gives a very high yield of polymer, 91%, and a smaller amount of carbazole side-product. The high yield is particularly significant in view of the fact that polymerization yields above 85% are difficult to obtain with the conventional peroxide melt polymerization,[1] and the polymerization initiated by dinitrogen tetroxide is complete in 5 min. in the absence of water, whereas the conventional peroxide-initiated polymerization requires a period of 24 hr.

Table II shows that the yield of higher molecular weight polymer from the gaseous initiations is considerably lower in the cases of hydrogen chloride and chlorine and somewhat lower in the case of dinitrogen tetroxide than that obtained from peroxide-initiated polymerization.

The mechanism of initiation by chlorine and sulfur dioxide gases was postulated by Tsuji et al.[6] to occur via the paramagnetic charge-transfer complexes, which are formed by the two electron acceptor gases chlorine and sulfur dioxide, the electron donor being *N*-vinylcarbazole. This mechanism is the same as that postulated for the initiation of solution polymerization of *N*-vinylcarbazole by charge-transfer acceptors. It has been suggested that the charge-transfer complex gives rise to the formation of *N*-vinylcarbazole radical cation, which then initiates cationic polymerization.[4] It was suggested that the solution polymerization was cationic, since the reaction was inhibited by water and by amines but not by free-radical scavengers. As the radical cation of *N*-vinylcarbazole was present in the reaction mixture, it was selected by inference as the cationic initiator. However, this theory is not without dispute. Meyers reports that chloranil (frequently reported as an *N*-vinylcarbazole charge-transfer initiator) does not cause polymerization in solution and actually may act as a polymerization inhibitor, when all reagents are carefully purified.[7] Dinitrogen tetroxide, which may act as a charge-transfer electron acceptor, could initiate polymerization via the same mechanism as chlorine and sulfur dioxide; however, hydrochloric acid, which is not a charge-transfer electron acceptor, could not function by this mechanism.

Since the inhibition of polymerization by water is a characteristic of charge-transfer-initiated polymerization, the effect of water on the solid-state initiation was investigated. Table I shows that the distributions of polymer and carbazole products remain roughly the same in the case of hydrochloric acid and chlorine and identical in the case of dinitrogen tetroxide. The time of initiation remained the same for hydrogen chloride, decreased for chlorine, but increased for dinitrogen tetroxide, whereas the time for polymerization, once initiation took place, remained roughly the same. Clearly, water has no well-defined effect on the course of initiation of polymerization of *N*-vinylcarbazole with the gases studied. The propagation is in all cases cationic in nature, since the base, triethylamine, is an inhibitor and the radical scavenger dinitrobenzene is not an inhibitor. In addition, it is important to note that the *N*-vinylcarbazole samples must have contained considerable adsorbed oxygen (a radical polymerization inhibitor) during the course of polymerization, because oxygen would not be completely removed by the short-term initiator gas flow. On the whole, the mechanism of the polymerization does not appear to involve charge-transfer initiation, since water is not an inhibitor, as was previously reported for solution charge-transfer polymerization, and since hydrogen chloride, an acid, which is not a charge-transfer acceptor, is a polymerization initiator. We wish to postulate that the three gases, all of which are Lewis acids, add at crystal surfaces heterolytically across the nucleophilic vinyl group of *N*-vinylcarbazole, forming the stabilized salts shown in Figure 1. Cationic polymerization then ensues with the evolution of 15.2 kcal./mole

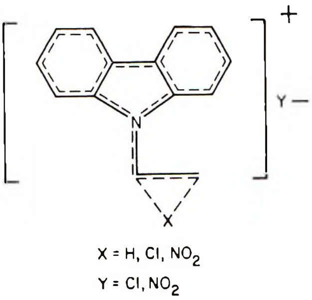

Fig. 1. Cationic initiator formed by action of Lewis acid gases on *N*-vinylcarbazole.

heat of polymerization.[8] The heat of polymerization is sufficient to melt adjacent *N*-vinylcarbazole monomer (the heat of fusion is 3.5 kcal./mole). The melted monomer dissolves the saltlike initiator, allowing polymerization to be propagated in the melt. This process of polymerization and melting proceeds until the sample is consumed. As a side reaction, carbazole is formed via the well-known acid-catalyzed devinylation of *N*-vinylcarbazole.

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Dehydrochlorination Reactions in Polymers. Part III. Vinylidene Chloride–Styrene Copolymers

R. A. HALDON, *The Department of Chemistry, The University of Southern California, Los Angeles,* and J. N. HAY,
The Department of Chemistry, The University, Birmingham 15 England

Synopsis

A systematic study of the effect of styrene units on the thermal stability of vinylidene chloride copolymers was made. In general, the copolymers were more easily dehydrochlorinated than the homopolymer. The copolymers eliminate HCl at rates that could only be interpreted in terms of styrene group activation. However, the elimination rate fell too rapidly with reaction extent to be accounted for by concentration changes or weak links and was consistent with retardation by the reaction products. The elimination was a radical process and accompanied by chain scission and crosslinking in competition.

INTRODUCTION

In a previous study of dehydrochlorination, of polyvinylidene chloride (PVdC)[1] analysis of the reaction was restricted to about 10% conversion by the rapid development of insolubility and the accompanying autocatalysis of the reaction. Nevertheless, the process was established as a radical zipper reaction initiated at unsaturated chain ends. The reaction was retarded by addition of triphenylmethane. The dehydrochlorination of poly-α-chlorostyrene was also interpreted[2] as a radical process but was retarded by the aromatic polyene products of the reaction.

Styrene copolymers are studied in this present paper for these mechanisms and also because copolymers are an obvious way of changing the reaction environment, reducing the inherent insolubility of PVdC in inert solvents, decreasing the zip length of the elimination process, and reducing crosslinking reactions. The reaction may then be studied at higher conversions.

EXPERIMENTAL

Copolymerizations were carried out at 60° with benzoyl peroxide as initiator and taken to less than 5% conversion. Reactivity ratios were determined by a Finemann-Ross plot.[3] The characteristics of the copolymers are listed in Table I.

TABLE I
Copolymer Characteristics

Serial no.	Initiator concn., wt.-%	Mol. wt. ($\times 10^{-3}$)	Styrene mole fraction	
			Monomer	Copolymer
A1	0.48	55.0	0.58	0.75
A2	0.48	—	0.47	0.70
A3	0.62	36.4	0.34	0.62
A4	0.52	46.0	0.37	0.63
A5	0.36	94.6	0.35	0.61
A6	0.52	35.8	0.12	0.46
A7	0.53	30.0	0.10	0.38
A8	0.48	33.5	0.10	0.39
A9	0.49	26.0	0.08	0.32
A10	—	—	0.03	0.14
A11	—	69.0	0.35	0.61
A12	—	55.4	0.35	0.61

The molecular weights of the styrene copolymers were measured in toluene with a Mechrolab high-speed osmometer, Model 501, and also by intrinsic viscosity at 25°.

Degradation Apparatus

The polymers in the form of finely divided powder and solution-cast films were degraded in an all-glass apparatus under high vacuum. Volatile products from the reaction vessel were condensed for a fixed period of time alternately into liquid nitrogen traps. The volatiles collected were isolated from the degradation vessel and measured by manometers at room temperature. They were removed from the measuring system by pumping to collector traps for further analysis. This apparatus was designed to remove the volatile products rapidly from the reacting system and so eliminate possible side effects.

The reaction vessel, which was made of thin-wall Pyrex tubing, was heated externally by a Wood metal bath controlled to 0.2°.

Accuracy of the Degradation Apparatus

The reproducibility of the degradation measurements was checked by degrading polymer samples to different extents and analyzing the products. In this way it was established that the copolymers did in fact lose only one molecule of hydrogen chloride per vinylidene chloride (VdC) monomer unit on pyrolysis below 200° and that there were no other volatile products to complicate the measurements.

The degradation of cast films of the copolymers showed that the rate of volatilization increased linearly with sample thickness beyond 0.2 mm. The rate studies were limited to films less than 0.1 mm. thick (i.e., 20–40 mg. samples).

COPOLYMERIZATION SYSTEM

The characteristics of the copolymers are listed in Table I. Analyses were carried out by chlorine content and infrared and ultraviolet spectroscopy with styrene adsorption bands. The reactivity ratios obtained for the system styrene and VdC were $r_1 = 1.75 \pm 0.10$ and $r_2 = 0.12 \pm 0.02$, respectively. These compared favorably with literature values.[4,5]

The molecular weights of the copolymers increased linearly with increasing styrene content in the monomer feed, after allowances for the variations in initiator concentration were made by means of the expression

$$p_n = K(\mathrm{M}) \cdot (\mathrm{init})^{1/2} \tag{1}$$

where p_n is the degree of polymerization and $K(\mathrm{M})$ a function of monomer feed composition and rate constants. This linear dependence is exactly that required by copolymerization theory,[6] although the reverse dependence ought to have been observed.

To check the postulate of neighboring group activation it was necessary to measure the sequence of blocks of monomer units along the chain. The reactivity ratio product, i.e. 0.2, suggested a strong tendency to produce an alternating copolymer. However, from the simple copolymerization theory,[4,5] the probability of obtaining the sequences of units A-B$_n$-A in a copolymer of A and B is

$$p_n = [dA/(dA + dB)]p_{AB}p_{BB}^{\,n-1}p_{BA} \tag{2}$$

where $dA/(dA + dB)$ is the mole fraction of A in the copolymer. When $f = (A/B)$ is the mole ratio in the monomer feed,

$$p_{AB} = 1/(1 + fr_1), \qquad p_{BB} = r_2/(f + r_2), \qquad p_{BA} = f/(f + r_2)$$

This simple copolymerization theory neglects termination and assumes that the reactivity of the growing radical depends only on its character and not on that of the penultimate group.[7-9]

TABLE II

Styrene Activation of Elimination

Styrene content, mole-%:	76	62	38	32	0
Activation energy, kcal./mole:	24.0	26.0	29.0	28.0	30.0

Serial no.	Sequence distribution Mole fraction of VdC units present, %			
	Initially	As A-B	A-B-A	Activated
A1	25	97	68	60
A3	38	93	58	49
A7	62	71	21	37
A9	68	64	16	36

Temperature dependence of activated VdC Units (sample A1)

Temperature, °C.:	153	159	166
Activated unit, mole-%:	34	42	60

From these equations the fractions of VdC units flanked by two styrene units, i.e. A-B-A, and adjacent to at least one styrene unit, i.e. A-B, were calculated and compared with the fraction of activated units observed experimentally; see Table II.

RESULTS

The volatile product of the reaction in the temperature range 150–220° was HCl (at least 98%) with no styrene monomer. At low reaction extents the solid residues were colored and readily soluble, but the color and solubility were dependent on styrene content and reaction extent. However, all the copolymer residues at complete dehydrochlorination were

TABLE III
Degradation Characteristics

Solubility of residue on dehydrochlorination (155°C. per 8 hr.)

Serial no.	VdC content, mole-%	Solubility, wt.-%
A1	25	100
A3	38	100
A4	37	100
A6	54	100
A7	62	95
A8	61	95
A9	68	50
A10	86	30
PVdC	100	1[a]

Viscosity changes

Serial no.	Reaction extent, %	Intr. viscy., dl./g.	Mol. wt. M_n ($\times 10^{-3}$)
A8	0	0.27	35.5
	32	0.17	
	45	0.16	
	53	0.15	
A9	0	0.23	26.0
	13	0.17	
	33	0.12	
	40	0.21	
	72	gel	

Molecular weight changes at 167° for sample A4

Time, hr.	Number-avg. chain length, A.	Number-avg. mol. wt. ($\times 10^{-3}$)
0.0	985	46.0
1.0	865	
2.0	811	
3.0	757	

[a] See Ref. 1, at 1% reaction.

either black or brown, and only the styrene-rich residue was completely soluble. Copolymers with VdC contents in excess of 60% showed appreciable amounts of insoluble fraction.

Viscosity and gel permeation chromatographic studies were carried out on degraded copolymers since osmometry proved to be meaningless, owing to excessive diffusion of low molecular weight material (not present with the undegraded copolymers). Substantial changes in viscosity and gel permeation chromatography elution volumes (Table III) occurred on elimination, consistent with crosslinking and chain scission processes. In VdC-rich copolymers an initial drop in viscosity was followed by an increase and, finally, with the development of increasing insolubility; see Table III. In a styrene-rich copolymer the number-average chain length decreased, consistent with the occurrence of random scission on elimination (the chain length varied inversely with reaction time).

The infrared and ultraviolet spectra of the degradation residues were consistent with the slow development of unsaturated and conjugated unsaturated carbon double bonds. The infrared absorption bands appeared at 1660 and 1625 cm.$^{-1}$.

Kinetic Studies of the Elimination

A typical series of reaction extent–time plots is shown in Figure 1 for various styrene copolymers at 166°. Figure 2 also shows the effect of temperature on the elimination from a typical copolymer, sample A1. These curves are very different from those obtained previously for PVdC,[1] since, in particular, there is no evidence of autocatalysis. Instead, the rates of elimination from all the copolymers fall off linearly but more rapidly than changing concentration. Attempts at relating rate and reaction conversion

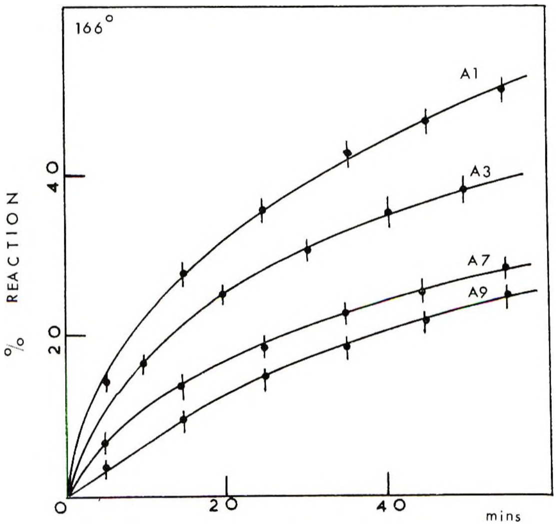


Fig. 1. Elimination characteristics of copolymers.

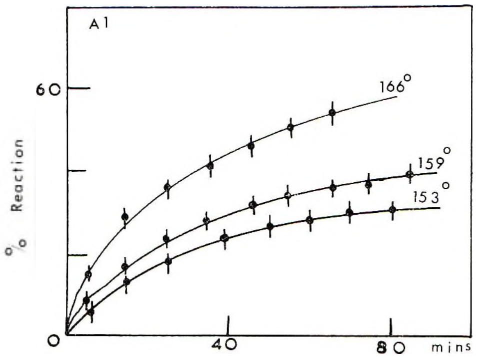


Fig. 2. Temperature dependence of elimination: copolymer A1.

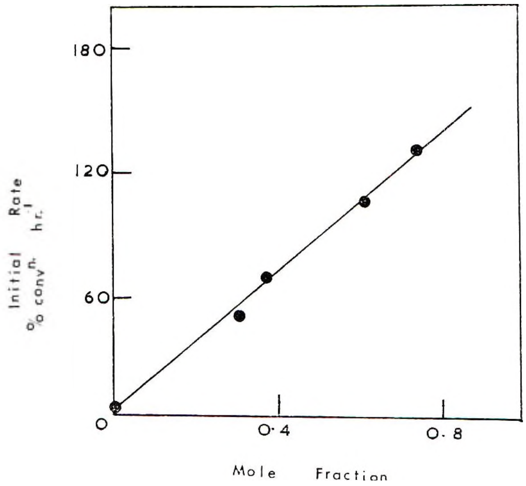


Fig. 3. Styrene dependence of reaction rate.

yielded nonconstant reaction orders between 3 and 7. The initial (extrapolated) rates increased with styrene content in the copolymer (see Fig. 3), and their temperature dependence showed evidence of activation by styrene units (see Table II).

Extrapolation of the rates to zero gave fractions of the VdC units which increased regularly with styrene content. These were considered to be the fraction of VdC units in the copolymer activated by styrene units and so capable of ready elimination. The overall process was analyzed as eliminations initiated at a number of activated sites, possibly superposed upon a very much slower elimination from the remaining VdC units. The fractions of VdC units in the copolymers adjacent to styrene units and flanked by styrene units in the chain were calculated by means of eq. (2). However, little agreement was observed between these fractions and those observed to be activated experimentally; see Table II. The presence of activated units alone could not explain the observed rate dependences, especially since it was also found that the fraction of activated units increased significantly with temperature; see Table II. Another mechanism must have been present.

Molecular Weight Dependence of the Elimination Rate

The dehydrochlorination of PVdC is initiated from chain ends, since the rate is dependent on the reciprocal molecular weight.[1] The observed differences in rate between the various copolymers may thus be partially attributed to molecular weight differences. To establish the effect of molecular weight on the elimination reaction and so establish the mechanism of initiation, copolymers of the same composition but of different molecular weights were made by varying the initiator concentration. However, in these copolymers no dependence of initial rates on molecular weight was observed and, accordingly, initiation appeared to be random rather than from unsaturated endgroups; see Table IV.

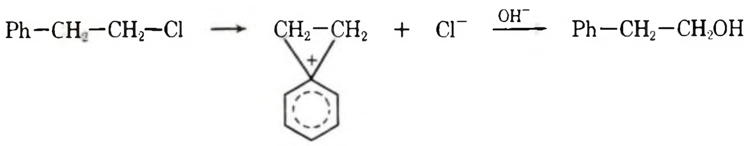
TABLE IV
Molecular Weight Dependence of the Rate

Serial no.	Molecular weight ($\times 10^{-3}$)	Initial rate, % convsn. per min.
A5	94.6	1.10
A11	89.0	1.03
A12	55.0	1.05

DISCUSSION

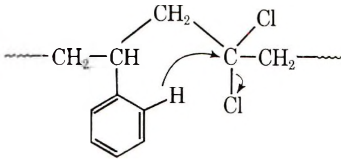
The low values of the activation energies (20–30 kcal./mole) are consistent only with "weak link" initiation, but since initiation is not from terminal unsaturated groups, styrene units must, clearly, activate VdC units to eliminate HCl. This is also apparent from the dependence of the rate of elimination and the activation energy on the styrene content of the copolymer. This activation most probably results from two effects: increased chain mobility and neighboring group interactions. The first would lead to changes in the Arrhenius factor and the second to changes in activation energy by altering the energy of the transition state.

Sykes[10] has explained the anomalous high rates of hydrolysis of 2-phenylethyl chloride in terms of an intermediate transition state involving a bridge ion:

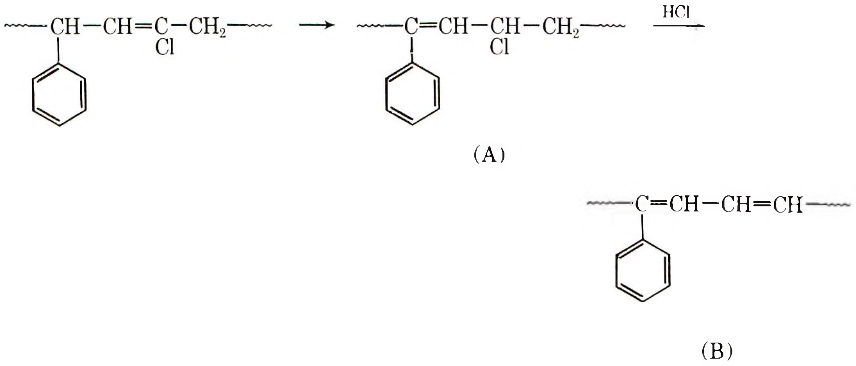


$$Ph-CH_2-CH_2-Cl \longrightarrow CH_2-CH_2 + Cl^- \xrightarrow{OH^-} Ph-CH_2-CH_2OH$$

A similar transition state for radical, unimolecular, or ionic mechanisms could be invoked to explain activation by styrene units:



The insertion of styrene units in the VdC chain ought to prevent the development of long, conjugated sequences on elimination. However, polymers having small amounts of VdC color extensively and early in the elimination reaction. Conjugation could be lengthened by double-bond shift:



Structure (A) ought to be labile and eliminate further HCl, producing (B). Analysis of the colored residues at almost complete reaction suggested that this occurred only to a small extent; see Table V. The early development of color is thus consistent only with the copolymers containing blocks of monomer units, and a zipper elimination process occurring within these blocks.

TABLE V
Analysis of the Residue

	Chlorine, %		
Serial no.	Initial	Observed	Calculated
A1	18.6	9.5	9.3
A9	49.5	24.7	25.2

A radical mechanism has been proposed for the dehydrochlorination of PVdC, since the transfer agent, triphenyl methane, was found to retard.[1] A transfer mechanism producing a stabilized radical was invoked,

$$Ph_3CH + R\cdot \rightarrow Ph_3C\cdot + RH$$

since triphenyl methane isolated from the degrading polymer was unreactive to HCl. The reduction in the elimination cannot be attributed to the removal of HCl, as has been shown for the stabilization with dibutyltin acetate.[11] The assumption of a radical elimination process can also explain many of the experimental observations on the elimination from the copolymers. The following kinetic scheme is then possible.

(*1*) Initiation: Nonrandom from units activated by adjacent styrene units, for which the rate of initiation, R_i, is $R_i = k_i[\text{styrene}]$.

(*2*) Propagation: Stepwise elimination of HCl from the radical along the block of VdC units, followed by transfer or termination, i.e. $-d/dt[\text{HCl}] = k_p[\text{R}^\cdot]$, where $[\text{R}^\cdot]$ is the stationary concentration of dehydrochlorinating radicals.

(*3*) Termination: First-order termination must be invoked, to account for the rate dependence on styrene concentration. First-order termination has been observed in PVdC dehydrochlorination and considered to arise either from termination by "geminate" radical pairs or by loss through distillation of volatile radicals and chlorine atoms:

$$\text{(a)}\quad \text{R}^\cdot + \text{R}^\cdot \rightarrow \text{R}_2 \nearrow$$

$$\text{(b)}\quad \text{R—Cl} \rightarrow \text{R}^\cdot + \text{Cl} \nearrow \qquad k_t$$

$$\text{R}^\cdot + \text{HCl} \rightarrow \text{RH} + \text{Cl}^\cdot$$

$$\text{Rate of termination, } R_t = k_t[\text{R}\cdot]$$

A radical mechanism explains four things, as follows.

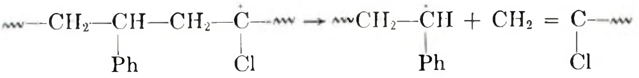
(*1*) The observed initial rate dependence on styrene concentration, since under stationary-state conditions

$$k_i[\text{styrene}] = k_t[\text{R}^\cdot]$$

$$-d/dt[\text{HCl}] = k_p k_i k_t^{-1}[\text{styrene}]$$

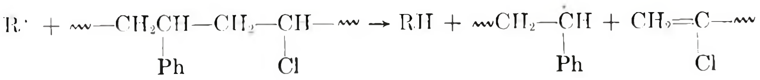
(*2*) The presence of crosslinking, by termination of radical pairs.

(*3*) The presence of chain scission by transfer to styrene units and subsequent chain cleavage, producing stabilized styryl radicals:



$$\sim\!\!\sim\text{—CH}_2\text{—}\underset{\text{Ph}}{\text{CH}}\text{—CH}_2\text{—}\underset{\text{Cl}}{\dot{\text{C}}}\text{—}\sim\!\!\sim \rightarrow \sim\!\!\sim\text{CH}_2\text{—}\underset{\text{Ph}}{\dot{\text{C}}\text{H}} + \text{CH}_2 = \underset{\text{Cl}}{\text{C}}\text{—}\sim\!\!\sim$$

or



$$\text{R}^\cdot + \sim\!\!\sim\text{—CH}_2\underset{\text{Ph}}{\text{CH}}\text{—CH}_2\text{—}\underset{\text{Cl}}{\text{CH}}\text{—}\sim\!\!\sim \rightarrow \text{RH} + \sim\!\!\sim\text{CH}_2\text{—}\underset{\text{Ph}}{\dot{\text{C}}\text{H}} + \text{CH}_2\text{=}\underset{\text{Cl}}{\text{C}}\text{—}\sim\!\!\sim$$

The styryl radicals cannot depolymerize at this low temperature, and they either terminate or transfer. Similar mechanisms have been invoked by Grant and Grassie[12] to explain chain scission on dehydrochlorinating copolymers of styrene and α-chloracrylonitrile.

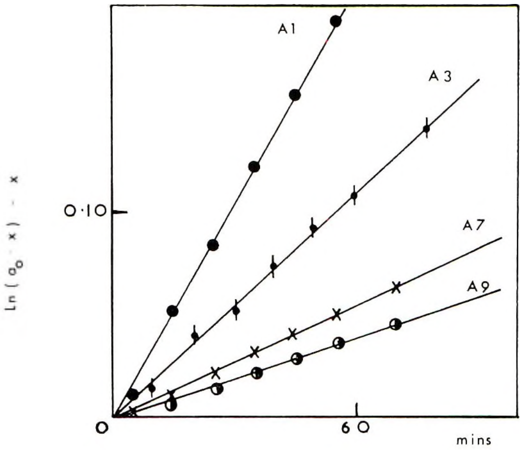
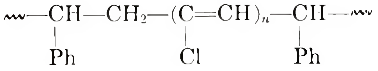


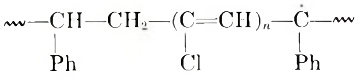
Fig. 4. Retardation by-products: copolymers.

(4) The rapid reduction in rate of elimination with conversion and the temperature dependence of the fraction of apparently activated VdC units, by retardation. The polyene products of the elimination have the final structure



$$\sim\!\!-\underset{\displaystyle Ph}{CH}-CH_2-(\underset{\displaystyle Cl}{C}{=}CH)_n-\underset{\displaystyle Ph}{CH}-\!\!\sim$$

in which the conjugation is limited by styrene groups. Such products ought to be as effective transfer agents as triphenyl methane[1] and should be similarly efficient at retardation, producing stabilized radicals:



$$\sim\!\!-\underset{\displaystyle Ph}{CH}-CH_2-(\underset{\displaystyle Cl}{C}{=}CH)_n-\underset{\displaystyle Ph}{\overset{\cdot}{C}}-\!\!\sim$$

For the products X to be retarders, then,

$$R\cdot + X \xrightarrow{k_x} \text{unreactive}$$

Although initially the elimination rate is determined by the termination steps, the retardation becomes increasingly important as the reaction proceeds and finally predominates. Eventually,

$$-d/dt[\mathrm{HCl}] = (k_p k_i/k_x)([\text{styrene}]/[X])$$

That is

$$(-d/dt)x = (k_p k_i/k_x)([\alpha_0 - x]/[x])$$

where $[\alpha_0 - x]$ is the concentration of elimination groups at time t. Plots of $\log_e(\alpha_0 - x) - x$ versus t were made for all the copolymers and for one copolymer at different temperature and proved to be linear; see Figures 4 and 5.

Items (*1*), (*2*), and (*4*) could also be explained by a unimolecular elimination of HCl from VdC units activated by styrene, followed by a stepwise elimination, by allylic activation, along the VdC sequence, if it is further assumed that the polyene products can reversibly add HCl:

$$\text{Polymer} \rightleftarrows X + \text{HCl}$$

This will give the observed linear decrease in rate with conversion. A pseudo-equilibrium must finally be established, at which

$$(-d/dt)[\text{HCl}] = 0 \qquad \text{and} \qquad [\alpha_0 - x]/[x]$$

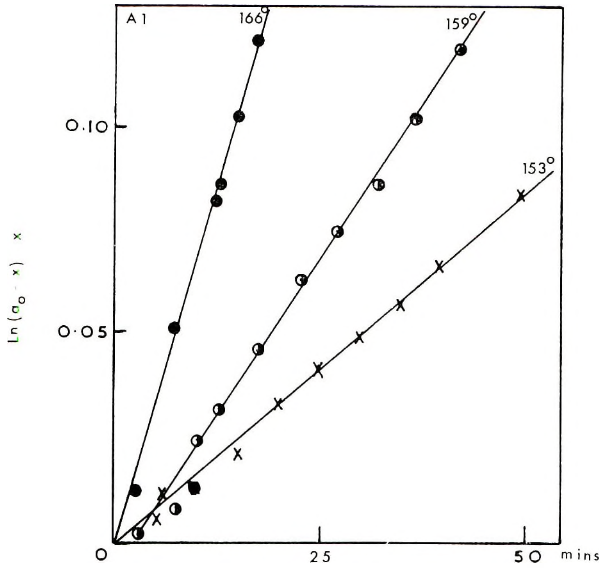


Fig. 5. Temperature dependence of retardation: copolymer A1.

are constant if [HCl] is constant. The kinetic data are not sufficiently accurate to distinguish between these two possible mechanisms. The unimolecular mechanism seems, however, to be very unlikely, since HCl was never observed to add to degraded polymer on reduction of the temperature, and under an atmosphere of HCl. Furthermore, the initial precaution of removing the HCl *in vacuo* from the degrading system ought to eliminate reversible addition reactions completely.

The bulk of the experimental evidence on the elimination of HCl from VdC–styrene copolymers favors a radical process initiated at styrene units but retarded by the polyene products of the reaction. This mechanism is analogous to that observed in the dehydrochlorination of poly-α-chlorostyrene.[2]

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JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 6, 963–967 (1968)

Part I. On the Synthesis and Pyrolysis of a Tetrafluoroethylene–Acrylonitrile Graft Copolymer

J. FOCK,* *Polytechnic Institute of Brooklyn, Brooklyn, New York 11201*

Synopsis

Radiation-induced grafting of acrylonitrile onto films of polytetrafluoroethylene has been studied. Irradiation has been carried out in a ^{60}Co gamma source at −78°C., and the graft polymerization was facilitated by being held at 100°C. for 150 hr. The amount of acrylonitrile grafted per unit surface area apparently increases with the thickness of the film. Grafting is also accompanied by slight swelling. This indicates that the reaction occurs in depth. The relative decrease of the amount of grafted acrylonitrile with thickness of the film, referred to the weight of the film, shows that grafting is controlled by the diffusion of the monomer. The rate of grafting was found to be lower in a material with a higher degree of crystallinity; i.e., grafting occurs faster in the amorphous areas of the polymer. The final yield of graft decreases with the temperature at which the reaction is carried out. This may be explained on the basis of kinetics or by assuming a simultaneous disappearance of free polymer radicals.

Introduction

Polytetrafluoroethylene is very inert toward most chemicals, and there is no common organic solvent known in which it swells at room temperature. Therefore, it is expected that in radiation-induced grafting the monomer does not penetrate the polymer film but that the reaction is limited to the surface.

Surface grafting of polytetrafluoroethylene has been achieved by the irradiation of its films immersed in an excess of acrylonitrile,[1] styrene,[2,3] methyl methacrylate,[4] vinyl pyrrolidone,[5] vinyl acetate,[6] and mixtures of styrene and acrylonitrile[7] at room temperature. The fact that the weight of grafted vinyl acetate has been found to be independent of the thickness of the film indicated that grafting is indeed limited to the surface.[6]

It has, however, been demonstrated that in the case of styrene, which is a solvent for its polymer, grafting occurs throughout the film when the irradiation is carried out at low dose rate or at elevated temperature.[8,9]

In this study an attempt was made to graft acrylonitrile into and throughout polytetrafluoroethylene through the establishment of experimental conditions that should favor penetration of the film by the monomer and subsequent graft polymerization.

*Present address: Th. Goldschmidt A.-G., 43 Essen, Goldschmidtstr. 100, Germany.

Experimental

Films of polytetrafluoroethylene (0.05 and 0.5 mm. thickness, 2.5 × 1.3 cm.^{2} area) were boiled in dimethylformamide for 24 hr. and then in chloroform for 24 hr. Subsequently the films were dried at 50°C. at 1 mm. Hg.

Acrylonitrile was freed from the stabilizer by washing with 0.1*N* KOH and then with water, dried over $CaCl_2$, and subsequently fractionated at 78°C. at 760 mm. over P_2O_5. The distilled monomer was flushed with nitrogen, stored in a refrigerator, and used within 2 days after distillation.

The films were immersed in 20 cm.^{3} of acrylonitrile in glass ampules and then degassed by repeated freezing and melting under high vacuum.

The irradiation was carried out in a ^{60}Co gamma source with a dose rate of 0.78×10^5 r./hr. in a Dewar container with Dry Ice–acetone at −78°C. The dose rate was determined by Fricke dosimetry.

After irradiation the samples were heated for 150 hr. at 100°C. The grafted films were stirred for 48 hr. in dimethylformamide in order to remove the formed homopolymer, stirred for 24 hr. in chloroform, and dried at 50°C. at 1 mm. for 48 hr. The graft yield was determined gravimetrically.

Results and Discussion

Figure 1, top, shows the weight of the acrylonitrile, grafted per unit surface area, onto films of polytetrafluoroethylene as a function of the gamma-dose. The film immersed in the monomer was irradiated under vacuum at −78°C. Immediately after irradiation the samples were heated for 150 hr. at 100°C. With increasing thickness of the films the yield increased per surface area; so it is obvious that the "surface yield" depends on the thickness of the film.

Figure 1, bottom, shows the conversion, i.e., the amount of grafted acrylonitrile in relation to the initial mass of the film, as a function of the dose. The grafting rate is greater in films of 0.05 mm. thickness than in those of 0.5 mm.

It was also found that grafting is accompanied by a slight swelling of the film. On irradiation with 1.24 Mr the initial area of a film of 0.55 mm. thickness was enlarged by a factor of 1.30.

In contradiction to many other examples of grafting, the initial reaction does not occur with a constant rate. This is demonstrated in both parts of Figure 1, in which is seen a constant decrease of rate with dose.

The results described indicate that radiation-induced grafting of acrylonitrile onto polytetrafluoroethylene is not limited to the surface when the irradiation is carried out at low temperatures and the sample is subsequently kept at high temperature. Irradiation at low temperature not only stabilizes the free radicals but also suppresses homopolymerization. The rate of radiation-induced homopolymerization of acrylonitrile at −78°C. is 100 times lower than at room temperature.[10] On the other hand, the subsequent heating facilitates the diffusion and the reaction of the monomer with

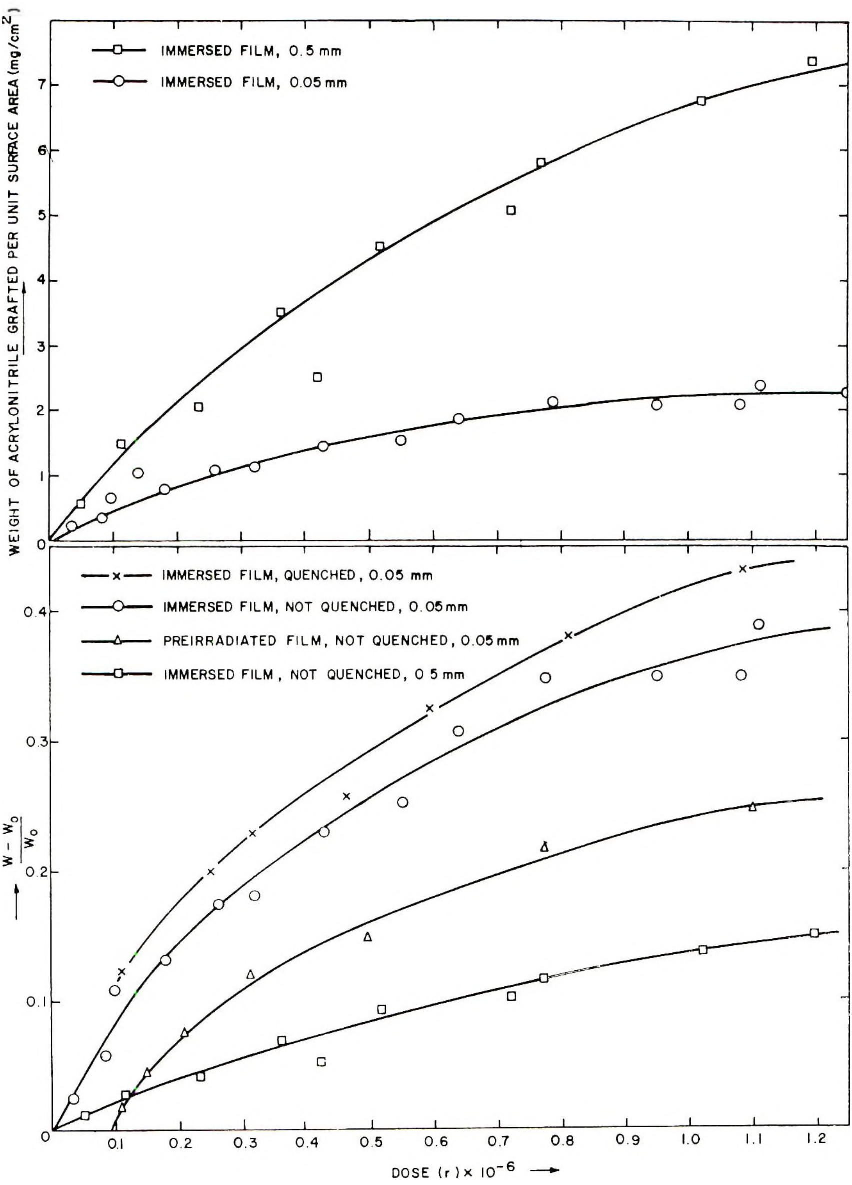

Fig. 1. Top: weight per unit surface area of polyacrylonitrile grafted onto polytetrafluoroethylene versus ^{60}Co gamma dose. Bottom: amount of grafted polyacrylonitrile, referred to initial weight of film, versus ^{60}Co gamma dose.

the free polymer radicals. Grafting in depth obviously occurs although the polyacrylonitrile formed is insoluble in its monomer. However, the lower graph of Figure 1 demonstrates that at 100°C., the grafting reaction is controlled by the diffusion of the monomer into the film, and therefore the concentration of the grafted polyacrylonitrile could be decreasing with the distance from the surface. This is also indicated by the self-retardation

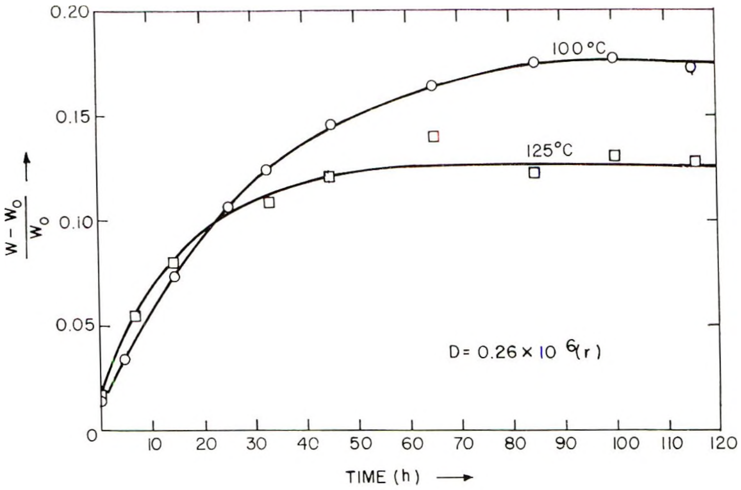

Fig. 2. Dependence of yield of graft on time of heating.

of the grafting reaction, which is shown by the curvature toward the abscissa in both graphs. Since the graft polymerization of the acrylonitrile first occurs in the outer layers of the film, one may assume that a barrier is formed, which retards further penetration of the monomer. This may also be associated with the fact that the diffusion occurs below the glass transition point of the polyacrylonitrile formed.[11] In addition, there is evidence from electron spin resonance measurements that radicals formed during the irradiation of polytetrafluoroethylene, in particular the primary radical $\sim\!\sim CF_2-CF_2\cdot$, start to disappear at about 75°C.[12] This would diminish the sites of chain initiation and would therefore contribute to the retardation of the graft polymerization. With increasing dose and, consequently, with increasing concentration of grafted polyacrylonitrile in the foil the penetration of the monomer becomes more difficult; simultaneously more free polymer radicals disappear during heating.[12]

The thermal history of the film has some influence on the rate of grafting, as shown in the lower graph of Figure 1. A film was quenched by heating it above the melting point and treating it subsequently with a cold press. The rate of grafting for a material thus treated is slightly higher than for an untreated material. The result indicates that grafting occurs with a faster rate in the amorphous area of the polymer. Similar, but much more pronounced, results have been obtained by Ballantine et al. in a work on grafting onto high-density and low-density polyethylene.[13]

Furthermore, the degree of swelling is higher when grafting is carried out with a quenched film. The initial area of the film is increased by a factor of 1.43, instead of 1.30, for the untreated material. This demonstrates that the crystalline fraction in the polytetrafluoroethylene hinders the expansion of the film and the loosening of the structure, and thus the grafting reaction is retarded.

The preirradiation technique, i.e. the irradiation of the film in the absence of the monomer at −78°C. and the subsequent addition of the degassed monomer under high vacuum and heating at 100°C., turned out to be less effective (see lower graph, Fig. 1). Grafting gave only about 60% of the yield obtained for the films that were immersed during irradiation. The induction period for the curve obtained for the preirradiation technique is about 10 times longer than that obtained when the irradiation is carried out in the presence of the monomer. It is conceivable that this is due to the fact that for the initial stage of the reaction a small amount of swelling is required, in order to facilitate the further penetration of the monomer. Such swelling, however, may already take place during irradiation in the presence of the monomer and, further, traces of impurities either in the monomer or in the film may be responsible for this phenomenon. These traces are already inactivated when film and monomer are irradiated simultaneously.

Figure 2 shows the conversion as a function of heating time for a dose of 0.26×10^5 r. Obviously, some grafting occurred before heating was started. If the sample is exposed to heating, then grafting occurs with a decreasing rate, until a limiting value is reached, indicating the completion of the reaction. The initial rate increases with temperature, but the yield at the end of the reaction drops. This result may be explained by the fact that the probability of chain termination in a highly viscous medium, such as a polymer film, increases with temperature. As a result, the preponderance of chain propagation over chain termination drops, which in turn lowers the yield. However, the lower final yield obtained at the higher temperature may also be caused by a faster depletion of polymer radicals.[12]

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Part II. Pyrolysis of a Tetrafluoroethylene–Acrylonitrile Copolymer

J. FOCK,* *Polytechnic Institute of Brooklyn, Brooklyn, New York 11201*

Synopsis

The pyrolysis of copolymers obtained by radiation-induced grafting of acrylonitrile onto polytetrafluoroethylene has been studied. Infrared spectroscopy shows disappearance of —C≡N and appearance —C=N— absorptions, indicative of the conjugation of the nitrile groups in the polyacrylonitrile segments. Aromatization is suggested by the appearance of aromatic C—H absorption and by the disappearance of aliphatic C—H absorption in the infrared spectra, as well as by the decrease of the C/H ratio and the constancy of the N content during exposure to 280°C. shown by elementary analysis. Melting and remelting was studied by differential thermal analysis with respect to temperature, extent, and shape of peak area. An increase in the melting temperature proportional to the content of acrylonitrile in the copolymer was explained in terms of entropy effects. The melting peak obtained after grafting appears as a doublet. The latter disappears after annealing for 14 hr. at 300°C. and does not reappear on crystallization or on remelting. In addition, the areas obtained on first and repeated meltings shows a decrease which is proportional to the content of grafted polyacrylonitrile. These results are taken as an indication of an exothermic reaction involving crosslinking. The rate of disappearance of the —C≡N absorption reaches a maximum at the melting temperature. It seems that the exothermic reaction occurring in the crystalline region is identical with "propagation crosslinking" suggested by Grassie and Hay. It is concluded that an interesting new type of polymeric material has been found.

Introduction

The results described in Part I of this series[1] lead to the conclusion that grafting of acrylonitrile onto films of polytetrafluoroethylene, induced by trapped radicals, is a process which is not limited to the surface but occurs in depth.

Furthermore, polytetrafluoroethylene is considered to be a polymer which predominantly suffers scissioning of the main chain when exposed to ionizing radiation.[2] Therefore, the product of radiation-induced grafting of this polymer should be a block copolymer with a large section of polytetrafluoroethylene and polyacrylonitrile:

$$\sim\!\sim\mathbf{TFE}\text{—}\mathbf{TFE}\sim\!\sim \xrightarrow{\;\sim\;} \sim\!\sim\mathbf{TFE}\cdot + \cdot\mathbf{TFE}\sim\!\sim$$

$$\sim\!\sim\mathbf{TFE}\cdot + n\mathbf{AN} \longrightarrow \sim\!\sim\mathbf{TFE}\text{—}\mathbf{AN}\sqcap\!\sqcap\!\sqcap$$

Several authors had found by infrared spectroscopy that the main result of the pyrolysis of polyacrylonitrile is the disappearance of the nitrile

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*Present address: Th. Goldschmidt A.-G., 43 Essen, Goldschmidtstr. 100, Germany.

group and the appearance of imino groups. Cyclization[3,4] and crosslinking[5] during pyrolysis were assumed. Furthermore, when the exposure to heat was drastic, such as at 300°C. for a longer time, evidence of aromatization was found and was explained in terms of the formation of fused pyridine systems.[3]

It was therefore interesting to investigate the pyrolysis of the tetrafluoroethylene–acrylonitrile copolymer obtained by the radiation-induced grafting of acrylonitrile onto films of polytetrafluoroethylene.

Experimental

The preparation of films of polytetrafluoroethylene grafted with acrylonitrile has been described in Part I.[1]

Pyrolysis experiments were carried out in a Mettler Thermalanalyzer under high vacuum or under purified nitrogen. The films were heated in an Alundum crucible, which was in contact with a Pt/Pt-Rh thermocouple controlling the temperature of the surrounding furnace. A sample of acrylonitrile homopolymer was dispersed in a KBr disk (0.15 g. per disk) and also heat-treated in the Alundum crucible.

Infrared spectroscopy was carried out with a Perkin-Elmer 521 Grating IR Spectrophotometer, the films mounted in a metal frame. Since it turned out that at temperatures higher than 230°C. gases were released, which led to a deterioration of the spectra, owing to the formation of microscopic bubbles, the determination of the rate of disappearance of nitrile groups depending on the fraction of polytetrafluoroethylene was carried out at 210°C. In addition, all pyrolysis experiments foreseen for infrared spectroscopy were carried out in a vacuum.

Differential thermal analyses and thermogravimetry were done in the Mettler Thermalanalyzer at a heating and cooling rate of 4°C./min. on 12 mg. samples. For the benefit of better accuracy of the differential thermal analyzer element these measurements had to be carried out under purified nitrogen.

Results and Discussion

Films of polytetrafluoroethylene grafted with acrylonitrile change their color from white to yellow and orange above 200°C. On further increase of the temperature, with a heating rate of 4°C./min., the color turns to reddish-brown; at about 300°C. it becomes a dark brown, and above 350°C., black.

Figure 1 shows a series of infrared spectra that was obtained from a film of polytetrafluoroethylene containing 12.5% polyacrylonitrile. The film first was analyzed as it was; then it was heated at 280°C. for 0.5, 3, and 18 hr. in a vacuum.

The spectra show the presence of the $-\text{C}{\equiv}\text{N}-$ group. In addition, there is a shift of the absorption at 2240–2195 cm.$^{-1}$, which is most likely caused by the formation of conjugated nitrile groups; as one may see, on longer exposure to heat this absorption disappears again. Appear-

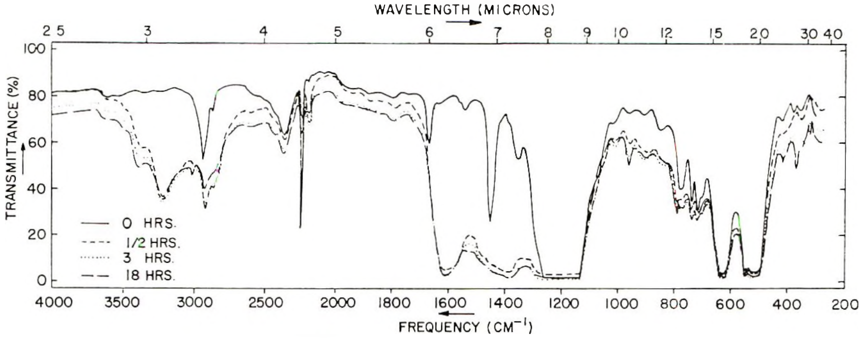

Fig. 1. Series of infrared spectra of film of polytetrafluoroethylene containing 12.5% polyacrylonitrile, heated at 280°C. in vacuum for various times.

ance of the —C=N— absorption and disappearance of the —C≡N absorption have been explained in terms of the formation of naphthyridine-like structures[3] and of crosslinking via azomethin groups.[5]

There is also a consecutive disappearance of absorptions at 2920 and 1455 cm.$^{-1}$, which may be taken for aliphatic C—H vibrations. Simultaneously there appear absorptions at 3050, 960, and 790 cm.$^{-1}$, and also a broad absorption between 1370 and 1410 cm.$^{-1}$, which strongly suggests aromatization. If, however, aromatization takes place, the major reason for the appearance of —C=N— groups should be ring formation and would not suggest crosslinking via an azomethin group as the prevailing reaction. The possibility that "propagation crosslinking" takes place, as suggested by Grassie and Hay,[4] is quite compatible with the concept of aromatization. It is interesting to see that the absorptions indicating conjugation or ring formation appear much faster than those indicating aromatization, which does not necessarily imply that the changes of the —C≡N and of the —C=N— absorptions are in the same relationship to one another. Absorptions at 2350 and between 1260 and 1130 cm.$^{-1}$

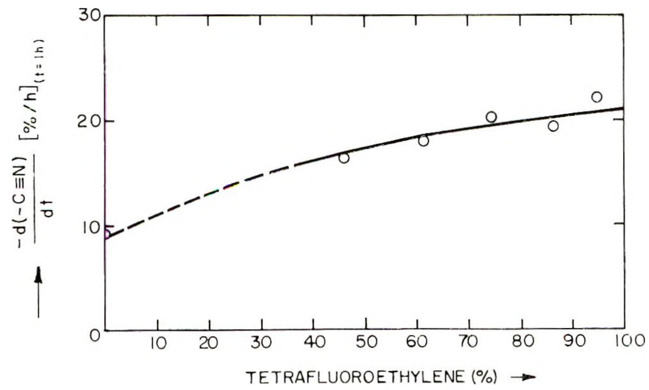

Fig. 2. Rate of disappearance of —C≡N absorption at 2240 cm.$^{-1}$ versus fraction of polytetrafluoroethylene at 210°C.

TABLE I

Transition Temperatures, Peak Areas, and Relative Decrease in Peak Area and in Weight of Virgin Polytetrafluoroethylene, Tetrafluoroethylene–Acrylonitrile Copolymers, and Acrylonitrile Homopolymer

Sample	1. Melting			Crystallization		2. Melting		Weight loss from 280 to 350°C.	
	T_1,°C.	T_2,°C.	A, cm.^{2}	T,°C.	A, cm.^{2}	T,°C.	A, cm.^{2}	$\Delta A/A$	$\Delta W/W_{\text{PAN}}$
Virgin polytetrafluoroethylene	338	—	1.60	320	1.57	338	1.57	0.019	—
10.7% polyacrylonitrile	347	352	1.28	322	1.19	339	1.13	0.117	0.35
21.2% polyacrylonitrile	353	358	0.97	327	0.76	343	0.73	0.247	0.277
28.0% polyacrylonitrile	356	359	0.77	329	0.50	345	0.52	0.322	0.238
28.0% polyacrylonitrile heated at 300°C. for 14 hr.	358	361	0.62	330	0.52	347	0.52	0.162	—
Polyacrylonitrile	—	—	—	—	—	—	—	—	0.175

TABLE II
Composition of a Tetrafluoroethylene–Acrylonitrile copolymer (13.3% Acrylonitrile) versus Time Exposure to Heat at 210°C.

Time, hr.	C	H	N	F	C/H
0	29.88	0.80	3.60	65.72	37.4
0.5	30.42	0.58	3.25	65.75	52.5
3	30.57	0.43	3.03	65.97	71.0
18	30.70	0.24	2.99	66.07	128.0

showing C—F bonds in polytetrafluoroethylene do not undergo a change during heating. The absorption at 3380 cm.$^{-1}$ most likely indicates absorbed water, which would show that the modified polyacrylonitrile was hygroscopic.

Figure 2 is a plot of the rate of the percent disappearance of the —C≡N absorption at 210°C. (related to the absorption in untreated material) versus the fraction of polytetrafluoroethylene. Obviously, the polyacrylonitrile segments in the block copolymer undergo pyrolysis faster than the acrylonitrile homopolymer. With increasing content of polytetrafluoroethylene the rate of pyrolysis is raised. It seems that the fluorine atoms act as a nucleophilic agent in a mechanism similar to that suggested by Grassie and Hay[4] for the acceleration of the pyrolysis in polyacrylonitrile copolymerized with acrylic acid. Faster pyrolysis of the polyacrylonitrile segments in the copolymer is also shown in Table I. The relative weight loss between 280 and 350°C. at a heating rate of 4°C./min. increases with increasing fraction of polytetrafluoroethylene.

Elementary analyses of a film with 13.3% acrylonitrile, which was heated for 0.5, 3 and 18 hr., shows (Table II) that the carbon content does not change significantly during the heat treatment.

Although there is a relatively rapid loss of nitrogen in the beginning of the pyrolysis, stabilization of the nitrogen content occurs after prolonged exposure to heat. The C/H ratio increased gradually and does not stabilize. All these results support the assumption of aromatization, i.e., the formation of aromatic heterocycles, including a nitrogen atom.

Figure 3 shows the results of differential thermal analyses of virgin polytetrafluoroethylene, of polytetrafluoroethylene grafted with different amounts of acrylonitrile, and of acrylonitrile homopolymer. Every sample was heated up to 375°C., cooled down to 300°C., and reheated at a rate of 4°C./min. under nitrogen. Figure 3 shows also the weight loss occurring with the heating between 280 and 350°C. In Table I the temperature T and the areas A of the peaks are given. The ratio $\Delta A/A$ represents the difference between the areas showing melting obtained on initial and repeated heating related to the initial area of melting.

Samples containing polyacrylonitrile and acrylonitrile homopolymer exhibit a sharp exothermic peak at about 275°C. The exotherm was also observed when a sample with 21.1% polyacrylonitrile was heated in oxygen. In addition, a secondary peak appears at 310°C., which is

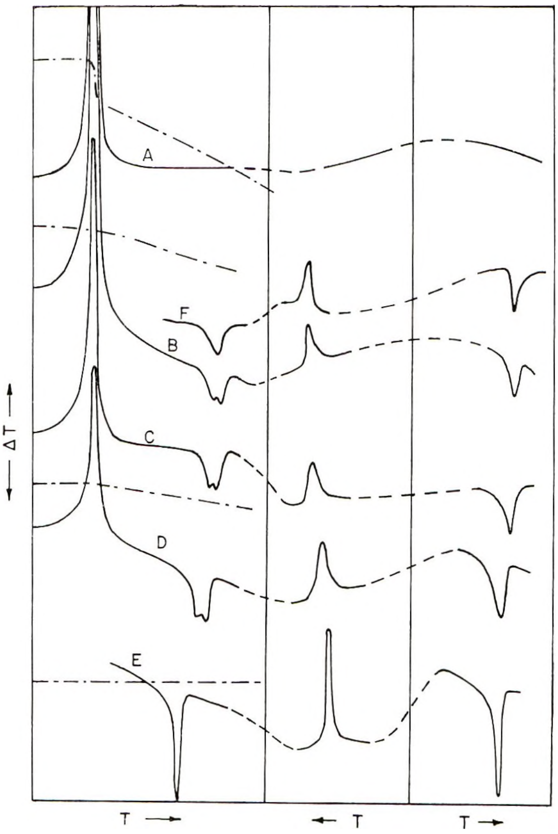

Fig. 3. Differential thermal analyses at heating and cooling at rate of 4°C./min.: (*A*) acrylonitrile homopolymer; (*B*) 28.0% acrylonitrile in copolymer; (*C*) 21.1% acrylonitrile in copolymer; (*D*) 10.7% acrylonitrile in copolymer; (*E*) virgin polytetrafluoroethylene; (*F*) 28.0 acrylonitrile in copolymer annealed at 300°C. for 14 hr.

absent when the thermal analysis is run in pure nitrogen. Obviously, the peak at 275°C. does not represent an oxidative nature. In previous thermoanalytical work on the homopolymer of acrylonitrile the exotherm has been assigned to the formation of naphthyridine-like structures.[6]

In general, a decrease of the melting temperature of copolymers compared with those of the homopolymer components is observed. This is true of random and of block copolymers.[7a] It is, however, obvious that the temperature at which melting of the crystalline fraction of polytetrafluoroethylene occurs is shifted toward higher values when the polymer is grafted with polyacrylonitrile (see also Table I). It seems that in the presence of the polyacrylonitrile segments modified by the heat treatment a situation is established in which the change or gain of the entropy of melting, ΔS_m, is considerably smaller than in the virgin material. This in turn affects the melting temperature T_m, which is defined as

$$T_m = \Delta H_m / \Delta S_m$$

In a first approximation it can be assumed that the enthalpy of melting ΔH_m is constant. Lowering of ΔS_m would therefore result in a higher melting temperature. The decrease of ΔS_m could be a consequence of a restricted mobility of initially melted chain segments of the crystalline fraction of the polytetrafluoroethylene. The unmeltable and supposedly rigid sections of the blocks of modified polyacrylonitrile would permit fewer possible conformations for the polytetrafluoroethylene. As melting progresses, the number of conformations increases, and the entropy change becomes greater. In other words, a kinetic barrier has to be overcome in order to initiate the transition from the crystalline to the completely amorphous phase. This assumption may also be associated with the result that grafting occurs faster in the amorphous regions of polytetrafluoroethylene films, and swelling occurs to a higher extent in a material with a lower degree of crystallinity, such as that due to quenching. The kinetic barrier involves entropy effects and leads to the phenomena of "superheating." Similar effects of superheating have been observed in polymers completely crystallized by the application of high pressures.[8]

The comparison of the first melting peak with the peak obtained on reheating of any of the copolymers in Figure 3 or Table I shows that there exists a considerable difference with respect not only to the temperature of the transition but also to the extent and shape of the peak. The first melting peak has been observed when polytetrafluoroethylene was melted for the first time after its synthesis, and it was ascribed to the presence of two different types of crystallite.[9] However, the doublet has not been found in the ungrafted material, even when the film was gamma-irradiated with a dose of 1 Mr. The doublet disappears when the copolymer is annealed at 300°C., i.e. below the melting temperature, for 14 hr. It is conceivable that the melting process induces an exothermic chemical reaction which compensates for the absorption of thermal energy and results in the doublet. Cooling and reheating of the sample showed that the doublet involves a reversible transition, since only single peaks are found during crystallization and remelting.

In order to receive more information on the nature of the assumed chemical reaction associated with melting, the per cent disappearance of the $-C{\equiv}N$ and the appearance of the $-C{=}N-$ absorption (both related to the initial intensity of the $-C{\equiv}N$ absorption) as a function of the temperature was investigated. Samples of identical materials (13.2% acrylonitrile) were heated to a certain temperature between 240 and 375°C. at a rate of 4°C./min. and cooled at the same rate. The results are shown in Figure 4. One can see two temperature ranges at which the rate of disappearance of the $-C{\equiv}N$ absorption reaches a maximum: at 260–290°C. and at 350–365°C. Simultaneously, the absorption of the $-C{=}N-$ group (conjugated or cyclic) reaches a maximum at 290°C. and then drops continuously. The maximum at 350–365°C. shows that a chemical reaction is indeed associated with the first melting. This reaction is probably identical with the conjugation of nitrile groups or the

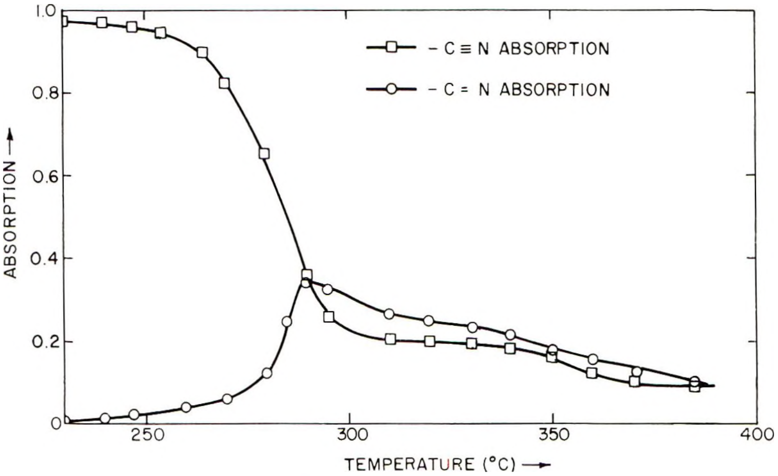

Fig. 4. Relative infrared absorption of —C≡N group at 2240 cm.$^{-1}$ and of —C=N— group at 2195 cm.$^{-1}$ versus temperature (related to absorption at 2240 cm.$^{-1}$ without previous heating).

process of cyclization, to judge by the strong exothermic peak at 275°C. and the first maximum in the rate of disappearance of the —C≡N group. Melting enhances the mobility and, subsequently, the reactivity of the chain segments of polyacrylonitrile in the crystalline part of the copolymer. One could therefore assume that the exothermic reaction which occurs during melting involves the chemical transition of "trapped" —C≡N groups.

The decrease of the —C=N— absorption above 290°C. could be taken as a proof of aromatization after the conjugation.

Comparing the peak areas representing melting and remelting, one finds a decline ΔA. With increasing concentration of grafted polyacrylonitrile in the copolymer the ratio $\Delta A/A$, where A is the area of the first melting peak, also increases; see Table I. Furthermore, when comparing the two melting peak areas one observes a depression of the melting temperature, which is also proportional to the concentration of acrylonitrile in the copolymer; see Table I. The decrease in the melting area and the depression of the melting temperature show that the exothermic reaction responsible for the discussed doublet involves, or is accompanied by, crosslinking. Because of the formation of interchain links the translatory diffusion of chain segments is hindered. This in turn restricts the crystallization in crosslinked polymers. A similar decrease of the degree of crystallinity has been observed for the crosslinking of polyethylene with the aid of dicumylperoxide.[7b] The decrease in crystallinity leads in turn to a comparatively larger change in the entropy of melting; concomitantly, there is a depression of the melting temperature.[10]

The nature of the crosslinking process is possibly identical with the propagation crosslinking suggested by Grassie and Hay,[4] which is supposed to be a part of the complex pyrolysis of polyacrylonitrile and constitutes the reason for the development of insolubility. This process does not seem to occur in the crystalline region of the copolymer unless melting takes place. After the transition of the crystalline fraction of the copolymer into the amorphous phase "propagation crosslinking" becomes possible, since pairs of nitrile groups on adjacent chains will be in a position more favorable for this reaction than in the crystalline phase.

It is possible that some crosslinking by formation of links between blocks of polytetrafluoroethylene and modified polyacrylonitrile takes place, which is initiated by ammonia or amines evolved in the pyrolysis of polyacrylonitrile.[3] Crosslinking at elevated temperature involving the release of hydrogen fluoride was observed in hydrofluorocarbon polymers when amines were added.[11]

The possibility that crosslinking occurs by reactions of radicals stemming from the gamma irradiation, such as $\sim\!\sim CF_2-\dot{C}F-CF_2\sim\!\sim$, which are supposed to be stable even at 200°C.,[12] has been ruled out, since electron spin resonance spectroscopy of copolymers that have not undergone pyrolysis does not give evidence of the presence of free radicals.

Finally, it may be concluded that through pyrolysis of the tetrafluoroethylene–acrylonitrile copolymer, which very likely results in the formation of pyridine-like structures and crosslinks, a new type of polymeric material has been obtained. This may find interesting applications with respect to its thermal and, possibly, its electrical properties, since pyrolized polyacrylonitrile is known as a semiconductor.

The author wishes to thank H. F. Mark and F. R. Eirich for their kind interest in this work, which was supported in part by the Office of Advanced Research Project Agency, Washington, D. C., under Contract Nonr-839(38).

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The Preparation of Polysiloxane–Vinyl Monomer Graft and Block Copolymers

YUJI MINOURA, *Research Institute for Atomic Energy, Osaka City University, Kitaku, Osaka*, and MINORU SHUNDO and YASUSHI ENOMOTO, *Sakai Chemical Industry Co. Ltd., Sumaku, Kobe, Japan*

Synopsis

In another paper the radical polymerization of styrene in the presence of various chlorosilanes was investigated, and polystyrenes having chlorosilyl groups as endgroups were obtained. In the present work attempts were made to obtain polysiloxane–styrene graft and block copolymers from chlorosilyl polystyrenes. Block copolymers were obtained with dichlorosilane and graft copolymers with tri- and tetrachlorosilanes. In the latter case the insoluble fractions increased, if a suitable stopper, such as butanol or trimethylchlorosilane [$(CH_3)_3SiCl$], was not used in the condensation reaction. Methyldichlorosilane was used for the preparation of the graft copolymer, because the Si—H bond was more effective than the Si—Cl bond for the chain transfer reaction.

INTRODUCTION

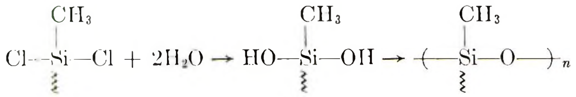
A few papers have been published concerning the synthesis of polysiloxane–vinyl monomer graft and block copolymers. For example, a graft copolymer was obtained by a chain transfer reaction in the radical polymerization of a vinyl monomer in the presence of a polysiloxane.[1] Recently Greber and his co-workers[2] prepared a block copolymer from an ω,ω'-dihalopolysiloxane and a living polymer and graft copolymers by anionic polymerization of styrene and methyl methacrylate with a macromolecular catalyst having a polysiloxane chain. Morton and his co-workers[3] synthesized block copolymers by the ring-opening polymerization of cyclic polysiloxanes with polystyryl lithium and polyisopropenyl lithium.

In an earlier paper[4] from this laboratory we showed that various chlorosilyl compounds undergo a chain-transfer reaction in the radical polymerization of styrene and methyl methacrylate. The present paper reports the preparation of siloxane–vinyl monomer graft and block copolymers by the chain-transfer reaction of chlorosilyl compounds in the radical polymerization of styrene and the condensation reaction of the chlorosilyl groups which have a vinyl polymer chain.

The following reaction scheme seems to hold for methyltrichlorosilane:

$$\text{polymer radical}\sim\sim\cdot + CH_3SiCl_3 \rightarrow \sim\sim Cl + \cdot SiCl_2CH_3$$

$$CH_3Cl_2Si\cdot + nM \rightarrow CH_3Cl_2Si\sim\sim\cdot \rightarrow \text{termination}$$



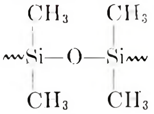
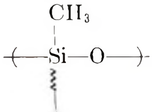
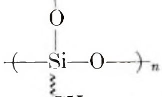
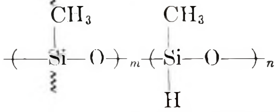
$$\mathrm{Cl{-}\underset{\wr}{\overset{CH_3}{Si}}{-}Cl} + 2H_2O \rightarrow \mathrm{HO{-}\underset{\wr}{\overset{CH_3}{Si}}{-}OH} \rightarrow \mathrm{(\!-\underset{\wr}{\overset{CH_3}{Si}}{-}O-\!)_n}$$

where M is the vinyl monomer and ∿∿ is the vinyl polymer.

Therefore, the structure of the copolymer changes according to the chlorosilane used.

The classification of the copolymers is given in Table I.

TABLE I
Classification of Copolymers

Chlorosilane used	Graft or block copolymer expected[a]
$(CH_3)_2SiCl_2$	 $\mathrm{\sim\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Si}}\sim}$ block copolymer
CH_3SiCl_3	 $\mathrm{(\!-\underset{\wr}{\overset{CH_3}{Si}}{-}O-\!)_n}$ graft copolymer
$SiCl_4$	 $\mathrm{(\!-\underset{\wr}{\overset{\overset{\wr}{O}}{Si}}{-}O-\!)_n}$ graft copolymer
CH_3SiHCl_2	 $\mathrm{(\!-\underset{\wr}{\overset{CH_3}{Si}}{-}O-\!)_m(\!-\underset{H}{\overset{CH_3}{Si}}{-}O-\!)_n}$ graft copolymer

[a] The wavy bond indicates vinyl polymer.

It was found that the chlorosilyl compounds did not initiate the cationic polymerization of styrene, and therefore the introduction of the chlorosilyl groups to the polymer ends is due to a chain-transfer reaction.

The experiments described below deal mainly with the effect of the conversion of styrene and the initial concentration of the chlorosilyl compounds on the yield of the graft or the block copolymer.

EXPERIMENTAL

Purification of Reagents

Styrene (St) was purified by the usual method. The boiling point was 54°C. at 30 mm. Hg. The chlorosilyl compounds were supplied by the Shin-etsu Chemical Company Ltd. and were redistilled before use.

	Boiling point, °C.
$(CH_3)_3SiCl$:	58
$(CH_3)_2SiCl_2$:	70.5
CH_3SiCl_3:	66.4
$SiCl_4$:	57.6
CH_3SiHCl_2:	41.0

Commercial azobisisobutyronitrile (AIBN) was recrystallized from ethanol. The melting point was 101 to 102°C. Benzene and toluene were washed with sulfuric acid and water and dried over calcium chloride and sodium and then distilled. Special-grade cupric sulfate, butanol, and methanol were used.

Reaction Method

The chain-transfer reactions were carried out in benzene at 80°C. in sealed tubes. The required amounts of the reactants were placed in the clear tubes and then degassed by repeated freezing and thawing cycles; then the tubes were sealed. They were placed in a thermostat regulated at 80°C.

After the chain-transfer reaction the polymer solution was poured into a three-necked reaction flask, where the condensation reagent, inhibitor, and solvent were added.

The condensation polymerization was carried out at the reflux temperature.

RESULTS AND DISCUSSION

Fractionation and Confirmation of Graft and Block Copolymers

It was found that the reaction mixture from the St–chlorosilane systems, which contained polysiloxane–polystyrene graft or block copolymers, polystyrene, and polysiloxane, were fractionated best by means of petroleum ether.

Since petroleum ether is a good solvent for polysiloxane and a poor solvent for polystyrene, and carbon disulfide is the opposite, mixtures of the two homopolymers were fractionated preliminarily with these solvents. The results are shown in Table II.

Of the two methods, the polymer mixture was fractionated best by method 1, and this was verified by means of infrared spectra. Therefore, method 2 was used for the series of St–chlorosilane systems.

TABLE II
Fractionation of Polymer Mixture[a]

Method 1		Method 2	
Pst 0.1987 g.	Psi 0.3208 g.	Pst 0.1691 g.	Psi 0.2338 g.
CS_3, 25 ml.		Petroleum ether, 25 ml.	
Soluble Pst, 0.2030 g. (102.7%)	Insoluble Psi, 0.2625 g. (81.8%)	Insoluble Pst 0.1727 g. (102.1%)	Soluble Psi, 0.2148 g. (93.4%)
Total: 89.6%		Total: 97.1%	

[a] Pst, polystyrene; Psi, polysiloxane.

On the other hand, for the purpose of investigating whether the fractionation with petroleum ether was adequate or not, it was compared with the fractionation results from a turbidimetric titration. The result of the turbidimetric titration is shown in Figure 1.

The sample was the benzene-soluble fraction from the reaction mixture of the St–CH_3SiCl_3 system. The turbidity curve was divided into three fractions, and therefore the reaction mixture was composed of three components.

In the fractionation with petroleum ether 63.8% of the mixture was soluble in petroleum ether and 36.2% was insoluble. The soluble fraction was homopolysiloxane, since the infrared spectrum did not show the absorption of polystyrene (Fig. 2A). However, the infrared spectrum of the insoluble fraction showed the characteristic absorption bands of polystyrene and polysiloxane. Therefore, a graft copolymer was contained in the insoluble fraction (Fig. 2B). It is considered that the three fractions in the turbidimetric titration curve were polystyrene (12.5%), polystyrene–polysiloxane graft (25.5%), and polysiloxane (62.0%), from their behavior toward the precipitant (methanol–acetone, 3:1 volume ratio). The sum of the polystyrene (12.5%) and the graft copolymer (25.5%) agreed well with the fraction insoluble in petroleum ether. The latter fraction was completely soluble in carbon disulfide. This solubility was due to the short length of the polysiloxane chain in the graft copolymer. The infrared spectrum of the fraction soluble in petroleum ether is shown in Figure 2A and is identical with that of dimethylpolysiloxane.

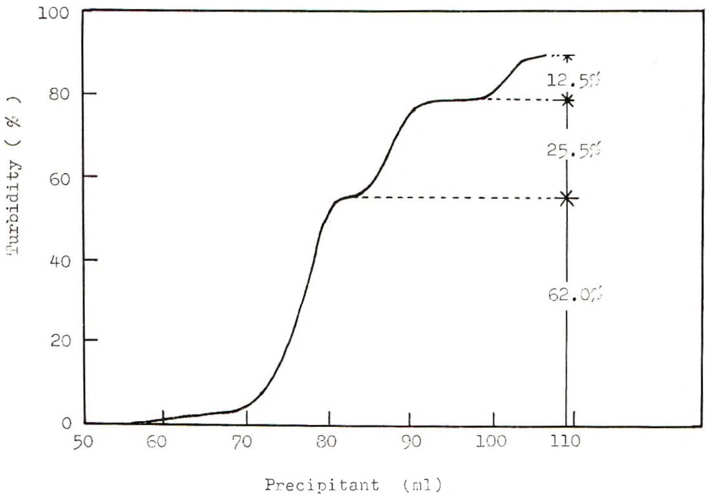


Fig. 1. Methanol–acetone (3:1) titration of benzene solution containing polystyrene, polysiloxane, and a polystyrene–polysiloxane graft. Sample: B-23, soluble in benzene, Concentration 1.3726 g. per 100 ml. of benzene.

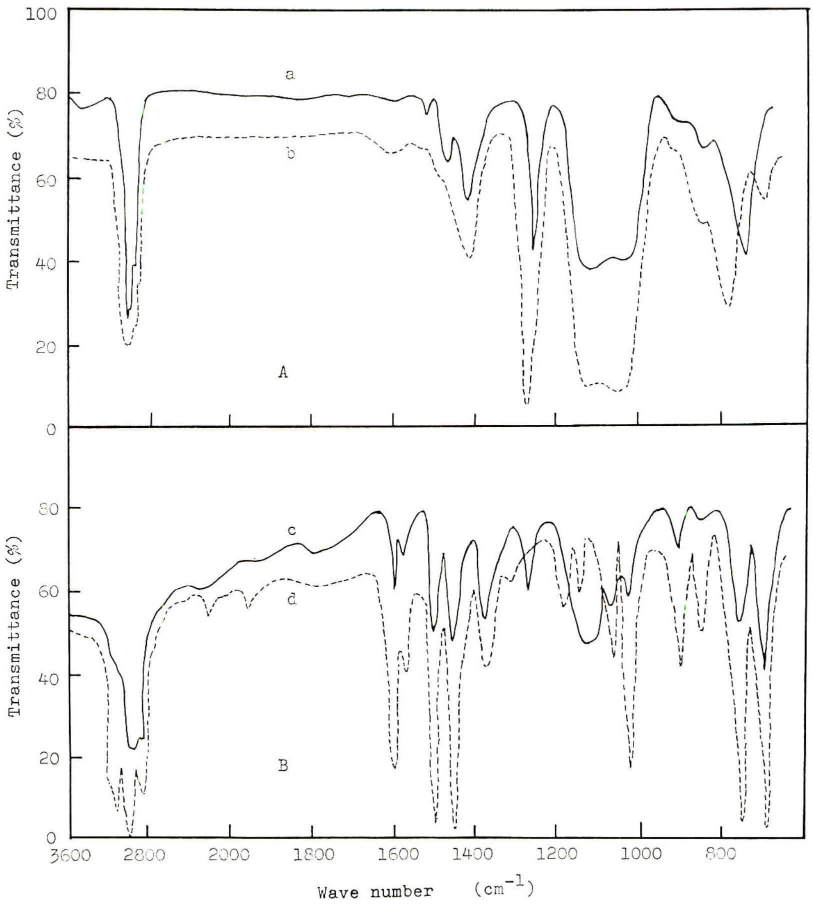
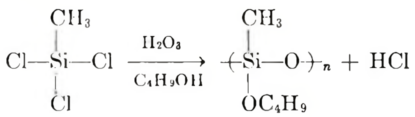


Fig. 2. Infrared spectra of sample B-23 fractionated with petroleum ether: (*a*) soluble in petroleum ether; (*b*) dimethylpolysiloxane; (*c*) insoluble in petroleum ether; (*d*) polystyrene.

In this spectrum the absorption band at 770 cm.$^{-1}$ seems to be the characteristic absorption band of the butoxy group:



$$\mathrm{Cl{-}\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{Si}}{-}Cl} \xrightarrow[\mathrm{C_4H_9OH}]{\mathrm{H_2O_3}} \mathrm{\left(\overset{\displaystyle CH_3}{\underset{\displaystyle OC_4H_9}{Si}}{-}O \right)_{\!n}} + \mathrm{HCl}$$

The absorption bands at 1270 and 1120 cm.$^{-1}$ in Figure 2B are characteristic of methylpolysiloxanes.

Preparation of Graft and Block Copolymers

In a series of experiments two identical reaction tubes were prepared for each sample composition. The conversion of styrene was measured by the polymer weight after the chain-transfer reaction, one of the tubes being used. The contents of the other were placed in a three-necked reaction flask, and hydrolysis of the chlorosilane and condensation reaction of the silanol were carried out.

Styrene–Dimethyldichlorosilane System

The conditions for the chain-transfer reaction and the relationship between the conversion of styrene and the polymerization time for various concentrations of dimethyldichlorosilane are shown in Figure 3. The initial concentration of dimethyldichlorosilane and the polymerization time were varied and the concentration of styrene was constant.

As may be seen from Figure 3, the rate of polymerization of styrene is independent of the concentration of the silane.

After the chain-transfer reaction all the contents (10 ml.) were poured into a three-necked flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser, and the hydrolysis and the condensation reaction were carried out according to the reaction conditions shown in Table III. After the reaction, the reaction system was cooled to room temperature and diluted with benzene. Then the cupric sulfate was filtered off, and the filtrate was evaporated. The nonvolatile material was the polymer mixture, which separated into two phases on standing for a long time. The yield of the polymer mixture and the result of the fractionation with petroleum ether are shown in Table III.

The fraction insoluble in petroleum ether was completely soluble in carbon disulfide. Although the infrared spectrum of this fraction showed the presence of the siloxane bond, it is thought that this solubility was due to the short length of the polysiloxane chain in the block copolymer.

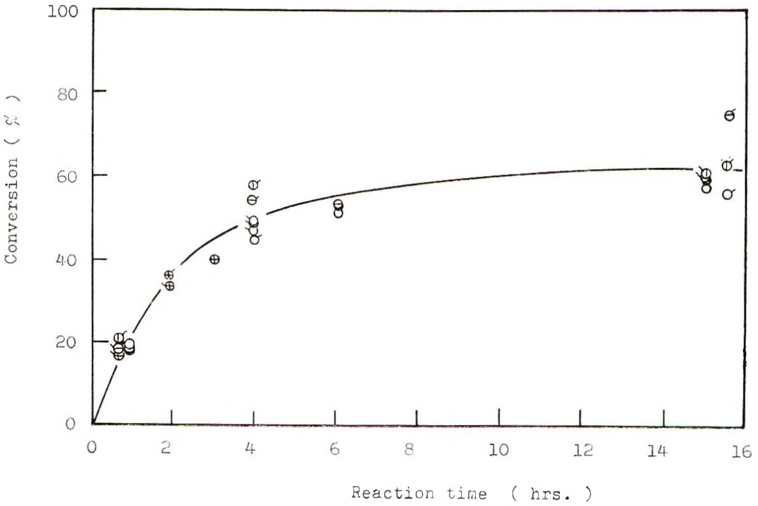


Fig. 3. Conversion of styrene versus reaction time in chain-transfer reaction. Styrene, 3.49 mole/l.; AIBN, 2.0×10^{-2} mole/l.; solvent, benzene; reaction temperature, 80°C. Concentration (moles/l.): (⊙) $(CH_3)_2SiCl_2$, 1.66; (⦶) same, 3.32; (⊖) same, 4.98; (⊙́) CH_3SiCl_3, 1.70; (⦶́) same, 3.41; (⊖́) same, 5.11; (⊙̀) $SiCl_4$, 1.75; (⦶̀) same, 3.50; (⊖̀) same, 5.25.

TABLE III
Conditions and Results of Condensation Reaction for Dimethyldichlorosilane System[a]

No.	St convsn., %	Cupric sulfate, g.	Yield, g.	Component		Sol. (Psi),[b] %	Insol. (block + Pst),[c] %
				St, %	Silox., %		
B-1	19.0	3	1.806	38.2	61.8	64.0	36.0
-2	40.1	"	2.588	56.4	43.6	30.8	69.2
-3	51.7	"	3.009	62.6	37.4	23.5	76.5
-4	57.4	"	3.459	60.4	39.6	16.4	83.6
-5	18.7	6	3.339	20.4	79.6	76.4	23.6
-6	40.8	"	3.420	43.3	56.7	43.4	56.6
-7	52.6	"	3.192	60.2	39.8	40.9	59.1
-8	58.9	"	2.915	73.4	26.6	42.8	57.2
-9	18.6	9	4.208	16.0	84.0	75.4	24.6
-10	39.2	"	3.650	39.0	61.0	58.8	41.2
-11	53.0	"	4.894	39.5	60.5	49.3	50.7
-12	59.1	"	4.654	46.2	53.8	39.5	60.5

[a] Initial amount of the reactants in chain-transfer reaction: St, 4 ml. (3.49 mole/l.); AIBN, 2.0×10^{-2} mole/l.; $(CH_3)_2SiCl_2$ (B-1 to B-4), 2 ml. (1.66 mole/l.), (B-5 to B-8) 4 ml. (3.32 mole/l.), (B-9 to B-12) 6 ml. (4.98 mole/l.). All in 10 ml. of toluene and about 0.1 g. of hydroquinone at reaction temperature of 100 to 110°C. for 12 hr.

[b] Psi, free polysiloxane; soluble in petroleum ether.

[c] Block + Pst, total of block copolymer and free polystyrene; insoluble in petroleum ether.

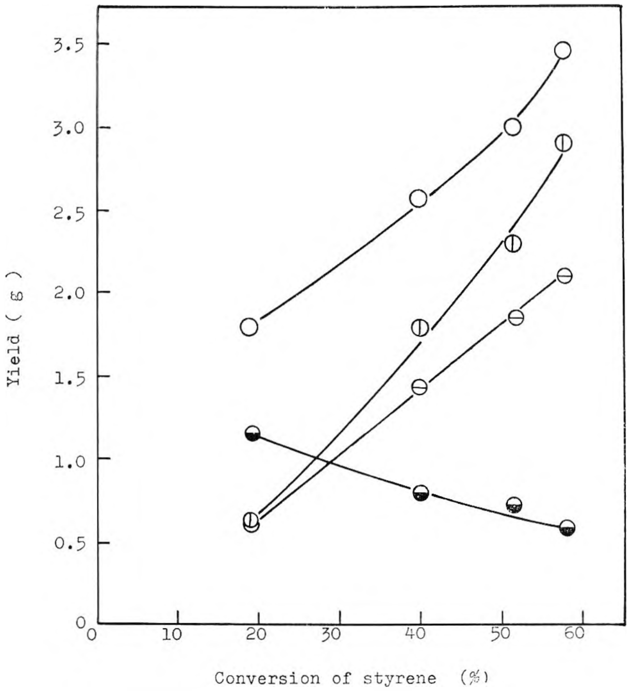


Fig. 4. Effect of conversion of styrene on various yields. Styrene, 4 ml. (3.49 mole/l.): $(CH_3)_2SiCl_2$, 2 ml. (1.66 mole/l.). (○) Total yield; (⦶) insoluble in petroleum ether (polystyrene–polysiloxane block + polystyrene); (◒) soluble in petroleum ether (polysiloxane); (⊖) theoretical yield of total polystyrene.

Figure 4 shows the effect of the conversion of styrene on the various yields. It is natural that the total yield of polymer mixture increases with the conversion of styrene; however, the free polysiloxane decreases, and the sum of the polystyrene and the polystyrene–polysiloxane block increases sharply. Therefore it was found that the yield of the block copolymer increased as the conversion of styrene increased.

In the same manner Figure 5 shows the effect of the initial amount of dimethyldichlorosilane on the various yields. In this case the conversion of styrene was constant, and therefore the sum of the polystyrene and polystyrene–polysiloxane block only need be considered. Because the mixture of polystyrene and block copolymer increased more than the free polysiloxane, with the initial amount of silane, the yield of the copolymer increased with it. In the mixture of polystyrene and copolymer the polysiloxane content was 35% by weight even at the highest yield.

Styrene–Methyltrichlorosilane System

The relationship between the conversion of styrene and the polymerization time for various concentrations of methyltrichlorosilane is shown in Figure 3. In this case the conversion of styrene was scattered with respect to the initial concentration of silane. For the formation of the siloxane

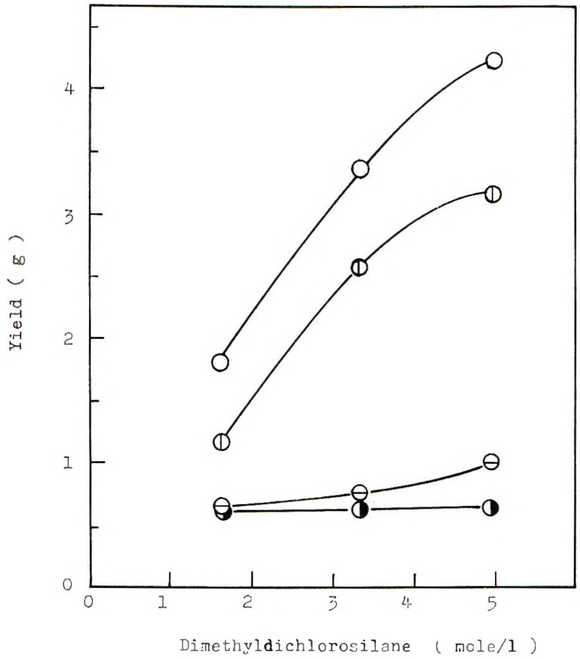
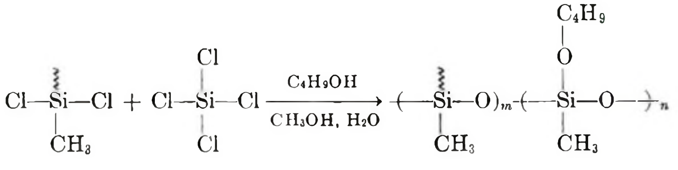
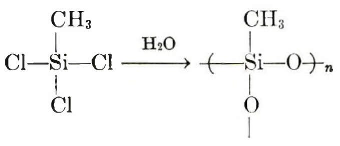


Fig. 5. Effect of initial amount of dimethyldichlorosilane on the various yields (styrene conversion, 20%): (⊙) total yield; (⊖) insoluble in petroleum ether (polystyrene–polysiloxane block + polystyrene); (⌽) soluble in petroleum ether (polysiloxane) (◑) theoretical amount of polystyrene.

chain the partial butoxylation of the chlorosilyl groups was carried out prior to the hydrolysis, with a mixture of methanol and water and the condensation reaction:


$$Cl-\overset{\wr}{\underset{CH_3}{Si}}-Cl + Cl-\overset{Cl}{\underset{Cl}{Si}}-Cl \xrightarrow[CH_3OH,\ H_2O]{C_4H_9OH} (-\overset{\wr}{\underset{CH_3}{Si}}-O)_m(-\overset{\overset{C_4H_9}{|}}{\overset{O}{\underset{CH_3}{Si}}}-O-)_n$$

The condensation reaction was continued for 5 hr. at the reflux temperature. After the reaction the system was diluted with benzene, and the gel fraction, produced by the following reaction (insoluble in benzene), was filtered off:


$$Cl-\overset{CH_3}{\underset{Cl}{Si}}-Cl \xrightarrow{H_2O} (-\overset{CH_3}{\underset{\underset{|}{O}}{Si}}-O)_n$$

The solvent, monomer, and silane were distilled off from the filtrate, and the nonvolatile material was fractionated with petroleum ether. The results are shown in Table IV.

TABLE IV
Total Yield and Result of Fractionation with Petroleum Ether for Styrene–Methyltrichlorosilane System[a]

No.	St convsn., %	Tot. yield, g.	Component St, %	Component Silox., %	Insol. in benz., gel. fract., %	Sol. in benz. Sol. (Psi),[b] %	Sol. in benz. Insol. (graft + Pst),[c] %
B-13	18.2	2.186	30.0	70.0	5.5	41.5	53.0
-14	35.6	2.773	46.5	53.5	4.7	35.8	59.5
-15	44.7	3.084	52.8	47.2	21.9	14.4	63.7
-16	57.0	2.940	70.5	29.5	22.6	8.4	69.0
-17	21.6	3.471	22.6	77.4	20.9	44.5	34.6
-18	36.5	3.941	33.8	66.2	8.7	52.9	38.4
-19	58.0	3.415	61.8	38.2	2.5	51.5	46.0
-20	64.5	4.442	52.6	47.4	19.2	23.6	57.2
-21	17.4	4.176	15.2	84.8	22.9	57.6	19.5
-22	37.1	4.178	32.4	67.6	19.1	47.5	33.4
-23	55.3	5.358	37.5	62.5	5.7	60.2	34.1
-24	76.7	5.115	54.5	45.5	10.2	41.8	48.0

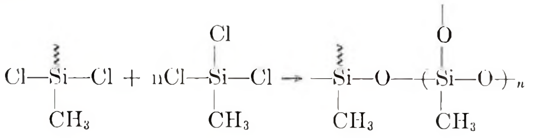
[a] Initial amount of reactants in chain-transfer reaction: St, 4 ml. (3.49 mole/l.); AIBN, 2.0×10^{-2} mole/l.; CH_3SiCl_3 (B-13 to B-16) 2 ml. (1.70 mole/l.), (B-17 to B-20) 4 ml. (3.41 mole/l.), (B-21 to B-24) 6 ml. (5.11 mole/l.).

[b] Psi, free polysiloxane; soluble in petroleum ether.

[c] Graft + Psi, total of graft copolymer and free polystyrene; insoluble in petroleum ether.

The fraction soluble in petroleum ether was free polysiloxane, from the infrared spectrum, which did not show the characteristic absorption of polystyrene.

On the other hand, the fraction insoluble in petroleum ether showed the characteristic absorption bands of polystyrene and polysiloxane in the infrared spectrum. Therefore it seemed that the polystyrene–polysiloxane graft was contained in this fraction. The gel fraction, which was insoluble in benzene, increased, and the fraction soluble in benzene decreased as the conversion of styrene increased at a constant concentration of methyltrichlorosilane (1.70 mole/l.). Therefore, it seems that the polystyrene having dichloromethylsilyl groups as endgroups increased as the polymerization proceeded and that cohydrolysis of the chlorosilylpolystyrene and methyltrichlorosilane occurred, causing crosslinking, which formed a three-dimensional network:



$$Cl{-}\underset{CH_3}{\overset{\wr}{Si}}{-}Cl + nCl{-}\underset{CH_3}{\overset{Cl}{Si}}{-}Cl \rightarrow {-}\underset{CH_3}{\overset{\wr}{Si}}{-}O{-}\!\left(\underset{CH_3}{\overset{\overset{|}{O}}{Si}}{-}O\right)_n$$

On the other hand, as the initial amount of methyltrichlorosilane increased, the gel fraction and the free polysiloxane had a tendency to increase, and then the graft copolymer decreased.

TABLE V

Total Yield and Result of Fractionation with Petroleum Ether for Styrene–Tetrachlorosilane System[a]

No.	St convsn.,	Tot. yield, g.	Component		Insol. in benz., gel fract., %	Theoretical amount of SiO_2 %	Sol. in benz.	
			St, %	Silox., %			Sol. (Psi),[b] %	Insol. (graft + Pst),[c] %
B-25	18.0	2.134	30.6	69.4	64.3	47.0	3.9	31.8
-26	34.8	2.484	51.0	49.0	54.9	40.4	1.9	43.2
-27	48.3	2.934	60.0	40.0	43.0	34.2	1.0	56.0
-28	59.0	4.476	47.6	52.4	27.1	22.4	17.5	55.4
-29	16.7	3.239	18.8	81.2	92.9	64.4	0.7	6.4
-30	34.0	4.382	28.2	71.8	64.4	47.5	11.3	24.3
-31	49.8	4.832	37.5	62.5	60.6	43.0	6.3	33.1
-32	61.8	6.495	34.6	65.4	46.1	32.0	17.9	36.0
-33	16.0	4.841	12.0	88.0	90.8	64.0	4.6	4.6
-34	33.8	4.908	25.0	75.0	81.8	63.2	0.3	17.9
-35	37.4	5.786	23.5	76.5	95.6	53.6	1.0	3.4
-36	59.5	6.150	35.1	64.9	67.6	50.4	2.4	30.0

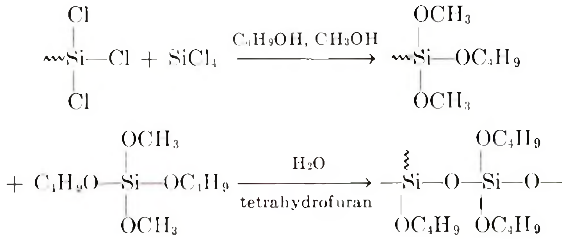
[a] Initial amount of the reactants in the chain transfer reaction. St = 4 ml. (3.49 mole/l.), AIBN = 2.0×10^{-2} mole/l., $SiCl_4$ = B-25 B-28; 2 ml. (1.75 mole/l.), B-29 B-32; 4 ml. (3.50 mole/l.), B-33 B-36; 6 ml. (5.25 mole/l.).

[b] Psi, free polysiloxane; soluble in petroleum ether.

[c] Graft + Pst, total of graft copolymer and free polystyrene; insoluble in petroleum ether.

Styrene–Tetrachlorosilane System

The relationship between the conversion of styrene and the polymerization time for various concentrations of tetrachlorosilane is shown in Figure 3. In this case, too, the polymerization rate was independent of the amount of silane. In the hydrolysis and the condensation reaction a small amount of chloranil was added as an inhibitor of the radical polymerization of styrene. After the alkoxylation of the chlorosilyl groups by means of methanol and butanol an aqueous solution of tetrahydrofuran was added dropwise, and the reactants were stirred at the reflux temperature for 3 hr.

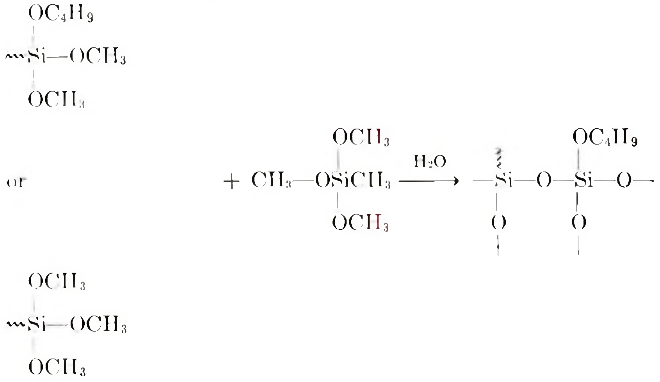


$$\sim\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{Si}}}\text{—Cl} + \mathrm{SiCl_4} \xrightarrow{\mathrm{C_4H_9OH,\ CH_3OH}} \sim\underset{\mathrm{OCH_3}}{\overset{\mathrm{OCH_3}}{\mathrm{Si}}}\text{—}\mathrm{OC_4H_9}$$

$$+\ \mathrm{C_4H_9O}\text{—}\underset{\mathrm{OCH_3}}{\overset{\mathrm{OCH_3}}{\mathrm{Si}}}\text{—}\mathrm{OC_4H_9} \xrightarrow[\text{tetrahydrofuran}]{\mathrm{H_2O}} \text{—}\underset{\mathrm{OC_4H_9}}{\overset{\wr}{\mathrm{Si}}}\text{—O—}\underset{\mathrm{OC_4H_9}}{\overset{\mathrm{OC_4H_9}}{\mathrm{Si}}}\text{—O—}$$

The rest of the procedure was similar to that mentioned above. The results are shown in Table V.

The gel fraction decreased as the conversion of styrene increased, and the mixture of polystyrene and polystyrene–polysiloxane graft (the fraction insoluble in petroleum ether) had a tendency to increase. Therefore, it is considered that the graft copolymer increases with the conversion of styrene. The fact that the gel fraction is much more than the theoretical amount indicates that the polystyrene having chlorosilyl endgroups underwent a crosslinking reaction.



$$\left.\begin{array}{l}\sim\underset{\mathrm{OCH_3}}{\overset{\mathrm{OC_4H_9}}{\mathrm{Si}}}\text{—}\mathrm{OCH_3}\\[2ex] \text{or}\\[2ex] \sim\underset{\mathrm{OCH_3}}{\overset{\mathrm{OCH_3}}{\mathrm{Si}}}\text{—}\mathrm{OCH_3}\end{array}\right.\ +\ \mathrm{CH_3}\text{—O}\underset{\mathrm{OCH_3}}{\overset{\mathrm{OCH_3}}{\mathrm{Si}}}\mathrm{CH_3} \xrightarrow{\mathrm{H_2O}} \text{—}\underset{\underset{|}{\mathrm{O}}}{\overset{\wr}{\mathrm{Si}}}\text{—O—}\underset{\underset{|}{\mathrm{O}}}{\overset{\mathrm{OC_4H_9}}{\mathrm{Si}}}\text{—O—}$$

Therefore, the graft copolymer did not increase with increase in the initial amount of tetrachlorosilane.

Styrene–Methyldichlorosilane System

Generally, the silicon-hydrogen bond is more reactive than the silicon-chlorine bond in a radical reaction. For example, triphenylsilane $[(C_6H_5)_3$-

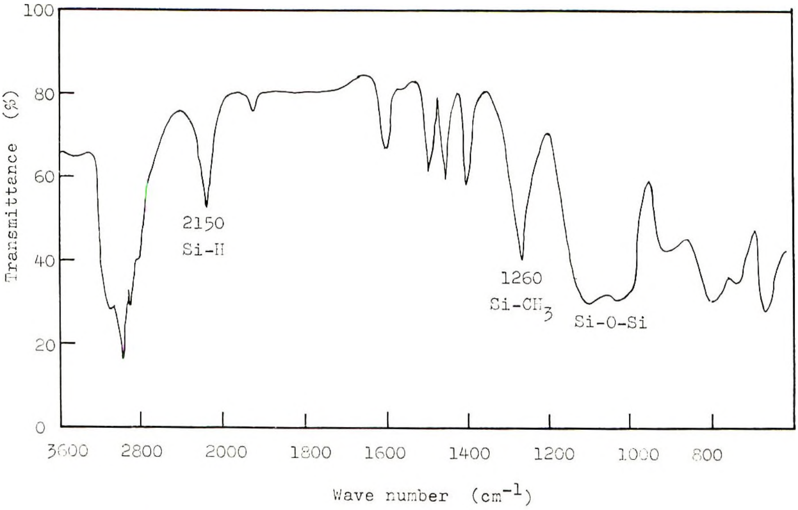


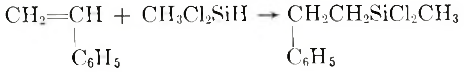
Fig. 6. Infrared spectrum of fraction soluble in acetone.

SiH] and triethylsilane [$(C_2H_5)_3SiH$] have larger chain-transfer constants in the radical polymerization of styrene than do alkylchlorosilanes and tetrachlorosilane.[4] Therefore, it is expected that with the chlorohydrosilane (Cl—Si—H) a block or a graft copolymer would be easily produced by the chain-transfer reaction and the condensation reaction. To confirm this, the styrene–methyldichlorosilane (CH_3SiHCl_2) system was studied. The conditions of the chain-transfer reaction in a sealed tube are shown in Table VI.

TABLE VI
Conditions for Chain-Transfer Reaction

Styrene, 5 ml. (4.35 mole/l.)
Methyldichlorosilane, 3 ml. (2.88 mole/l.)
AIBN, 1.0×10^{-2} mole/l.
Solvent: benzene
Polymerization temperature: room
Polymerization time: 8 days

The conversion of styrene in this reaction was 13.6%. It seems that this low conversion is due to the addition of silane to the double bond of styrene, but this was not confirmed.


$$\underset{\displaystyle C_6H_5}{CH_2{=}\overset{}{CH}} + CH_3Cl_2SiH \rightarrow \underset{\displaystyle C_6H_5}{CH_2}CH_2SiCl_2CH_3$$

The condensation reaction was carried out in a three-necked flask equipped with a condenser, a stirrer, and a dropping funnel, as follows. All the contents of the sealed tube were poured into the reaction flask and benzene (10 ml.), butanol (10 ml.), water (20 ml.), and dimethyldichlorosilane (10 ml.) were added. The mixture was stirred for 5 hr. at 80°C. After the reaction, the volatile materials were distilled off. The residue (1.45 g.) was extracted with acetone, which is a poor solvent for polysiloxane. The extract (0.56 g.) showed the characteristic absorption bands of polystyrene and polysiloxane in its infrared spectrum, as shown in Fig. 6.

It is evident that a polystyrene–polysiloxane graft was produced. Moreover, the characteristic band of Si—H appeared in the spectrum. This is probably due to the hydrolysis of the methyldichlorosilane, which did not react in the chain-transfer process.

Polystyrene–polysiloxane block and graft copolymers were prepared by a new method, in which the radical chain-transfer reactions of chlorosilanes are used.

We are grateful to the Shin-etsu Chemical Industry Co. Ltd. for supplying various chlorosilyl compounds.

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Structure and Reactivity α,β-Unsaturated Ethers. II. Cationic Copolymerizations of Propenyl Isobutyl Ether*

T. OKUYAMA, T. FUENO,† AND J. FURUKAWA, *Department of Synthetic Chemistry, Kyoto University, Kyoto, Japan*

Synopsis

cis- and *trans*-Propenyl isobutyl ethers were copolymerized with each other and each with vinyl isobutyl ether separately under various conditions. In homogeneous polymerizations a *cis*-β-methyl substitution on vinyl isobutyl ether apparently enhanced the reactivity, whereas the *trans* substitution tended to reduce it slightly. In heterogeneous catalysis, on the other hand, a β-methyl group on the vinyl ether, whether *cis* or *trans*, greatly reduced the reactivity, probably because of the steric hindrance toward the adsorption of monomers on the catalyst surface. The relative reactivities of *cis*- and *trans*-propenyl isobutyl ethers ranged from 2 to 20, depending on the polymerization conditions. The polymer end formed from the *cis* monomer exhibited special steric effects. It was concluded that even in homogeneous media the rotation of the polymer end around the terminal carbon–carbon bond is restricted.

INTRODUCTION

It has been well known that α,β-disubstituted olefins are generally reluctant to add to themselves in free-radical polymerization. However, they are often brought into polymers of sufficiently high molecular weight by ionic mechanisms, particularly by cationic mechanism. This contrasting behavior in radical and ionic polymerizations might be attributed to the difference in stereochemistry for the transition state. β-Substituents on vinyl monomers largely restrict the geometry of the transition state of radical polymerization. Although an adverse steric effect of a β-substituent may be moderate in ionic polymerizations, the effect should practically appear also in these cases. Thus, an investigation of the effects of β-substitution and geometrical isomerism of monomers on the relative ionic polymerizabilities will be of great use in understanding the nature of the transition state of ionic polymerizations, especially of stereospecific polymerizations. Yet no investigations have been reported so far concerning such polymerizabilities, except for β-alkylstyrenes.[1,2]

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† Present address: Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan.

Heck and Breslow[3] and Natta et al.[4] have reported the stereospecific polymerization of propenyl ethers by a modified Ziegler-type catalyst and by diethylaluminum chloride, respectively. The former[3] noticed that the *cis* isomers were polymerized much more rapidly than the *trans* but did not undertake any further investigations.

In the present paper the *cis–trans* copolymerizations of propenyl isobutyl ether (PIBE) and the copolymerizations of PIBE with vinyl isobutyl ether (VIBE) were investigated under various cationic polymerization conditions, in order to examine the effects of geometrical isomerism as well as β-methyl substitution on the vinyl ether polymerization. In the succeeding paper of this series[5] we shall report the results of similar copolymerizations of various alkenyl ethers and deal primarily with the effects of the various alkyl substituents in comparison with the behavior of the β-methyl group studied here.

EXPERIMENTAL

Materials

cis- and *trans*-PIBE and VIBE were obtained as previously described[6] and distilled from lithium aluminum tetrahydride. Vapor-phase chromatography showed that isomeric purities of *cis*- and *trans*-PIBE used for polymerization were above 97.5 and 95.5%, respectively.

Methylene dichloride (CH_2Cl_2) and *n*-heptane were dried over calcium hydride and fractionally distilled. Nitroethane (NO_2Et) was dried over calcium chloride and distilled. The middle fraction was further dried over Drierite and fractionally distilled under dry nitrogen; b.p. 114°C. Toluene (PhMe), triethylaluminum ($AlEt_3$), and stannic chloride ($SnCl_4$) were purified in the manner as described previously.[7] Boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$) was commercially obtained and distilled immediately before use; b.p. 125.5°C.

Polymerization Technique

Polymerization was carried out in a 20 ml. flask with a filling tube having a side-arm for nitrogen inlet. Monomer solution containing a small amount of *n*-heptane as an internal standard was introduced into a flask and adjusted to the desired temperature. Catalyst solution was then added with shaking by means of a syringe, when the polymerization temperature was 0°C. In the low-temperature polymerization a 1 ml. ampule for catalyst solution was placed in a flask in advance, into which monomer and catalyst solutions were introduced. The flask was immersed in a Dry Ice–methanol bath. After the system reached thermal equilibrium, the ampule containing catalyst solution was broken with a glass rod, and the reaction was started. After standing for an appropriate time the reaction was stopped by adding a small amount of methanolic potassium hydroxide. Concentrations of initial total monomers and internal standard were 7 and 3 vol.-%, respectively; the catalyst concentrations arbitrarily chosen for various systems are given in Table I.

TABLE I

Monomer Reactivity Ratios in the Mutual Copolymerizations of *cis*- and *trans*-PIBE

Expt. no.	Polymerization condition Solvent	Catalyst	Catalyst concn., mmole/l.	Temp., °C.	Polymn. time, min.	No. of runs	r_c[a]	r_t[a]	$(r_c/r_t)^{1/2}$	r_cr_t
1	CH_2Cl_2	$BF_3 \cdot OEt_2$	3–5	−78	5–15	6	2.21 ± 0.02	0.46 ± 0.01	2.19	1.02
2	CH_2Cl_2	$BF_3 \cdot OEt_2$	0.15	0	1–6	7	1.85 ± 0.09	0.33 ± 0.03	2.37	0.61
3	PhMe	$BF_3 \cdot OEt_2$	3–5	−78	5–15	11	4.45 ± 0.53	0.25 ± 0.09	4.22	1.11
4	NO_2Et	$SnCl_4$	0.1	0	1–6	8	1.16 ± 0.03	0.59 ± 0.02	1.40	0.68
5	PhMe	$AlEt_3$–$SnCl_4$	3–7	−78	3–30	12	2.88 ± 0.33	0.27 ± 0.08	3.27	0.78
6	PhMe	$Al_2(SO_4)_3$–H_2SO_4	2–3 g./l.	0	50–200	7	5.94 ± 0.50	0.17 ± 0.06	5.91	1.01

[a] Uncertainties are the probable errors of independent runs.

Catalyst Preparations

The $AlEt_3$–$SnCl_4$ catalyst, in which the molar ratio of the two components was unity, was prepared in the same way as before.[7]

The $Al_2(SO_4)_3$–H_2SO_4 catalyst was prepared as follows.[8,9] Anhydrous aluminum sulfate was digested in concentrated sulfuric acid 5 times its volume and was maintained at 180°C. for 2 hr. After cooling dry ether was added, and the precipitate was filtrated, washed several times with dry ether under nitrogen, and dried *in vacuo*. The catalyst was used as a suspension in toluene.

Determination of Monomer Concentrations

The concentrations of the respective comonomers, both at the start of reaction and when reacted, were determined by vapor-phase chromatography. A Shimadzu gas chromatography, Model GC-2C, with a Disc chart integrator, Model 239, was used. It was found by calibration that the internal-standard method with integrated peak areas fully sufficed for determining the ether concentrations.

Calculations of Monomer Reactivity Ratios

The monomer reactivity ratios were calculated by use of the integral form of the Mayo-Lewis copolymerization equation. The lines of r_1 versus r_2 obtained from the equation converged reasonably, as is shown in Figure 1. A line obtained for each run was regarded as straight, $r_1 = mr_2 + b$, and the constants r_1 and r_2 (or r_c and r_t) were evaluated by least-squares treatments of the observed quantities m and b.

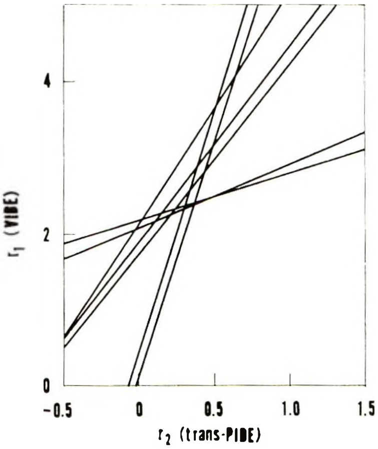

Fig. 1. Plots of r_1 versus r_2 for VIBE-*trans*-PIBE (M_1 and M_2, respectively) copolymerization in toluene with $BF_3 \cdot OEt_2$ at −78°C.

RESULTS

In the mutual copolymerization of *cis*- and *trans*-PIBE catalyzed by $BF_3 \cdot OEt_2$ in toluene at −78°C. the monomer consumptions obeyed the first-order decay law with respect to each monomer component separately, as is seen in Figure 2. From the slopes of the plots, *cis*-PIBE is about 4.2 times more reactive than *trans*-PIBE. Similar observations were made in CH_2Cl_2 by Higashimura et al.[10]

When one of the isomeric pairs of PIBE was polymerized, the other isomer was not found in the remaining monomer under any polymerization conditions studied here. This observation and the first-order consumption of monomer, described above, may be taken as evidence that neither isomer suffers geometrical isomerization during the course of polymerization.

The conversions of monomers estimated from the VPC analysis were in essential agreement with those obtained from the yield of the resulting copolymers. Besides, the copolymer yield of 100% was attainable after a sufficient time of reaction. These observations indicate that no appreciable side reaction was taking place during the polymerization. Thus, the monomer reactivity ratios calculated from the VPC analysis of remaining monomers were proved to be reliable.

Table I summarizes the results of the mutual copolymerizations of *cis*- and *trans*-PIBE under various polymerization conditions. The values of $(r_c/r_t)^{1/2}$ indicate average monomer reactivity ratios of *cis* to *trans* ethers. Table I shows that the *cis* isomer is the more reactive in all cases investigated.

In Table II the monomer reactivity ratios for the copolymerizations of VIBE (M_1) with *cis*- or *trans*-PIBE (M_2) are given. The monomer reactivities estimated from $1/r_1$ and r_2 values were higher for the *cis*-PIBE than for its trans isomer under all the conditions studied, regardless of the structure of attacking polymer ends. Except for case 6, in which the catalyst used was heterogeneous, *cis*-PIBE was more reactive than VIBE,

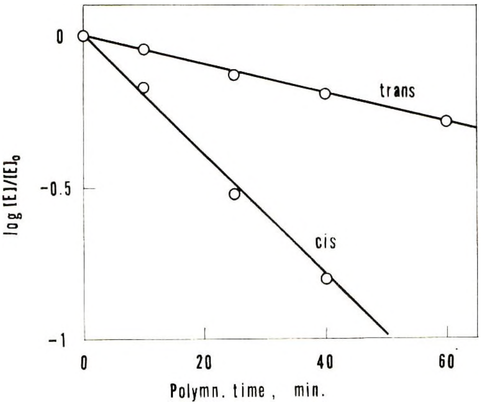

Fig. 2. First-order plots for the mutual copolymerization of *cis*- and *trans*-PIBE in toluene with $BF_3 \cdot OEt_2$ (2.5 mmoles/l.) at −78°C.

TABLE II

Monomer Reactivity Ratios in Copolymerizations of *cis*- or *trans*-PIBE (M_2) with VIBE (M_1)

	cis				*trans*			
Expt. no.[a]	No. of runs	r_1[b]	r_2[b]	r_1r_2	No. of runs	r_1[b]	r_2[b]	r_1r_2
1	8	0.29 ± 0.05	2.20 ± 0.14	0.64	5	1.04 ± 0.05	0.90 ± 0.03	0.94
2	9	0.29 ± 0.08	0.85 ± 0.12	0.25	8	1.05 ± 0.03	0.71 ± 0.02	0.75
3	7	0.18 ± 0.04	2.17 ± 0.09	0.39	7	2.64 ± 0.16	0.35 ± 0.04	0.92
4	7	0.44 ± 0.03	0.81 ± 0.03	0.36	7	0.96 ± 0.14	0.79 ± 0.06	0.76
5	6	0.13 ± 0.04	1.78 ± 0.08	0.23	5	1.67 ± 0.02	0.65 ± 0.01	1.09
6	7	1.56 ± 0.16	0.29 ± 0.05	0.45	8	31.4 ± 2.3	0.10 ± 0.04	3.1

[a] Numbers refer to the polymerization conditions shown in Table I.

[b] Uncertainties are the probable errors of independent runs.

and *trans*-PIBE showed much the same polymerizability as VIBE. In case 6 the β-methyl substitution reduced the polymerizability of VIBE considerably.

DISCUSSION

Effect of Geometrical Configurations on the Polymerizabilities

As has been described above, *cis*-PIBE is more reactive than *trans*-PIBE, regardless of the structure of attacking polymer chain end. The same order of reactivity was found in various related cationic reactions.[6,11,12] Moreover, *cis*-PIBE was proved to be thermochemically less stable than *trans*-PIBE by our separate experiments on isomerization equilibrium.[13] Thus, the reactivity differences given above are qualitatively in accord with those to be expected from the relative stabilities of the ground states, even though the stability difference of the transition states, which is another contributing factor to the reactivity, was clearly discerned, as will be shown later.

The difference in polymerizabilities seems to be larger in less polar solvents. The temperature dependence of the relative monomer reactivities is very small except for those toward the polymer end derived from *cis* monomer.

Effect of β-Methyl Substitution

The reactivity increase by the β-methyl substitution on VIBE observed in homogeneous catalysis may be understandable from the viewpoint of the electronic state of the monomers, as will be discussed in a succeeding contribution.[12] A β-methyl group exerts little adverse steric effect on the vinyl ether polymerization in homogeneous medium.

In contrast to the above results, the β-methyl substitution remarkably reduced the polymerizability of VIBE when a heterogeneous catalyst, $Al_2(SO_4)_3$–H_2SO_4, was used. This might have been caused by large steric hindrance of a β-methyl group, probably exerted when the monomer was adsorbed on the catalyst surface before or during the attack of a polymer end. This type of steric effect was observed in the complexation of alkenyl ethers with the silver ion.[11,12]

Abnormal Steric Effect Caused by *cis* Cation in Homogeneous Polymerization

In the copolymerizations of *cis*-PIBE with VIBE the products r_1r_2 are apparently less than unity, while the products are close to unity for *trans*-PIBE–VIBE copolymerizations in the homogeneous media. A similar tendency was observed also for cationic polymerizations of various alkenyl ethers.[5] In the *cis*-PIBE–VIBE copolymerizations r_2 varies remarkably with temperature; i.e., $r_2 \approx 2$ at -78°C. and $r_2 \approx 0.8$ at 0°C., although the variation in r_1 is very small. In the mutual copolymerizations of *cis* and *trans* isomers the $r_c r_t$ products are less than unity at 0°C., though the values are nearly equal to unity at −78°C. These observations imply that the propagating polymer end units derived from *cis* and *trans* monomers are different in structure. That is, the rotation of the end units around the carbon–carbon bond is restricted. The transition states may also be different in the reactions of *cis* and *trans* monomers. The end unit derived from the *cis* monomer appears to exert a special steric effect. Perhaps it is this steric effect that reduces the tendency to self-addition of cis monomer ($r_1 r_2 < 1$). Because the effect is more marked at higher temperatures (cf. Nos. 1 and 2 in Table II), it must be concluded that the effect is entropy-controlled in the temperature range studied here.

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Structure and Reactivity of α,β-Unsaturated Ethers. III. Cationic Copolymerizations of Alkenyl Alkyl Ethers

T. OKUYAMA, T. FUENO,* J. FURUKAWA, and K. UYEO,
Department of Synthetic Chemistry, Kyoto University, Kyoto, Japan

Synopsis

The relative cationic polymerizabilities of the geometrical isomers of various alkenyl alkyl ethers were studied both in copolymerizations with each other and in their respective copolymerizations with vinyl isobutyl ether as standard. Copolymerizations were carried out in methylene dichloride at −78°C. with boron trifluoride etherate as catalyst. The *cis* isomers have been found to be more reactive than the corresponding *trans* isomers. A primary alkyl substituent on the β-*cis* position of vinyl ethyl ether enhances the reactivity. Yet the steric effect is noticeable when the substituents are bulky. Compounds substituted with *cis*-β-isobutyl and with β-dimethyl showed little tendency to homopolymerization. It was proved that the polymer ends derived from *cis* and from *trans* monomers are respectively different in character because of the restricted rotation of the end unit around the terminal carbon–carbon bond. The alternation tendency, remarkable in the copolymerization of *cis* monomers with vinyl ether, was explained in terms of the *cis*-opening mechanism.

INTRODUCTION

Alkenyl alkyl ethers are easily polymerized by a cationic mechanism. Although several investigations concerning the polymerization of propenyl alkyl ethers have been reported from the viewpoints of the stereospecificity[1-4] and the relative polymerizability,[5,6] other alkenyl ethers than propenyl ethers have not been reported on, except that Natta et al.[4] referred to the formation of poly(*trans*-1-butenyl ethyl ether).

In the preceding paper[5] of this series the effect of β-methyl substitution on the cationic polymerization of vinyl isobutyl ether (VIBE) was investigated under various polymerization conditions. The *cis* isomer was found to be the more reactive in all cases. It was shown that a β-methyl group on VIBE increases its polymerizability in homogeneous catalysis, while it reduces the polymerizability in heterogeneous catalysis. A remarkable alternating tendency was observed in the copolymerization of the *cis* ether with vinyl ether.

In the present paper geometrical isomers of various alkenyl alkyl ethers

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* Present address: Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan.

were copolymerized both with each other and each with VIBE separately, with boron trifluoride etherate ($BF_3 \cdot OEt_2$) at −78°C., and the effects of substituents, both β-alkyl and α-alkoxyl, on the relative polymerizabilities were investigated. As the substituents become bulkier, the steric effect became more appreciable, and in some cases an adverse steric effect of polymer end apparently overshadowed the electronic effect of substituents on the monomer reactivity. It was also confirmed that bond rotation in polymer end units is restricted.[5]

EXPERIMENTAL

Materials

All the alkenyl ethyl ethers were prepared in the way described previously.[7] Vinyl, propenyl, and 1-butenyl isopropyl ethers were prepared by pyrolyses of the appropriate acetals:[7]

Vinyl isopropyl ether: b.p. 55°C., n_D^{25} 1.3812.

cis-Propenyl isopropyl ether (isomeric purity 98.5%): b.p. 81–82°C., n_D^{25} 1.3956.

trans-Propenyl isopropyl ether (isomeric purity 96.5%): b.p. 91–92°C., n_D^{25} 1.3988.

cis-1-Butenyl isopropyl ether (isomeric purity 99.2%): b.p. 105–106°C., n_D^{25} 1.4035.

trans-1-butenyl isopropyl ether (isomeric purity 98.4%): b.p. 116–117°C., n_D^{25} 1.4071.

The ethyl and isobutyl vinyl ethers were commercially obtained. All the monomers were distilled from lithium aluminum hydride immediately before use, and their purities were checked by vapor-phase chromatography.

Methylene chloride, toluene, *n*-heptane, and $BF_3 \cdot OEt_2$ were purified as before.[5]

Procedure

Both the polymerization procedure and the method of calculation of the monomer reactivity ratios were identical with those described previously.[5]

RESULTS

During the polymerization of one of any isomeric pair studied here the other isomer was not found in the reaction mixture containing unreacted monomer. This indicates that neither *cis* nor *trans* ether isomerizes into the other during the polymerization, in agreement with the results found for the case of propenyl isobutyl ether.[5]

Table I summarizes the monomer reactivity ratios r_c and r_t, obtained in the copolymerizations of *cis* and *trans* isomer pairs with each other. The values of $(r_c/r_t)^{1/2}$ indicate the relative polymerizabilities of the *cis* and *trans* ethers. It may be noted that *cis* isomers are more reactive than *trans* for all the ethers except 4-methyl-1-pentenyl ethyl ether (No. 7 in Table I).

TABLE I

Mutual Copolymerization of *cis*- and *trans*-Alkenyl Alkyl Ethers[a]

No.[b]	Cat. concn., mmole/l.	Polymn. time, min.	No. of runs	r_c[c]	r_t[c]	$(r_c/r_t)^{1/2}$	$r_c r_t$
2	5–10	2–7	9	1.37 ± 0.29	0.72 ± 0.16	1.38	0.99
3	25	10–20	7	1.23 ± 0.06	0.92 ± 0.04	1.16	1.13
4	25	60–120	11	1.76 ± 0.08	0.23 ± 0.01	2.77	0.40
6[d]	25	10–15	9	1.16 ± 0.05	0.88 ± 0.03	1.15	1.02
7	25	15–50	7	0.46 ± 0.15	0.74 ± 0.07	0.81	0.36
9	5	4–10	7	2.04 ± 0.05	0.48 ± 0.02	2.06	0.98
10[d]	5	60–120	9	1.18 ± 0.05	0.49 ± 0.02	1.55	0.58

[a] Polymerization was carried out in CH_2Cl_2 at −78°C. with $BF_3 \cdot OEt_2$ as catalyst; *n*-heptane was used as internal standard unless otherwise noted.

[b] For substituents R_1 and R_2 see Table II.

[c] Uncertainties are the probable errors of independent runs.

[d] Toluene was used as internal standard.

TABLE II

Copolymerization of Alkenyl Ethers, $R_1CH{=}CHOR_2$ (M_2) and VIBE (M_1)[a]

No.[b]	R_1	R_2	Cat. concn., mmole/l.	Polymn. time, min.	No. of runs	r_1[c]	r_2[c]	$1/r_1$	r_1r_2
1	H	C_2H_5	3	1.5–3	5	0.92 ± 0.02	1.30 ± 0.02	1.09	1.20
2c	CH_3	"	5	0.5–1	6	0.23 ± 0.07	2.25 ± 0.10	4.35	0.52
2t	CH_3	"	5	0.5–1	7	0.56 ± 0.03	1.44 ± 0.02	1.79	0.81
3c	C_2H_5	"	12	15–30	7	0.26 ± 0.04	0.81 ± 0.03	3.85	0.21
3t	C_2H_5	"	12	10–20	6	0.68 ± 0.03	1.54 ± 0.14	1.47	1.05
4c	i-C_3H_7	"	5	10–30	6	1.71 ± 0.20	0.09 ± 0.04	0.58	0.15
4t	i-C_3H_7	"	5	30–100	5	14.44 ± 0.21	0.09 ± 0.01	0.07	1.30
5t	t-C_4H_9	"	10	10–20	7	ca. 100	ca. 0.01	ca. 0.01	
6c[d]	n-C_5H_{11}	"	5	30–100	7	0.17 ± 0.05	0.46 ± 0.05	5.88	0.08
6t[d]	n-C_5H_{11}	"	5	30–90	6	2.10 ± 0.21	0.59 ± 0.09	0.48	1.24
7c	i-C_4H_9	"	10	30–50	7	0.20 ± 0.10	0.032 ± 0.038	5.00	0.01
7t	i-C_4H_9	"	10	20–40	9	2.48 ± 0.10	0.33 ± 0.03	0.40	0.82
8	H	i-C_3H_7	5	3–5	4	0.22 ± 0.03	2.70 ± 0.11	4.55	0.81
9t	CH_3	i-C_3H_7	5	8–10	6	0.18 ± 0.08	2.37 ± 0.19	5.56	0.43
10c[d]	C_2H_5	i-C_3H_7	5	10–60	10	0.32 ± 0.05	0.93 ± 0.06	3.13	0.30
10t[d]	C_2H_5	i-C_3H_7	5	20–60	9	0.50 ± 0.06	0.90 ± 0.05	2.00	0.45
11[e]	$(CH_3)_2$	C_2H_5	12	3–10	8	1.48 ± 0.03	0.00 ± 0.01	0.68	0.00

[a] Polymerization condition: solvent, CH_2Cl_2; temp., −78°C.; catalyst, $BF_3\cdot OEt_2$. As internal standard n-heptane was used unless otherwise noted.

[b] The suffixes *c* and *t* refer to *cis* and *trans*, respectively.

[c] Uncertainties are the probable errors of independent runs.

[d] Toluene was used as internal standard.

[e] Isobutenyl ethyl ether.

In Table II the results of copolymerizations of various alkenyl alkyl ethers (M_2) with VIBE (M_1) are given. The values of $1/r_1$ stand for the reactivities of the various alkenyl ethers relative to VIBE toward the polymer end cation formed from VIBE. For all the ethers studied here the *cis* isomers are more reactive toward the VIBE cation than are the *trans*. The *cis* alkenyl ethyl ethers bearing a primary alkyl group on their β carbon are several times more reactive than the parent vinyl ether.

DISCUSSION

Effects of Geometrical Isomerism

The *cis*-alkenyl alkyl ethers were more reactive than the *trans* isomers in the cationic polymerization. One unusual result was obtained in the copolymerization of the isomers of 4-methyl-1-pentenyl ethyl ethers (No. 7) where the values of r_c and r_t were both less than unity. In this particular case, however, the r_c value is smaller than the r_t, so that the *cis* isomer appears to be less reactive than the *trans:* $(r_c/r_t)^{1/2} < 1$. On the other hand, the respective copolymerizations of the isomeric ethers (No. 7) with VIBE show that the *cis* isomer is the more reactive to the VIBE end. When the *cis* isomer of this compound was copolymerized with VIBE, the product r_1r_2 was remarkably small, and the *cis* monomer hardly showed a tendency to self-addition ($r_2 \ll 1$). That is, the corresponding rate constant k_{cc} might be unusually small. In other words, the reactivity of the *cis* monomer toward the polymer end arising from the *cis* monomer is unusually small. Hence, the monomer reactivity should be discussed for the polymer end formed from a pertinent monomer unit other than the *cis* monomer. Probably the value of r_t or $1/r_1$ will provide a better criterion of the relative reactivities of the *cis* and *trans* ethers (No. 7) than does the value of $(r_c/r_t)^{1/2}$. If this is true, the *cis* monomer must be judged to be more reactive than the *trans*.

As has been reported previously,[7] *cis*-alkenyl alkyl ethers are more vulnerable to acid-catalyzed hydrolysis than their *trans* isomers.[7] Moreover, it was elucidated that alkenyl ethers are thermochemically less stable in the *cis* configuration than in the *trans*.[8] One of the origins of the reactivity difference might be the difference in stability of the ground state of the ethers.

Although the effect of substituents upon the relative reactivities of *cis* and *trans* monomers in the *cis–trans* copolymerizations does not seem to be simply explained, the relative *cis–trans* reactivities judged from $1/r_1$ (reactivities to VIBE end) are roughly parallel to the bulkiness of the β-alkyl groups.

Effect of β-Substituents

β-Monomethyl substitution (No. 2) on ethyl vinyl ether enhances its reactivity by factors of 4 and 1.6 for the *cis* and *trans* placements, respectively. A similar trend is seen with β-ethyl substitution (No. 3). Thus, a β-methyl or β-ethyl group exerts little adverse steric effect on the polymerization of ethyl vinyl ether. For isopropyl vinyl ether the β-ethyl substitution (No. 10) reduces the reactivity, although the effect of methyl substitution (No. 9) remains the same as in the case of propenyl ethyl ether (No. 2).

When the β substituent is a bulkier primary alkyl group in ethyl ethers (Nos. 6 and 7), the *cis* ether is more reactive than the *trans*, the latter being less reactive than the parent ethyl vinyl ether. As a β-alkyl group becomes secondary (No. 4) and tertiary (No. 5), the monomer reactivity is reduced remarkably.

Dimethyl substitution (No. 11) on the β carbon of vinyl ether reduces the reactivity considerably. It will be worth noting that isobutenyl ethyl ether (No. 11), the disubstituted, hardly undergoes homopolymerization ($r_2 = 0$), even though its reactivity to the VIBE end is only moderately lower than that of vinyl ethyl ether ($r_1 = 1.48$). This is understandable again in terms of the steric hindrance that may accompany the attack of carbonium ions on the isobutenyl ether.

Effect of Alkoxyl Groups

In the present study several alkenyl isopropyl ethers were investigated besides ethyl ethers. Isopropyl ethers were several times more reactive than ethyl ethers both for vinyl and propenyl homologues. This trend of reactivities has already been observed in the vinyl ether polymerizations.[9] However, ethyl (No. 3) and isopropyl (No. 10) 1-butenyl ethers showed practically the same reactivity to the VIBE cation, as is seen in Table II. An adverse steric effect might appear for the isopropyl ether. The steric effect of the isopropoxyl group is apparent in the copolymerizations of VIBE–*trans*-ether pairs (Nos. 9t and 10t), where the product r_1r_2 is remarkably small compared with those of ethyl ethers (Nos. 2t and 3t).

In the copolymerization of isomers of ethers the values of $(r_c/r_t)^{1/2}$ were larger in isopropyl (Nos. 9 and 10) than in ethyl ethers (Nos. 2 and 3) for both propenyl and 1-butenyl compounds.

Restricted Rotation in Polymer End Units

The data listed in Table I indicate that the products r_cr_t are practically equal to unity when the bulkiness of the substituents R_1 and R_2, is relatively small, whereas they become sensibly less than unity as the branching of the alkyl substituents develops. Thus, in the latter cases the chain-end carbonium ions formed on additions of *cis* and *trans* ethers must be different in structure, as has been concluded previously for the polymerization of propenyl isobutyl ether.[5] When the substituents become considerably bulky, this difference is reflected in the selectivities toward the isomeric monomer pairs. Rotation of the end unit around its carbon–carbon bond is restricted and, hence, the polymer end is not entirely free even in homogeneous cationic polymerizations.

TABLE III
Relation Between Taft's Steric Substituent Constants E_s of R_1 and the Products r_1r_2 for VIBE–*cis*-$R_1CH{=}CHOC_2H_5$ Copolymerizations

No.	R_1	E_s	r_1r_2
1	H	1.24	1.20
2	CH_3	0	0.52
3	C_2H_5	−0.07	0.21
6	n-C_5H_{11}	−0.40	0.08
4	i-C_3H_7	−0.47	0.15
7	i-C_4H_9	−0.93	0.01

Inspection of the data listed in Table II shows that in the series of ethyl ethers the products r_1r_2 are considerably less than unity for the *cis* monomers, while they are close to unity for the *trans* isomers. This is indicative of a distinction in character between the *cis* and *trans* chain ends, lending support to the view that rotation of the chain end units must be restricted.

The observed alternating tendency in copolymerizations of the *cis* monomers with VIBE may be ascribed to a special geometrical factor involved in the chain propagation step. The r_1r_2 values for the *cis* ethyl ethers are inversely correlated to Taft's steric substituent constants E_s of β-alkyl groups,[10] as is shown in Table III. The steric effects of polymer ends derived from *cis* monomers are apparently dependent on the bulkiness of β substituents. The steric interaction of the β-substituent on the polymer end with catalyst and monomer can be larger for the *cis* cation than for the *trans* cation in the *cis*-opening mechanism, since the catalyst may have a certain interaction with the alkoxyl oxygen atom of the polymer end. In the *trans*-opening mechanism, on the contrary, the β substituent on the polymer end seems to be too far apart from the catalyst to affect the stereochemistry of the polymerization. Thus, the steric effect of polymer end structure seems to be explainable more satisfactorily in terms of the mechanism involving a *cis* opening of the monomer double bond.

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Preparation of Ion-Selective Membranes from Crosslinked Copolymers of Styrene and *p*-Vinylbenzenesulfonic Acid

T. G. BRYDGES,* D. G. DAWSON, and J. W. LORIMER,
Department of Chemistry, University of Western Ontario, London, Ontario, Canada

Synopsis

Ion-selective membranes similar to those described by Graydon and Stewart [*J. Phys. Chem.* **59,** 86 (1955)] were prepared by improved methods involving copolymerization of styrene, *n*-propyl-*p*-vinylbenzenesulfonate, and divinylbenzene (DVB) with subsequent hydrolysis of the ester. Both the highly reactive ester and DVB were purified by column chromatography and were well characterized by their infrared and proton magnetic resonance spectra. For preparation of membranes about 25% by weight of *N,N*-dimethylformamide (DMF) was included with the vinyl monomers in the polymerization mixture. Thermal polymerization was initiated by benzoyl peroxide, and membranes were formed in special molds of two types. In one type a free surface of the mixture was exposed, while in the other the mixture filled the mold. The DMF in the fresh membranes was replaced with aqueous KOH by diffusion, and hydrolysis was then carried out. By this method hydrolysis times were decreased from several days to a few hours. Capacity, water content, and thickness were determined for all membranes, and density, swelling in salt solutions, and Young's modulus were measured for selected membranes. The Vermaas-Hermans-Flory theory of polyelectrolyte gels was found to account satisfactorily for the swelling properties and water content of these membranes, the solvent interaction parameter χ_1 increasing with increasing volume fraction of polymer from 0.7 to 1.0 at zero external salt concentration and up to 1.8 for membranes deswollen in 1*M* KCl. No differences in average water contents for given densities of fixed charge and crosslinking were observed with (*1*) different molds, (*2*) commercial or pure DVB, and (*3*) a swelling agent (DMF) or no swelling agent. The results in general indicate that the state of the membrane at a given temperature and pressure can be specified by any two of the parameters: degree of ionization per unit volume of an average structural unit, concentration of crosslinking agent, and degree of swelling. Young's modulus decreased markedly with increasing water content, but data were not sufficiently extensive or precise to permit a quantitative treatment.

INTRODUCTION

Fundamental studies of the interaction and transport of ions and neutral molecules in ion-selective membranes require, ideally, membranes which satisfy a formidable number of requirements. The membranes should be homogeneous (no binder present),[1] with well-defined and reproducible compositions that can be varied with respect to charge, crosslinking, and

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* Present address: Ontario Water Resources Commission, Toronto, Canada.

water content over wide ranges. Preferably only one type of exchangeable, charged group should be present. The mechanical properties should include availability in various forms (sheets, rods, tubes, of various dimensions), high flexibility, and strength, and freedom from defects such as bubbles and cracks. Physicochemical properties should include isotropy, rapid establishment of swelling equilibrium without stress cracking, and stability with respect to decomposition in a variety of solvents and over a wide temperature range.

Of the large number of types of ion-selective membranes that have been prepared[2] only a few satisfy a significant number of these requirements. One of these types has been described by Graydon and his co-workers[3–10] and is prepared by the copolymerization of styrene, various esters of *p*-vinylbenzenesulfonic acid, and divinylbenzene, with subsequent hydrolysis of the ester. Although the value of these membranes has been recognized, it has been claimed that their preparation "requires some details which are not given in the literature and without which the attempts to prepare the membranes prove unsuccessful."[2] While we do not agree that the published directions preclude successful preparation of membranes, we do find that several significant improvements in these directions can be made.

This paper describes (*a*) new data on the preparation, purification, and characterization of *n*-propyl-*p*-vinylbenzenesulfonic acid, (*b*) new methods of preparing membranes, which result in more rapid hydrolysis of the ester and more uniform, flexible membranes, and (*c*) data on, and interpretation of, capacity, water content, swelling, and elastic modulus of these membranes.

EXPERIMENTAL

Preparation and Characterization of Monomers

The general procedures were the following.

Melting points: Hoover capillary apparatus (A. H. Thomas Co.), corrected.

Infrared spectra: Beckman IR-5A spectrometer with NaCl prism and cell windows for the 2–16 μ range and CsBr prism and 0.05 mm. polyethylene windows for the 11–35 μ range.

Proton nuclear magnetic resonance spectra: Varian A-60 60 Mc./sec. spectrometer, with $CDCl_3$ solutions. Chemical shifts are given in parts per million (δ) from the tetramethylsilane (TMS) reference.

Column chromatography: alumina (acid form, anionotropic), volume 4–5 times the sample volume, in columns 30–40 cm. long and 1–2 cm. in diameter, with benzene as eluant.

Elemental analyses: Organic Microanalyses, Dr. C. Daesslé, Montreal, Quebec.

***p*-(β-Bromoethyl)benzenesulfonyl Chloride.** This compound was prepared by the method of Spinner et al.,[3] except that recrystallization was from ether only; m.p. 53–55°C. (lit.[3] 54–55°C.); yield (purified) 13%.

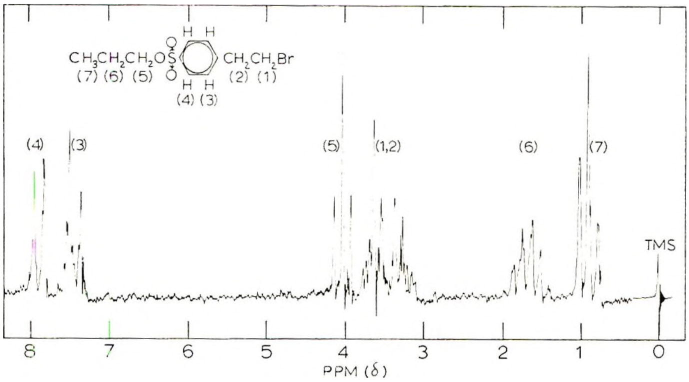

Fig. 1. 60 Mc./sec. NMR spectrum of *n*-propyl-*p*-(β-bromoethyl)benzenesulfonate. Sweep offset 0 cps, sweep width 500 cps, sweep time 250 sec.

Recrystallization from methanol[3] gave an amorphous product. The presence of only the *para* isomer was established by preparation of *p*-(β-bromoethyl)benzenesulfonamide, m.p. 182–185°C. (lit.[11] 185.5–186°C.), and by the NMR spectrum, which is almost identical with that shown in Figure 1 for hydrogens 1, 2, 3, and 4. Hydrogens 1 and 2 comprise an A_2B_2 system centered on 3.48 δ (cf.[12] spectrum 529), whereas hydrogens 3 and 4 comprise an A_2X_2 system with chemical shifts (estimated by treating the spectrum as two AB systems[13]) of 7.51 δ for hydrogens 3 and 8.03 δ for hydrogens 4 (cf.[12] spectra 196, 495). *Ortho* substitution would give a more complex spectrum (cf.[12] spectrum 195), of which no trace was found. The infrared spectrum between 2 and 16 μ (2% in $CHCl_3$), Figure 2, curve (*a*) is almost identical with the published spectrum of benzenesulfonyl chloride,[14] while between 11 and 35 μ (dispersed in Nujol), Figure 2, curve (*b*), the S—Cl and C—Br stretching frequencies at 373 and 635 cm.$^{-1}$, respectively,[15,16] are observed.

***n*-Propyl-*p*-(β-bromoethyl)benzenesulfonate.** This compound was prepared as described previously,[3] except that purification was by column chromatography; yield (purified) 40%, n_{D}^{25} = 1.5388 (lit.[4] 1.5442), d_{25}^{25} = 1.43 (lit.[4] 1.385). The NMR spectrum (Fig. 1) has absorptions assigned as indicated and chemical shifts centered on 3.47 δ for hydrogens 1 and 2, on 7.45 δ for hydrogens 3, on 7.89 δ for hydrogens 4, on 4.04 δ for the triplet due to α-methylene hydrogens, on 1.68 δ for the β-methylene hydrogens, and on 0.89 δ for the triplet due to the methyl hydrogens (cf.[12] spectra 42, 43). The infrared spectrum between 2 and 16 μ (2% in $CHCl_3$), Figure 2, curve (*c*) is similar to that of the sulfonyl chloride with the broad SO—C frequency[14] at 950 cm.$^{-1}$ superposed. Between 11 and 35 μ (sample spread in a thin layer), Figure 2, curve (*d*) the S—Cl stretching frequency[15] at 373 cm.$^{-1}$ is absent.

Purification of this compound by molecular distillation[3] was also attempted. A still with 60 mm. path and 65 mm. diameter (Fisher Scientific No. 9-124) failed to give any distillate in 24 hr. under a backing pressure of

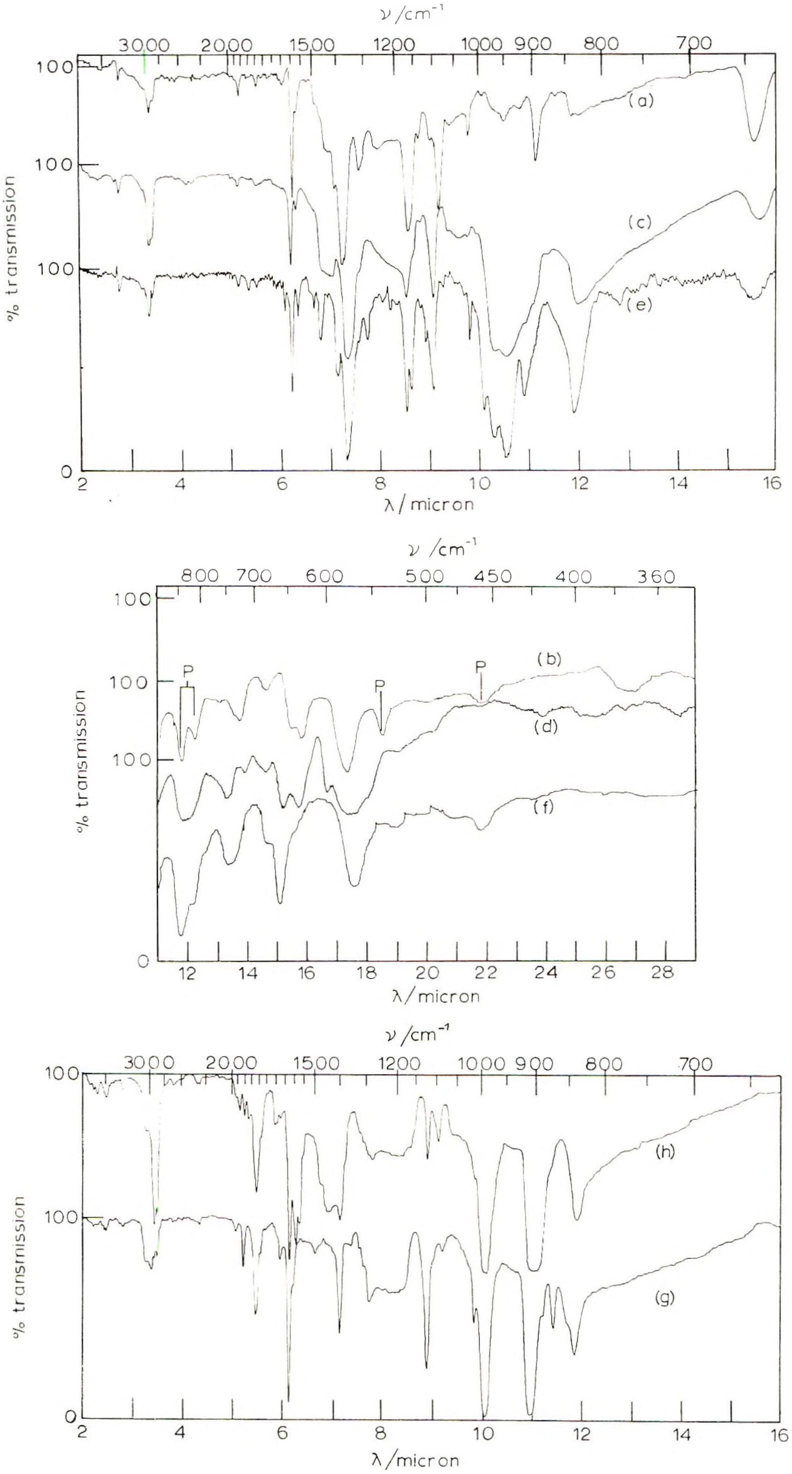

Fig. 2. Infrared spectra (*P* indicates absorption due to polyethylene cell window): (*a*, *b*) *p*-(β-bromoethyl)benzenesulfonyl chloride; (*c*, *d*), *n*-propyl-*p*-(β-bromoethyl)-benzenesulfonate; (*e*, *f*) *n*-propyl-*p*-vinylbenzenesulfonate; (*g*) *p*-divinylbenzene; (*h*) commercial DVB.

TABLE I
Properties of *n*-Propyl-*p*-vinylbenzenesulfonate

Preparation	Elemental analyses, %				d_{25}^{25}	n_D^{25}
	C	H	O	S		
1	58.90	6.16	21.57	13.92	1.153	1.5442
2	58.40	6.00	21.34	14.00	1.145	1.5384
3	—	—	—	—		
				chromatography	1.150	1.5384
				distillation	1.145	1.5377
Spinner et al.[3]	58.07 ± 0.03	6.33 ± 0.07	(21.39)[a]	14.21 ± 0.06	1.165	1.5374
Theoretical for $C_{11}H_{14}O_3S$	58.38	6.24	21.21	14.17		

[a] By difference; other values by direct analysis.

10^{-4} torr and a temperature difference of 60°C. A second still (Kontes Glass Co., Model K 28460) with 22 mm. path and 30 mm. diameter gave 1 ml. of distillate over five days under the same conditions; $n_D^{25} = 1.5380$, $d_{25}^{25} = 1.40$.

***n*-Propyl-*p*-vinylbenzenesulfonate.** A higher concentration of KOH than that reported[3] was found necessary to debrominate the bromoethyl ester completely. Bromoethyl ester, 55 ml., and 4-*tert*-butylpyrocatechol stabilizer, 0.5 g., in ethanol, 100 ml., were mixed at 50°C. with KOH, 30 g. in 100 ml. of ethanol. The mixture was boiled and after being stirred for 1 min. was quenched with 200 ml. of ice water, cooled to 0°C., extracted with ether, dried, and purified by column chromatography; yield (purified) 42%. Qualitative halogen tests were negative, and colorimetric bromine analysis[17] indicated the presence of less than 0.1 mole-% of bromoethyl ester. The saponification number was 99.1%. Analyses and properties of three samples are given in Table I. A trace of 4-*tert*-butylpyrocatechol was added, and the product was stored at 0°C.

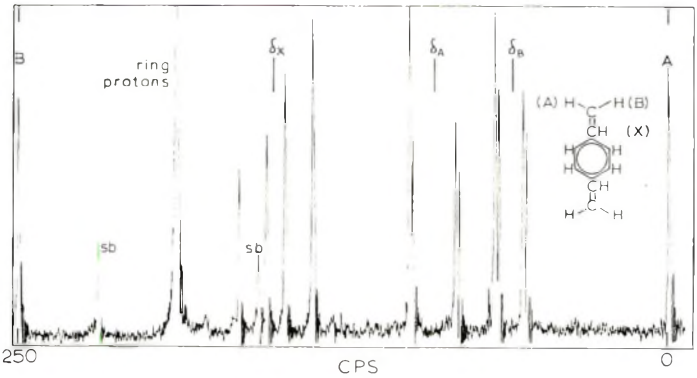

Fig. 3. Mc./sec. 60 spectrum of *p*-divinylbenzene. Sweep offset 250 cps, sweep width 250 cps between the two audio sidebands A and B, sweep time 250 sec.

The infrared spectrum between 2 and 16 μ (1.3% in $CHCl_3$), Figure 2, curve (*e*) is similar to that of the bromoethyl ester, with the addition of vinyl absorptions[16] at 918, 990, and 1400 cm.$^{-1}$, while between 11 and 35 μ (sample spread in a thin layer), Figure 2, curve (*f*) the C—Br frequency at 635 cm.$^{-1}$ is absent.

Purification by molecular distillation was reported to be successful only in a still of special design.[18] Distillation as described above was indeed unsuccessful, but a still similar to that in Figure 7 of Hickman and Sandford,[19] which had a diameter of 65 mm. and a path of 30 mm., gave 1.5 ml. of distillate in 24 hr. under a backing pressure of 10^{-4} torr and a temperature difference of 30°C. Stabilizer was necessary to hinder polymerization at the distillation temperature, 40°C.

Membranes prepared from distilled ester were lemon-yellow in color, presumably because of decomposition products of the stabilizer.

p-Divinylbenzene (DVB). This compound was isolated from commercial divinylbenzene (Monomer-Polymer Laboratories; analysis, 51.7% divinylbenzene, 43.3% ethylvinylbenzene, 3.4% diethylbenzene) as described by Storey[20] but was purified by column chromatography. It could be stored as a solid at 0°C. without stabilizer.

Purity checks by gas chromatography[20] were unsuccessful, presumably because of rapid polymerization on the column. The NMR spectrum (Fig. 3) shows the ring proton absorption at 7.31 δ, with spin sidebands at 6.79 and 7.82 δ. The remainder of the spectrum is a twelve-line ABX spectrum (protons 1, 2, and 3, respectively), which has been investigated recently.[21] The three chemical shifts obtained from the midpoints of the three groups of bands in the spectrum are $\delta_A = 5.69$, $\delta_B = 5.20$, and $\delta_X = 6.68$, in good agreement with the values 5.70, 5.19, and 6.66 δ obtained by computer analysis.[21] No trace of absorptions due to ethyl protons was observed. The infrared spectrum between 2 and 16 μ (1% in $CHCl_3$), Figure 2, curve (*g*) shows vinyl absorptions[16] at 912, 995, and 1400 cm.$^{-1}$ and *para*-substituted ring absorption[16] at 843 cm.$^{-1}$. For comparison, the spectrum of commercial DVB is shown in Figure 2, curve (*h*).

Preparation and Properties of Membranes

Membrane Casting Molds. Type I (free surface) molds were made by sealing a glass cylinder 6 mm. high and cut from 70 mm. tubing to a 6-mm. glass plate with epoxy cement. The mold was closed by a cover consisting of a layer of aluminum foil, a rubber pad, and a second glass plate. The whole assembly was clamped between two 6-mm. metal plates by means of screws and could be leveled accurately. The foil provided a warm surface that prevented condensation of the monomers.

Type II (closed) molds consisted of two Teflon sheets 1.5 mm. thick, between which Teflon sheets of the required thickness, each with a hole 60 mm. in diameter, could be placed. The three sheets were clamped between two 6-mm. aluminum plates by means of screws. Two small holes were drilled through the edge of the center Teflon sheet with an 18-gage hypodermic needle. Two needles, one for filling and one for escape of air, were placed in these holes.

Monomer Charges and Polymerization. The polymerization mixture consisted of styrene, commercial or pure (DVB), vinyl ester, and *N,N*-dimethylformamide (DMF) in the amounts given in Table II, plus 40 mg. of benzoyl peroxide. The charges were prepared by weighing into a stoppered tube and were transferred to the mold by means of a hypodermic syringe. Gravimetric checks on material balances were carried out. Polymerization was carried out by heating a 110°C. for 1 hr. in a forced-convection oven and then cooling the mold and contents to room temperature.

Type I molds were accurately leveled before polymerization was started. Type II molds were filled completely except for a small air bubble that allowed expansion and contraction in the mold. The filling needles were

TABLE II
Composition and Properties of Membranes[a]

Membrane no.	Composition of polymerization mixture, g. Styrene	*n*-Propyl-vinylbenzene-sulfonate	DVB	DMF	DVB,[b] mole-%	Capacity X, meq. per g. dry H-form	Water content $\bar{w}$, g. per g. dry H-form	Thickness, mm.
1	7.2586	4.5947	0.4683	2.8313	1.99	1.72	0.856	1.65
2	"	"	"	"	"	1.63	0.711	0.43
3	"	"	"	"	"	1.70	0.704	0.71
4	"	"	"	"	"	1.68	0.924	1.12
5	8.1575	3.4608	0.4689	2.8585	1.92	1.25	0.421	0.56
6	"	"	"	"	"	1.25	0.578	1.02
7	"	"	"	"	"	1.28	0.621	1.65
8	1.0175	0.8410	0.2272	0.4173	5.96	1.74	0.500	0.53
9	1.1259	0.8412	0.0843	0.4200	2.21	1.77	0.788	0.57
10	0.7910	1.1810	0.2329	0.4273	6.37	2.39	0.755	0.58
11	0.8905	1.1827	0.0884	0.3670	2.44	2.47	1.36	0.81
12	1.0745	1.3730	0.1082	0.5798	2.50	2.24	0.710	0.76
13	0.9268	1.1829	0.0546	0.2794	1.49	2.30	0.826	0.56
14	0.9079	1.1811	0.0640	0.2909	1.76	2.51	1.83	0.69
15	1.0659	1.4987	0.1046	0.5604	4.55	2.57	1.28	1.03
16	1.1911	0.8367	0.0591	0.4127	2.91	1.77	0.613	0.64
A1	3.2227	0.9947	0.2218	1.2110	2.38	1.14	0.372	1.24
A2	2.2519	1.8731	0.2148	1.2219	2.71	1.73	0.885	1.47
A3	1.5864	2.5781	0.2213	1.1950	3.11	2.72	1.72	1.61
A4	0.8873	3.2705	0.1965	1.1593	3.20	3.59	3.42	—

[a] Membranes 1–16 made in free surface (Type I) molds; membranes A1–A4 made in closed (Type II) molds. DVB refers to a commercial sample containing 51.7% divinylbenzene, except for membranes 15 and 16, which were made with pure *p*-divinylbenzene.

[b] Number of moles of DVB per 100 moles of vinyl monomers.

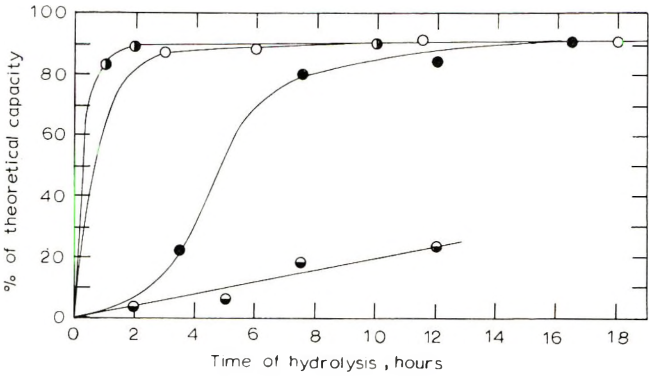

Fig. 4. Rate of hydrolysis of membranes. Composition of polymerization mixture: 0.30 g. of DMF, 0.061 g. of DVB (commercial), 1.15 g. of styrene plus vinyl ester. Weight ratio styrene to ester: (◑) 1:1; (○) 1.4:1; (●) 3:1; (◒) 5:1.

plugged, and the mold was inclined at a slight angle to the horizontal. In heated molds that stood vertically small air bubbles were released from the hot Teflon, rose through the polymerizing mixture, and were trapped in it, spoiling the membrane.

Membranes prepared in this way could be removed easily from glass or Teflon surfaces. However, the two surfaces of membranes made in Type I molds were of different smoothness and had thickened rims corresponding to the shape of the curved liquid meniscus. Membranes made in Type II molds modified by replacing the Teflon sheets with glass plates showed small, irregular channels on both surfaces. These were evidently caused by adhesion of the membrane to the glass during the contraction in volume accompanying polymerization. Use of Teflon sheets gave membrane surfaces that were uniform and flat.

Hydrolysis. The coherent membranes were removed carefully from the molds and placed in $1N$ KOH in 1:3 DMF–water solution for at least 6 hr. Immediate immersion in KOH solution caused cracking of the membrane surfaces. The membranes were boiled in $2N$ aqueous KOH for a time sufficient for complete hydrolysis (Fig. 4). To prevent serious warping, the thick rims of membranes prepared in Type I molds were cut off, and the membranes were held between two glass plates separated by glass spacers a few millimeters in thickness. After hydrolysis the membranes were thoroughly washed and were stored under conductance water.

Membranes prepared without the addition of DMF could be boiled in $2N$ KOH for a week and still have only a small fraction of their theoretical capacity.

Total Membrane Capacity. Whole membranes were agitated in $4N$ HCl for at least 12 hr. and then washed free of chloride with conductivity water. Exchange was carried out in 125 ml. of $2N$ KCl for 12 hr. with agitation and then repeated. The exchange solutions were titrated with standard NaOH. Two exchanges were sufficient.

The procedure was checked successfully by discontinuous pH titration[22] using a Radiometer PHM3 meter. The titration curve had the steep rise at pH 7 typical of a strong acid membrane.[22]

Water Content and Specific Capacity. A small piece (0.5 g.) of leached membrane in hydrogen form was blotted with filter paper, placed in a tared weighing bottle containing water, and weighed.[23] The piece was removed and dried to constant weight at 110°C. under nitrogen. Exchange (before drying) and titration as described above permitted calculation of the capacity. The water contents and capacities, both on a dry-weight, hydrogen-form basis, are listed in Table II.

It is apparent from Figure 4 that the maximum capacity is less than the theoretical value computed from the amount of vinyl ester, a phenomenon that has been noted elsewhere.[3,9] The data in Table II give 0.996 ± 0.043 eq. of acid per mole of ester. A freshly prepared, unhydrolyzed membrane was soaked for 12 hr. in 10 ml. of 1:3 DMF–water, and this solution was extracted with 2 ml. of CCl_4. The infrared spectrum of the extract was compared with blank extracts of the DMF solution and of a styrene–DVB–benzoyl peroxide solution. The 10.24 μ (977 cm.$^{-1}$) absorption was found to provide a unique identification of the ester, and by this means it was established that ester was lost to the DMF solution after polymerization. This loss is presumably in the form of low molecular weight polymer.

Water contents showed variations across the membranes. A membrane made in a Type I mold had water contents of 1.09, 2.04, and 1.99 g. per gram of dry samples taken from the rim, 1 cm. from the rim, and 2 cm. from the rim, respectively. A membrane made in a Type II mold showed variations from 0.283 to 0.376 (average 0.333 ± 0.039) g. per gram of dry membrane over five samples taken across a diameter. In this case no correlation of water content with geometry of the membrane was found.

Thickness. Membrane thickness was measured with a micrometer gage and varied less than ±0.02 mm., in general, over the surface of the membrane, provided that the rims of membranes made in Type I molds were ignored.

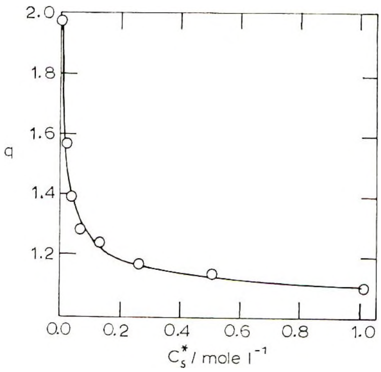

Fig. 5. Dependence of degree of swelling q on external salt (KCl) concentration C_s^*.

Swelling. Four pieces of membrane 12 in potassium form were equilibrated in various aqueous KCl solutions. The thickness t of each sample was determined, and the degree of swelling, $q = q_0(t/t_0)^3$, where t_0 and q_0 refer to the salt-free membrane, was calculated. The density of the dry membrane was found to be 1.25 g. cm.$^{-3}$ by hydrostatic weighing in CCl_4. No sorption of CCl_4 by the dried membranes was observed. The results (Fig. 5) show the strong deswelling in dilute salt solutions.

The degree of swelling of the leached membranes listed in Table II was found from the water content, $\bar{w}$ (grams of H_2O per grams dry resin), the density of the dry resin, d_2 = 1.25 g. cm.$^{-3}$, and the density of water, d_1, with the use of the equation

$$q = 1 + d_2\bar{w}/d_1 \tag{1}$$

The equation assumes additivity of volumes of resin and water. This assumption gives densities of swollen membranes which agree reasonably well with the observed values obtained by hydrostatic weighing in water. For example, two membranes with $\bar{w}$ of 1.93 and 2.40 had actual densities of 1.0667 and 1.0661 g. cm.$^{-3}$, respectively, the calculated values being 1.073 and 1.063 g. cm.$^{-3}$. It appears that the reported densities[6] of 1.3 to 1.6 g. cm.$^{-3}$ for swollen membranes are much too high.

Modulus of Elasticity. A membrane was clamped in a transport cell[24] filled with water. One of the calibrated capillary arms, 1.0 mm. bore, of this cell was connected to a ballast flask, mercury manometer, and nitrogen cylinder. The volume displacement of the membrane was found to be proportional to the applied pressure, with no hysteresis, up to pressures of at least 5 cm. Hg, corresponding to volume displacements of about 0.04 cm.^{3}. The modulus of elasticity (Young's modulus) E was found by using the formula[25] for the displacement z at a radial distance r of a circular plate of radius R and thickness d, clamped at the edge and subjected to a uniform pressure P:

$$z = P(R^2 - r^2)^2/64D \tag{2}$$

Here $D = Ed^3/12(1 - \nu^2)$ is the flexural rigidity, and ν ($= {}^1/_2$) is Poisson's ratio for the plate. Integration over r gives for the total volume displacement:

$$V = 9\pi PR^6/192Ed^3 \tag{3}$$

A second method was used as a check. A membrane strip of width a (about 1 cm.) and thickness d (about 1 mm.) was clamped horizontally and deflected by a load W (balance weights to a maximum of 20 g., corrected for density, on a platinum wire hanger) applied at a distance l (about 4 cm.) from the point of support. The membrane and weights were kept under water, the deflection z was measured with a cathetometer, and the modulus was obtained from[25]

$$z = 4Wl^3/Ead^3 \tag{4}$$

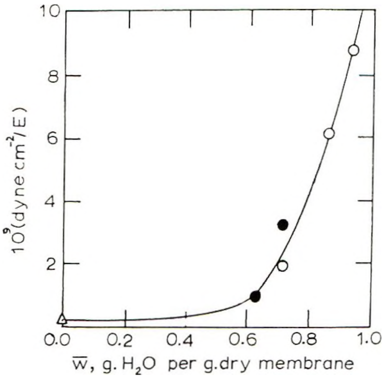

Fig. 6. Dependence of reciprocal Young's modulus E on water content of membranes; (○) from bending of a circular plate; (●) from bending of a strip; (△) for pure polystyrene.

The reciprocal modulus is plotted as a function of water content in Figure 6, including a value for zero water content, which was taken as that tabulated for pure polystyrene.[26]

DISCUSSION

The theory of polyelectrolyte gels developed by Vermaas and Hermans[27] and by Flory[28] will be used as a basis for discussion of the properties of the copolymer membranes described above. Although other more complete theories are available,[29] it is found that the simpler theory is adequate for all membranes if the solvent interaction constant χ_1 is treated as a parameter.

For a polyelectrolyte gel immersed in a uni-univalent electrolyte of concentration C_s^* Flory[28] gives

$$(i/v_u)(1 - 2\eta/Y) = [q \ln (1 - 1/q) + 1 + \chi_1/q]/v_1 + (\nu_e/V_0)(q^{2/3} - 1/2) \quad (5)$$

In this equation i is the degree of substitution of the singly ionized, fixed charge groups in the membrane, v_u the molar volume of a structural unit of the polymer, q the degree of swelling, v_1 the molar volume of the solvent (here 18.0 cm.^{3} mole^{-1}), ν_e the number of effective chains in the gel, V_0 the volume of the gel when crosslinks were introduced, and

$$Y = i/v_u q C_s^* \quad (6)$$

$$\eta = 1 + (Y/2)\{1 - [1 + (2/Y)^2]^{1/2}\} \quad (7)$$

The first group of terms on the right-hand side of eq. (5) reflects the contribution of mixing of polymer and solvent to the free energy of the gel, and the second group of terms reflects the contribution of elastic forces of the stretched polymer network.

The degree of swelling was calculated by using eq. (1) for the twenty membranes listed in Table II and for eleven membranes listed by Graydon

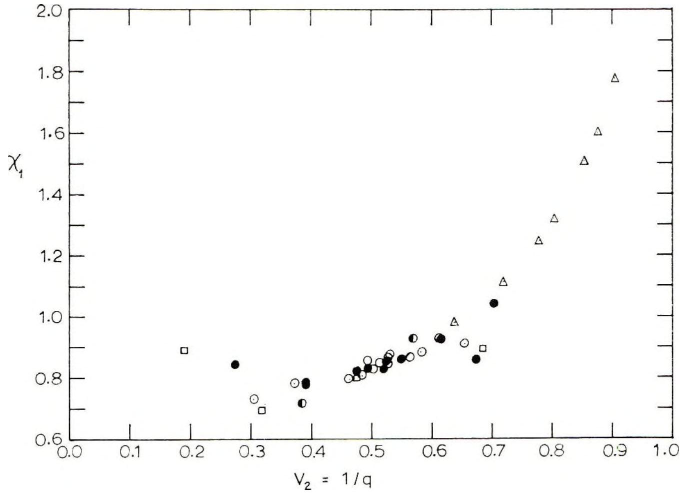

Fig. 7. Solvent interaction parameter χ_1 as a function of $v_2 = 1/q$, volume fraction of polymer in membrane. Swelling at zero salt concentration: (○) Type I mold; (◐) Type I mold and pure DVB; (□) Type II mold; (●) membranes of Graydon and Stewart. Swelling at finite salt concentrations: (△).

and Stewart.[4] The number of moles of crosslinks was assumed to be $\nu_e/2$ and equal to the number of moles of DVB in the initial polymerization mixture, n_c. The volume V_0 was assumed to be the volume of the dry gel, with density $d_2 = 1.25$ g. cm.$^{-3}$. Hence $\nu_e/V_0 = 2\, n_c d_2/w_p$, where w_p is the weight of vinyl monomers in the polymerization mixture.

If X is the capacity of the membrane in milliequivalents per gram of dry gel, then $i = Xw_p/1000n_p$, where n_p is the number of moles of vinyl monomers of weight w_p. The molar volume of a structural unit, v_u, was assumed to be the number-average molar volume of all vinyl monomers, with the molar volumes (cubic centimeters per mole) of 115 for styrene, 148 for ethylvinylbenzene, 155 for vinylbenzenesulfonic acid, and 140 for DVB. These values were found from tabulated density data or by estimation from benzene compounds of related structure. The values of v_u ranged from 121 to 140 cm.^{3} mole^{-1}.

In these calculations the analysis given above for commercial DVB was used, and it was assumed that negligible losses occurred during polymerization and hydrolysis.

Substitution of values of q, i/v_u, v_1, and ν_e/V_0 in eq. (5) at $C_s^* = 0$ permits calculation of χ_1 for each membrane. For most membranes the elastic term is only about 10–20% of the mixing term, and for the small degrees of swelling encountered the magnitude of the mixing term is very sensitive to the value of χ_1. The values of χ_1 ranged from 0.70 to 1.04, with an average of 0.842 ± 0.049, and are plotted as a function of $v_2 = 1/q$, the volume fraction of polymer, in Figure 7. With the exception of the two most highly swollen membranes, χ_1 is an increasing function of v_2. The decrease of χ_1 with decreasing v_2 has been observed in solutions of polymers (cf. Flory,[28] p. 515). In ionic networks at low degrees of swelling the nearest-neighbor ion interaction energies should be taken into account,[29] and the observed trend in χ_1 may reflect neglect of these interactions. It should be noted that membrane A4 (the most highly swollen) was very fragile and tended to disintegrate when swollen, so that the data for this membrane are suspect.

Although the membranes described in this paper were formed in the presence of a swelling agent, it is evident from Figure 7 that their water contents, for given concentrations of fixed charges and of crosslinking agent, are the same as the water contents of membranes prepared without swelling agents.[4] It is also evident that diluents associated with commercial DVB have no effect on the swelling properties of the membranes, provided that ethylvinylbenzene is treated as a monomer and diethylbenzene is ignored. Membranes prepared in the free surface molds (Type I) and in the closed molds (Type II) have the same overall properties, although the closed molds give membranes that are more uniform in water content and thickness. Reduction of the time of hydrolysis by the use of a swelling agent in which base (KOH) is soluble is very striking (Fig. 4). Graydon and Stewart[4] quote times of 30 hr. to 5 days for hydrolysis of their membranes.

The scatter of the experimental points in Figure 7 or the variations in capacity and water content for membranes of apparently identical composition (Table II) can be ascribed to several causes. Unavoidable losses occur during preparation of the membranes, mobile ionic impurities can cause deswelling, and crosslinking may not be reproducible. The first two causes should give consistently low water contents, while variations in crosslinking are presumably random.

The success of eq. (5) in accounting for the swelling properties suggests that any three of the parameters i/v_u, ν_e/V_0, q, and χ_1 are sufficient to describe the state of the membrane at a given external salt concentration. Treatment of swelling data at different salt concentrations (Fig. 5) by means of the full eq. (5) supports this view. As the external salt concentration increases from zero to 1M, χ_1 increases from 0.87 to 1.78. These values have been included in Figure 7, from which it appears that χ_1 is a smooth function of q alone. Knowledge of this function means that the state of the membrane can be specified by two parameters only, for example, i/v_u and ν_e/V_0.

The marked dependence of the modulus of elasticity on water content is as expected. However, the measurements are not of sufficient precision and do not cover a wide enough range of densities of charge and crosslinking to warrant further interpretation.

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Molecular Weight Distribution of Liquid Poly(ethylene Glycols): Determination by Gas Chromatography

J. P. FLETCHER and H. E. PERSINGER, *Research and Development Department, Chemicals and Plastics, Union Carbide Corporation, South Charleston, West Virginia 25303*

Synopsis

The molecular weight distribution of liquid polyethylene glycols 200, 300, and 400 can be determined by gas chromatography by using trimethylsilyl ether derivatives. The relative response factors for the first five members of the homologous series were determined experimentally. Attempts are made to extrapolate the experimental data to relative response factors for higher members of the homologous series.

INTRODUCTION

Molecular weight distributions of poly(ethylene glycols) (PEGs) have been determined by liquid–liquid extraction,[1] paper chromatography,[2] thin-layer chromatography,[3] gas chromatography,[4–6] fractional precipitation,[7] and gel permeation chromatography.[8] Gas chromatography, when applicable, is much simpler and considerably faster than other methods for PEGs.

Mikkelsen[4] reported a gas chromatographic analysis of PEG 400; the original sample injected directly into the gas chromatograph, a technique also employed by Puschmann.[5] Celades and Pacquot[6] converted the PEGs into methyl ethers in a reaction with dimethyl sulfate before injection into the gas chromatograph.

The rapid formation of trimethylsilyl ether derivatives of polyhydroxy compounds, followed by their separation and estimation by gas chromatography, has been described by Sweeley et al.[9] In this laboratory Crabb[10] applied this most useful technique to the liquid polyethylene glycols 200, 300, and 400. We have studied this application and wish to report the determination of response factors relative to ethylene glycol for conversion of peak areas to weight per cent when a thermal conductivity detector is used.

EXPERIMENTAL

Materials

Hexamethyldisilazane and chlorotrimethylsilane were obtained from K and K Laboratories and used without further purification. Ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, and the poly(ethylene glycols) 200, 300, and 400 were provided by Union Carbide Corporation, Chemicals Division. Pentaethylene glycol was separated from poly(ethylene glycol) 300 by fractional distillation under reduced pressure in the presence of nitrogen, and a hearts cut of the fraction boiling at 218–220°C. at 14 mm. Hg was collected. Hexa- and heptaethylene glycol fractions were also collected, but because of decomposition during distillation they were considered too impure for use in determining response factors for gas chromatography.

For gas chromatography the column packing was prepared from silicone gum rubber SE-30, obtained from F and M Scientific, Division of Hewlett-Packard, Avondale, Pa., and acid-washed Chromosorb G (45-60 mesh), obtained from Johns-Manville Corp., New York, N. Y.

Preparation of Trimethylsilyl Derivatives

Trimethylsilyl (TMS) ether derivatives of PEGs were prepared by reacting 0.1 ml. sample with 1.0 ml. reagent (2 parts by volume of hexamethyldisilazane to 1 part of chlorotrimethylsilane) in an ampule with a serum cap. The mixture was shaken vigorously for about 30 sec. and allowed to stand for at least 15 min., after which it was centrifuged. A 20 μl. amount of the supernatant liquid was removed for injection into the gas chromatograph.

Gas Chromatographic Conditions

The instrument used for analyses by gas chromatography was an F and M model 810 with thermal conductivity detector (W-2 filaments). The dual columns were aluminum tubing 3 ft. by 0.25 in. o.d., packed with 5% SE-30 on Chromosorb G. The column temperature was programmed from 100 to 370°C. at 10°C./min. and then held isothermally at 370°C.

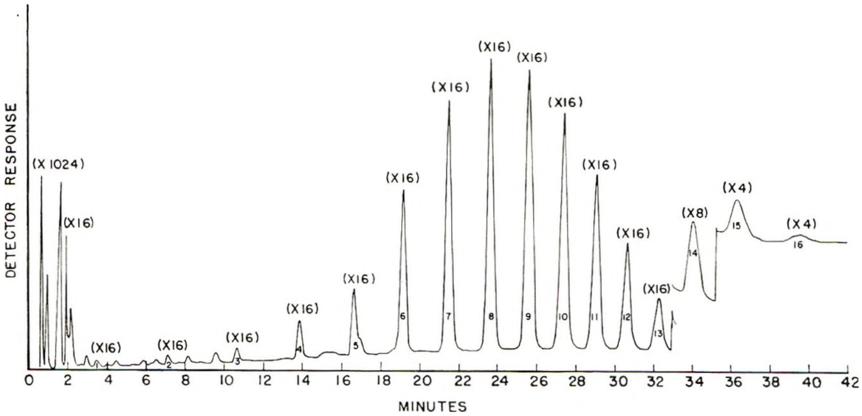

Fig. 1. Gas chromatogram of TMS derivative of PEG 400. Dual columns, 3 ft. by 0.25 in. o.d., 5% SE-30 on Chromosorb G. Temperature programmed from 100 to 370°C. at 10°C./min. and then isothermal at 370°C.

The injection port temperature was 320°, and the detector temperature was 310°. Helium was used as carrier gas with a flow of about 40 ml./min. (rotometers at 2.5 with 40 psig inlet pressure). The chart speed of the 0–1 mv. recorder was 1 in./min. A typical chromatogram of PEG 400 is shown in Figure 1.

RESULTS AND DISCUSSION

Response Factors

Mono- to Pentaethylene Glycol. Each of the relatively pure glycols was analyzed a number of times by the gas chromatographic method, the peak areas were converted to area per cent, and the determinations were averaged. Mixtures of ethylene glycol with each of the other glycols in 1:1 ratio were prepared and analyzed at least four times each. The relative areas of the ethylene glycol peak and the other principal component peak were measured and averaged. By a process of successive approximations the compositions of the pure materials were used to calculate the compositions of the binary mixtures, the compositions of the binary mixtures were used with the gas chromatographic relative areas to calculate approximate response factors relative to a value of 1.000 for ethylene glycol, and the approximate response factors were then used to recalculate the compositions of the pure glycols. The entire set of calculations was repeated until there were no further changes in the compositions of the pure glycols or in the relative response factors. Table I shows the average area per cent values for the five glycols along with the fourth and final approximation of weight per cent values. Table II shows how the values for response factors changed during approximations.

Extrapolation of Relative Response Factors. To obtain relative response factors for higher members of the homologous series of TMS ether derivatives of PEGs, we must somehow extrapolate the experimentally determined values for the first five members. Possibly the best summary to date on the quantitative interpretation of gas chromatograms in general and the relationship between relative response corrections and molecular weight in particular has been made by Andreev et al.[11] Using a thermal conductivity detector and helium or hydrogen carrier gas, several workers have observed a linear variation of molar relative response factors with molecular weight within a given homologous series, with a slight deviation from linearity in the first few members. Other workers have shown relationships varying with the $^1/_2$, $^2/_3$, $^3/_4$, and $^4/_3$ power of the molecular weight. Many workers conclude that relative response with thermal conductivity is related to the square of the average molecular diameter. As Hoffmann[12] points out, one can expect linearity with molecular weight only if the molecules form straight or nearly straight chains. If the molecules are coiled into spheres, the relative response may be proportional to a $^2/_3$ power of molecular weight.

TABLE I

Gas Chromatographic Analysis of Starting Materials

	Ethylene glycol		Diethylene glycol		Triethylene glycol		Tetraethylene glycol		Pentaethylene glycol	
	Area-%	Wt.-%	Area-%	Wt.-%	Area-%	Wt.-%	Area-%	Wt.-%	Area-%	Wt.-%
Ethylene glycol	99.96	99.94	0.07	0.05	0.04	0.02	0.24	0.09	0.58	0.18
Diethylene glycol	0.04	0.06	99.64	99.57	0.10	0.075	0.16	0.10	1.56	0.74
Triethylene glycol			0.29	0.38	99.86	99.905	4.63	3.65	1.75	1.10
Tetraethylene glycol							94.96	96.16	2.52	2.03
Pentaethylene glycol									92.98	95.21
Hexaethylene glycol									0.66	0.74
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

TABLE II
Relative Response Factors for Starting Materials, Successive Approximations

	First approx.	Second approx.	Third approx.
Ethylene glycol	1.000	1.000	1.000
Diethylene glycol	1.542	1.542	1.542
Triethylene glycol	2.039	2.042	2.042
Tetraethylene glycol	2.583	2.619	2.621
Pentaethylene glycol	3.237	3.325	3.329

We have obtained straight-line plots of relative response factors versus carbon number on semilogarithmic paper for some homologs. So we made one such extrapolation, as shown in Figure 2. Another extrapolation, Figure 3, was based on linearity between the homologs and their relative response factors. An attempt was made to select the better of these two extrapolations in the following way.

Samples of PEGs 300 and 400 and a 1:1 mixture of the two were chromatographed in triplicate, and the area per cent values were determined and averaged. With the use of one set of relative response factors the weight per cent value of each component in the 1:1 mixture was calculated from the compositions of PEG 300 and PEG 400 and their known weights. The calculated composition of the 1:1 mixture was then compared with the composition found.

Starting with the area per cent results, the entire procedure is repeated with the second set of relative response factors. The data, presented in

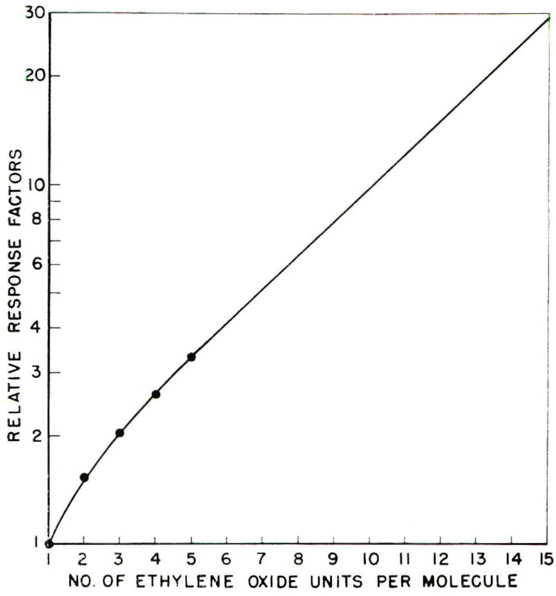

Fig. 2. Correlation of relative response factors with molecular weight (number of ethylene oxide units). TMS derivatives of PEGs. Semilogarithmic.

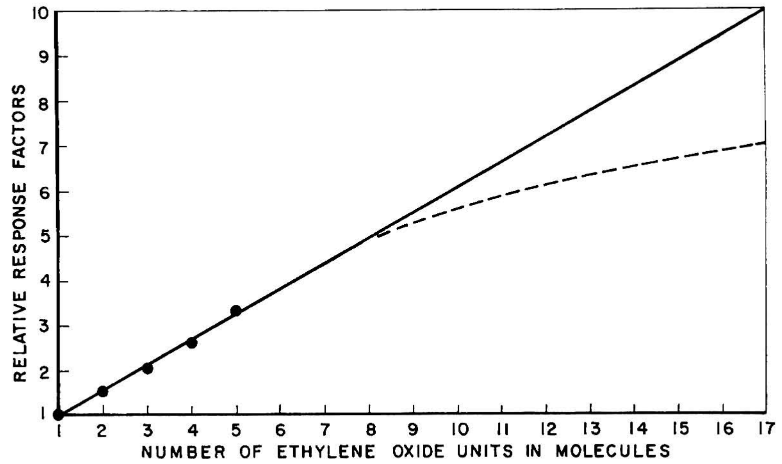

Fig. 3. Correlation of relative response factors with molecular weight (number of ethylene oxide units), TMS derivatives of PEGs: (A, ——) assuming a completely linear relationship; (B, – – –) Supposed deviation based on coiling of polymer chains.

Table III, indicate that the higher relative response factors from the first extrapolation give inconsistent results. Lower members of the homologous series are lower in concentration, whereas higher members are higher in concentration than they are calculated to be. Results from the use of the linear extrapolated relative response factors are more in line with the calculated results. The differences between results calculated and results

TABLE III

Test for Which Extrapolation of Relative Response Factors Gives More Consistent Data: 1:1 Mixture of PEG 300 and PEG 400

No. of ethylene oxide units	Wt.-% values based on response factors from logarithmic extrapolation			Wt.-% values based on response factors from linear extrapolation		
	Found	Calcd.	Diff.	Found	Calcd.	Diff.
1	0.04	0.03	+0.01	0.06	0.04	+0.02
2	0.08	0.08	—	0.12	0.10	+0.02
3	0.57	0.68	−0.11	0.83	0.86	−0.03
4	1.98	2.42	−0.44	3.42	3.71	−0.29
5	5.39	6.10	−0.71	7.78	7.93	−0.15
6	8.26	9.31	−1.05	10.93	11.27	−0.34
7	12.61	13.10	−0.49	15.38	15.03	+0.35
8	14.26	14.81	−0.55	15.79	15.98	−0.18
9	14.86	14.57	+0.29	14.69	14.46	+0.23
10	12.21	12.81	−0.60	10.72	11.69	−0.97
11	11.66	10.22	+1.44	9.09	8.41	+0.68
12	8.90	7.26	+1.64	6.06	5.32	+0.74
13	5.41	5.20	+0.21	3.19	3.35	−0.16
14	2.86	2.42	+0.44	1.47	1.36	+0.11
15	1.05	0.81	+0.24	0.47	0.40	+0.07
16	—	0.18	−0.18	—	0.08	−0.08

TABLE IV
Internal Standard Test of Linear Extrapolated Relative Response Factors on PEG 300

No. of ethylene oxide units	Wt.-%, intern. std. calculation[a] 1	2	3	Previous results, area normalization	Relative response factors used
1	0.12	0.11	0.10	0.05	1.000
2	0.38	0.26	0.32	0.16	1.542
3	—	—	—	1.60	2.042
4	8.87	8.11	7.71	6.59	2.621
5	17.56	15.64	14.61	13.29	3.329
6	22.43	19.43	17.55	17.35	3.82
7	24.84	23.24	19.45	19.75	4.38
8	22.12	20.75	16.32	16.67	4.94
9	16.14	13.98	11.64	11.77	5.50
10	9.35	8.71	6.88	6.44	6.06
11	4.41	4.39	3.42	3.78	6.62
12	2.51	2.29	1.86	1.64	7.20
13	1.15	0.91	0.85	0.67	7.74
14	0.46	0.34	0.35	0.24	8.30
15	0.22	0.15	0.17	—	8.86
	130.56	118.31	101.23	100.00	

[a] Weight per cent component = (area) × (relative response factor) × (normalizing factor). Normalizing factor = (grams internal standard) ÷ [(grams sample) × (area internal standard) × (relative response factor for internal standard)].

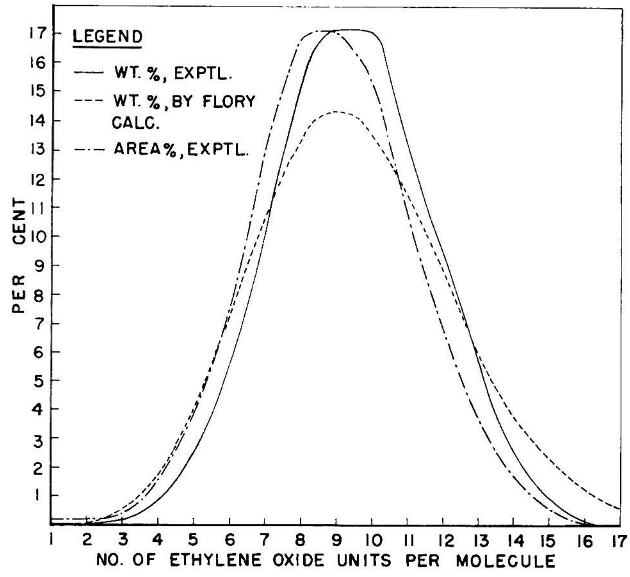

Fig. 4. Molecular weight distribution of poly(ethylene glycol) 400: (——) weight per cent, experimental; (- - -) weight per cent, calculated from Flory's equation; (— · —) area per cent, experimental.

found are smaller and more random than the differences observed with the first set of response factors.

Therefore, the linear extrapolation gets us a little closer to the actual relative response factors. But because the polymer chains may be coiling, and because we expect relative response factors to approach a limiting value, we might expect the extrapolation to drop off and look like the dashed line in Figure 3. Actually, however, the area normalization method for calculating quantitative results from gas chromatographic data allows so much variation in response factors without significantly affecting the calculated results that the use of response factors from the dashed line in Figure 3 will not change tremendously the results for PEGs 200, 300, and 400.

An attempt to use triethylene glycol as an internal standard failed to prove whether or not the linear extrapolated relative response factors were too high, because the gas chromatographic peak areas were not sufficiently precise for this type of calculation. The data, shown in Table IV, do indicate that they may be slightly too high, but they are too sensitive to the triethylene glycol area, which was apparently somewhat erratic.

For our purposes the relative response factors from the linear extrapolation are adequate, and the closer approach to weight per cent values is more satisfying than area percent values. Figure 4 shows a molecular weight distribution of PEG 400 in terms of area and weight per cent arrived at by the gas chromatographic method and a theoretical curve of weight percent calculated from Flory's equations.[13] This figure indicates that the molecular weight distribution produced industrially is narrower than that predicted by the Flory calculations.

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NOTES

Activation Energies for Styrene Polymerization by Differential Thermal Analysis

Current applications of differential thermal analysis (DTA) to polymer systems have been primarily concerned with the physical properties of the polymer. Except for some limited work, such as that of Klute and Viehmann,[1] little attention has been directed toward the polymerization reaction itself. This is probably due to the difficulty of running DTA's under the temperature and pressure conditions prevailing during polymerization reactions.

We have found that slight modifications of the sample-handling technique, described below, allow us to look at reactions at high temperatures and at pressures up to 45 atm. The variation in technique has enabled us to analyze systems not previously susceptible to differential thermal analysis, such as heterogeneous catalysis,[2] *cis-trans* isomerization,[2] and the Diels-Alder reaction.[3] Using this modified procedure, we have been able to follow the catalyzed and uncatalyzed polymerization of styrene, styrene in toluene, and the polymerization of this monomer with persulfate catalyst in a heterogeneous medium of water, monomer, and soap.

Thermograms were run using the calorimeter cell of the du Pont Model 900 Differential Thermal Analyzer with, as reaction vessels, the 4-mm. glass vials supplied with the instrument. When appropriate, the monomer, after preliminary purification by fractional distillation, was distilled under vacuum directly into the vials. The vials were then sealed under nitrogen.

Thermograms typical of the results obtained are shown in Figure 1. The activation energies of the reactions were calculated by the method of Piloyan et al.[4]

Figure 1, curve I, the thermogram of the thermally induced polymerization of pure styrene, shows an exotherm corresponding to the onset of polymerization at 140°C. and

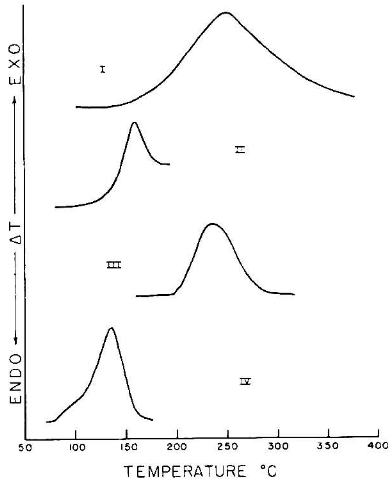

Fig. 1. Thermograms: (I) thermally induced polymerization of styrene; (II) polymerization of styrene benzoyl peroxide; (III) polymerization of styrene in toluene; (IV) heterogeneous polymerization of styrene.

a peak at 250°C. The activation energy for this process was calculated to be 21.3 ± 0.6 kcal./mole. Reported values have ranged between 19.2 and 23.5 kcal./mole. Flory[5] has calculated the value of 22.1 kcal. based on data of Mark and Raff[6] and 21 kcal., based on data of Suess et al.[7] and Schulz[8] and Husemann.

Figure 1, curve II, a thermogram of the polymerization induced by benzoyl peroxide, shows peaking at a much lower temperature, 160°C., as well as a more gradual onset of polymerization at about 100°C. The activation energy was calculated to be 24.0 ± 0.3 kcal./mole, which may be compared with the value of about 23 kcal./mole reported by Flory.[9]

Little difference can be seen in the thermally induced polymerization of styrene, whether carried out with a solution in toluene or with pure monomer. This is apparent from Figure 1, curve III, which shows that the peak for the thermally induced solution polymerization occurs at about 250°C., similar to that found for the pure monomer. The activation energy was found to be 21.4 ± 1 kcal./mole, virtually the same as that of the bulk polymerization.

Attempts were made to carry out an emulsion polymerization of styrene by a persulfate-catalyzed recipe. The results were erratic. The problems included the difficulty of establishing a baseline from which calculations could be made and, perhaps more important, the instability of the emulsion under the conditions necessary for the polymerization in the DTA apparatus. This instability was revealed by partial flocculation of the emulsion at the end of the reaction. We therefore feel that it was a heterogeneous reaction comprising the elements of both emulsion and suspension polymerization. Although we calculated an average activation energy of 19.4 ± 1.2 kcal./mole for this system from thermograms similar to that in Figure 1, curve IV, we hesitate to attach any significance to this value.

In conclusion, we feel that the procedure we have described provides a rapid and accurate means of obtaining kinetic parameters for systems which, because of pressure and temperature variables, were not previously readily accessible to differential thermal analysis.

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HORST W. HOYER
ANGELO V. SANTORO
EDWARD J. BARRETT

Department of Chemistry
Hunter College of
The City University of New York
New York, New York 10021

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Thermal Degradation of Polymers through an Inductively Heated Insert

It was previously reported[1] that the inductive heating of pre-cured thermosetting resins reinforced by inserts of stainless steel, graphite, or carbon cloth increased the mechanical strength of the composite over that obtained by a conventional post-cure in an oven or a press. In the course of an interface study into the causes of this phenomenon, observations were made which may be of more general interest. Since the conclusions drawn from these observations are not directly related to the purpose of the interface study, it seemed appropriate to summarize them briefly in a separate note.

A number of cylinder-shaped specimens were prepared by casting disks of stainless steel into an epichlorohydrin-bisphenol A type epoxide resin catalyzed by *m*-phenylenediamine, and precuring for 6 hr. at 50°C. plus 2 hr. at 85°C. Each of these cylinders was then subjected to inductive heating (27 Mc./sec.) for a different preselected length of time, with the longest heating time extended to the point where signs of charring were noted on the edges of the metal disc. Following proper machining, the resin cylinders could be broken clean along the surface of the metal. The matching resin and metal surfaces were then examined for water wettability by the (advancing) angle-of-contact test.[2] Figure 1 shows the observed relationships between contact angle (averages of five measurements; standard deviations on the order of 1.0 to 1.5 degrees) and induction heating time for the various specimens.

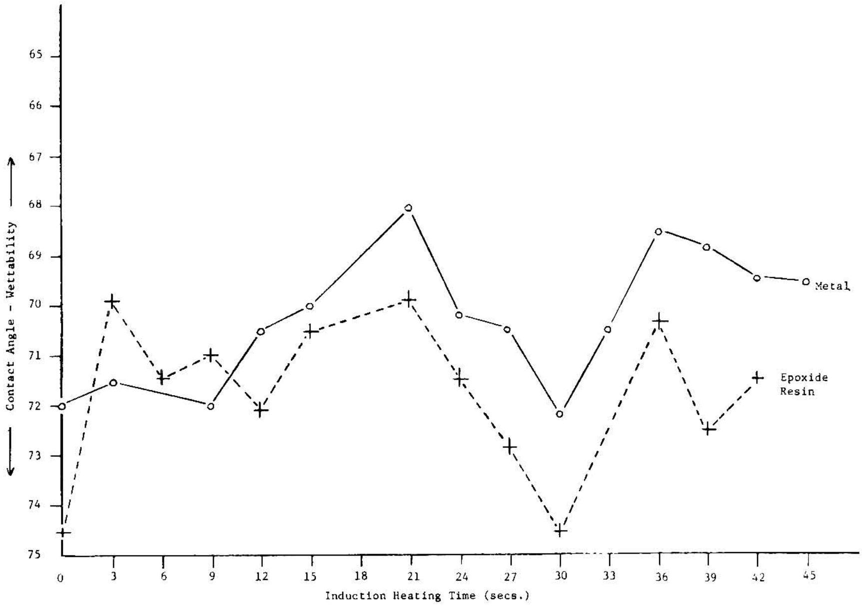

Figure 1.

The two curves given in the figure are approximately sinusoidal in that the wettabilities of both surfaces go through about three maxima and two minima as the induction heating time is increased. Also, the maxima and minima coincide quite well for matching metal and resin surfaces. Furthermore, as will be reported at a later date, maxima in wettability correspond to maxima in bonding strength. Under the assumption that changes in the wettability of a surface indicate changes in its chemical structure, one may interpret these curves by assuming sequences of formation, destruction and recombination of polymeric structures.

This conclusion does not seem unreasonable in view of the results reported by Keenan and Smith[3] of an investigation into the degradation, by hot-wire pyrolysis, of an epoxide resin similar to that used in our study, followed by gas chromatographic examination of the decomposition products. Keenan and Smith conclude that the first step in the thermal degradation of the resin consists of a homolytic rupture of bonds to produce resonance-stabilized free radicals for which there is evidence both from ESR and from reaction with 2,2-diphenyl-1-picryl hydrazyl. These free radicals are assumed to react further in a complex manner, and the products formed thereby are themselves likely to undergo additional secondary reactions. In all, a spectrum of products varying from small molecules of the phenol or cresol type through to compounds not greatly varying from the parent resin was identified.

Keenan and Smith worked, however, in an open system where degradation products are continually removed from the heating zone. Contrarywise, our tests were done in a closed system. Here, the degradation products formed through energy transmitted to the resin by the inductively heated insert cannot escape. The products of degradation will be different for various induction times, and so will be the products of recombination formed on cooling after the induction heating is discontinued. These differences in structure are indicated by the changes in wettability observed for the different levels of inductive heating shown in the figure. Identification of the newly formed products by method of polymer characterization might then be undertaken.

It is suggested that this procedure of inductive heating through an electrically conductive insert may be applied to study polymer degradation processes at various temperatures, up to carbonization, under conditions which do not permit the escape of degradation products, and to characterize the reformed polymeric structures.

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R. A. V. Raff
A. M. Sharan

Department of Metallurgy
College of Engineering
Washington State University
Pullman, Washington 99163

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Synthesis of Low Molecular Weight Hydroxy-Terminated cis-*1,4-Polybutadiene*

The value of the *cis*-1,4 structure in synthetic rubbers has been known for some time and yet, curable, low molecular weight liquid polymers high in *cis*-1,4 content have been previously unknown. In general, polymer chemists have sought very high molecular weight materials rather than the short-chain polymers. The advantage in having low molecular weight curable liquid polymers is that formulations can be prepared while the ingredients are fluid, and casting and molding operations can be done with greater ease. While the rubber, gumstock, or filled gumstock is in the liquid state, it can be molded into the desired shape and then cured to a rubber by heating.

Prerequisites for this type of operation are liquid polymers with functional groups which will react with conventional curing agents upon heating.

Since no liquid butadiene polymers are known which are high in *cis*-1,4 content and have curable terminal functional groups, it was decided to investigate the possibility that high molecular weight *cis*-1,4-polybutadiene rubber could be cleaved into low molecular weight liquid fragments with terminal functional groups. It was hoped that the liquid polymers obtained in this manner could be cured to give rubbery materials, and it was planned to study the properties of both the liquid polymer and of the cured gumstock.

The technical approach to the synthesis of these materials involved the cleavage of high molecular weight *cis*-1,4-polybutadiene rubbers, which are synthesized relatively easily, into shorter liquid fragments. Although several methods of cleavage of double bonds were available, ozonolysis presented an attractive route because of the possibility of placing a carboxylic acid group at each end of the shorter chains. The desirability of having carboxylic acid groups is easily seen when one considers the number of epoxides, isocyanates, and other curing agents which are available for curing and crosslinking carboxyl-modified or carboxyl-terminated polybutadiene.

The high molecular weight *cis*-1,4-polybutadiene rubber used in this study was prepared by polymerization of butadiene with a Ziegler catalyst composed of cobaltous chloride, aluminum chloride, and triethylaluminum. Ozonization of the rubber was effected by passing ozonized oxygen through a solution of the high polymer in chloroform. Several different methods of oxidative hydrolysis failed to yield carboxylic-acid terminated liquid butadiene polymers. Infrared analysis at various stages of ozonolysis and oxidative hydrolysis indicated that the hydroxyl group, rather than the carboxylic acid group, was generated by hydroperoxide formation as a result of ozone attack, or by partial hydrolysis of ozonides to dihydroperoxides or hydroxy hydroperoxides.[1,2]

Since it was felt necessary to prepare liquid polymers with only a single type of functionality, and since it did not seem possible to readily eliminate the formation of the hydroxyl group in the ozonization process, it appeared logical to prepare hydroxy-terminated polymers directly by reduction of the ozonides. Consequently, the direct reduction of the polymeric ozonides was undertaken with lithium aluminum hydride in ether solution. The results of this approach were most gratifying, in that low molecular weight polymers were obtained which were very high in *cis*-1,4-structure and had a hydroxyl functionality of two.

DISCUSSION

The ozonization of *cis*-1,4-polybutadiene was done in the following manner. The high molecular weight (100,000–900,000) polymer was dissolved in chloroform, and ozonized oxygen was bubbled through the solution at room temperature until the required amount of ozone had been absorbed. Upon evaporation of the solvent under vacuum, the ozonide was left as a very viscous liquid. The ozonides were somewhat sensitive to shock, partial initiation occurring at about 40 kg.-cm. The degree of impact sensitivity, of course, was dependent upon the amount of ozone absorbed by the polymer.

Efforts at decomposition of the ozonides to yield carboxylic acid terminal groups were unsuccessful. In some instances, products have low values of unsaturation because of the presence of succinic acid as a degradation product. A comparison of the infrared spectra of one ozonide with that of the product after hydrolysis attempts with formic acid and hydrogen peroxide suggested that the band at 1725 cm.$^{-1}$ was due to the reaction of performic acid with the polymer. This conclusion was supported by disappearance of the absorption upon aqueous saponification of the hydrolyzed ozonide. This interpretation is easily understood in view of the reaction of performic acid with olefins.[3]

To form a hydroxy-terminated, liquid *cis*-1,4-polybutadiene, high molecular weight *cis*-1,4-polybutadiene rubbers were dissolved in chloroform, and a stream of ozonized oxygen was bubbled through the solution to form the ozonides. The chloroform was evaporated and the ozonides were then dissolved in ethyl ether. An ether solution of lithium aluminum hydride was added cautiously to the solution of the ozonide at −5°C. After the reduction was completed, the product was isolated by solvent, nonsolvent precipitation. The yellow fluid product had an average molecular weight between 200 and 400. In most instances, the polymer was found to be difunctional. Usually the degree of unsaturation was between 90 and 100% of theory, with approximately 95% of the olefinic linkages having the *cis*-1,4 structure, 2% having the *trans*-1,4 structure, and 3% the vinyl-type unsaturation.

Because of the desirability of controlling the molecular weight, two approaches were made at obtaining hydroxyl-modified liquid *cis*-1,4-polybutadiene with a molecular weight in the range of 1000. Several butadiene polymers with molecular weights below 5000 are liquids.[4,5] The first approach to molecular weight control involved limiting the amount of ozone used in the ozonolysis of high molecular weight polymer. The second approach involved selective solvation of the ozonide before the reduction.

Attempts to control the molecular weight by limiting the ozone added to the *cis*-1,4-polybutadiene rubber did not prove feasible, since a small amount of ozone gave only low yields of short-chain hydroxy-modified *cis*-1,4-polybutadiene. Within working limits,

TABLE I
Results of Lithium Aluminum Hydride Reductions of Ozonized *cis*-1,4-Polybutadiene Rubber

Experiment no.	Ozonization time, min.	$[\eta]$[a]	Molecular weight (Rast)	Hydroxyl equivalents/100 g.	Unsaturation, %		
					Reported	Corrected[b]	Functionality
1	60	0.035	306	0.60	61	93	1.84
2	60	0.017	272	0.48	60	89	1.31
3	60	0.020	226	0.77	57	94	1.71
4	45	0.016	295	0.62	63	90	1.86
5	45	0.018	289	0.79	66	95	2.25
6	45	0.025	287	0.40	71	105	1.15
7	60	0.019	331	0.66	68	95	2.18
8[c]	—	—	313	0.66	78	109	2.08

[a] Since the molecular weights are very low, the intrinsic viscosities may not be significant.

[b] Corrected values are calculated from reported unsaturation and molecular weight determinations and include the effect of two CH_2CH_2OH terminal groups on each molecule.

[c] Represents a combination of several additional experiments.

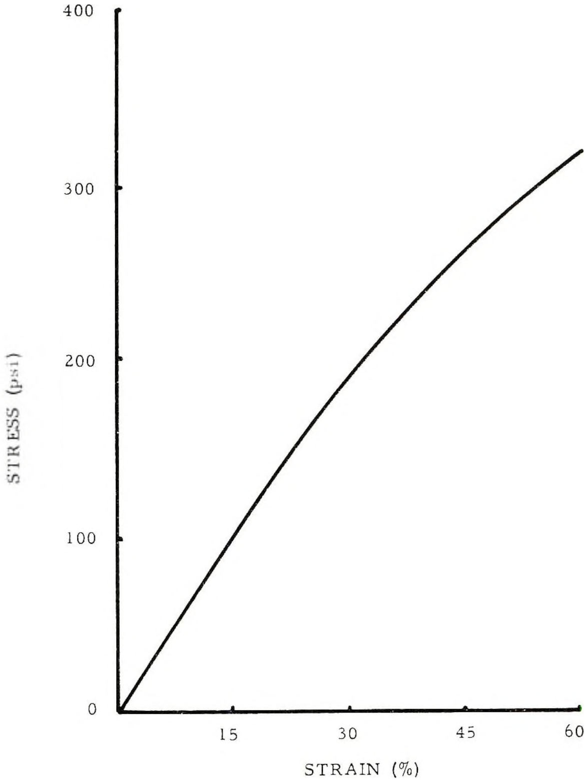

Fig. 1. Stress–strain curve for isocyanate-cured hydroxy-terminated *cis*-1,4-polybutadiene.

variation in the amount of ozone used gave polymers with molecular weights in the 200–400 range (see Table I).

Regulation of the molecular weight of the product was attempted also by trying to find a more powerful solvent for the ozonides. Di-*n*-butyl ether, diethyl ether, tetrahydrofuran, ethylene glycol dimethyl ether, and pyridine were each used in attempts to dissolve higher molecular weight ozonides before the reduction with lithium aluminum hydride. With di-*n*-butyl ether, the product was a brown, viscous liquid. Ethylene glycol dimethyl ether and diethyl ether both gave fluid, yellow liquid polymers as described above. Attempts with tetrahydrofuran and with pyridine gave brown intractable tars.

The polymers produced by this ozonolysis–reduction procedure were fairly fluid yellow liquids as described above. It was decided to attempt to cure the polymer to a firm rubber and to investigate briefly the physical properties of the gumstock.

The curing agent used in this study was a mixture of a di- and tri-functional isocyanate. The difunctional agent used was 1,6-hexamethylene diisocyanate. The trifunctional isocyanate was prepared in a manner similar to that described in the literature,[6] by adding a solution of trimethylolpropane dropwise to a warm solution of excess 1,6-hexamethylene diisocyanate. After completion of reaction, solvent and excess diisocyanate were removed by distillation under vacuum. The ratio of di- to trifunctional curing agent was calculated from isocyanate assay assuming the alcohol had reacted with three moles of 1,6-hexamethylene diisocyanate. It was found that a ratio of one mole of 1,6-hexamethylene diisocyanate to three moles of the triisocyanate gave a good gumstock with the hydroxy-terminated *cis*-1,4-polybutadiene (using a stoichiometric amount of hydroxyl and isocyanate groups).

The liquid polymer was mixed with the curing agent and heated in an oven at 57°C. for 64 hr. The cured gumstock was a firm, light yellow rubber. Tensile properties measured on the gumstock have the following values: average tensile strength, 311 psi; average elongation, 59%. A typical stress–strain curve is shown in Figure 1. It can be seen from Figure 1 that the gumstock is a soft tough rubber with moderate elongation (the apparent initial modulus, 7.1, was measured graphically).

EXPERIMENTAL

Ozonization of *cis*-1,4-Polybutadiene

A stream of ozonized oxygen from a Welsbach T-23 ozonator was bubbled through a solution of *cis*-1,4-polybutadiene for 75 min. at room temperature. A 5 g. portion of the high molecular weight polymer was used in 300 ml. of chloroform. The ozone concentration was such that 1.87 g. of ozone was produced in $1^1/_4$ hr. The solvent was removed under reduced pressure, leaving 6.7 g. of the ozonide as a viscous fluid with a small amount of tacky rubber present.

Impact sensitivity was measured with a Model 7 Olin-Mathieson drop weight tester (Technoproducts, Inc.). Initiation of decomposition occurred at about 40 kg.-cm. but did not appear to be an explosion. Impact in the drop weight tester resulted only in carbonization of the sample. If the ozonide was unconfined, explosions could be induced but would not propagate through the viscous liquid.

The infrared spectrum of the ozonide showed strong absorption peaks at 3500, 2900, 1450, 1110, and 750 cm.$^{-1}$. Medium to weak absorption peaks appeared at 1725, 1660, 1415, 1350, 1215, 1040, and 950 cm.$^{-1}$.

Hydrolysis of Ozonides

In early attempts at hydrolysis to obtain carboxyl groups the ozonides were dissolved in chloroform and stirred rapidly with water or aqueous hydrogen peroxide. Potassium iodide or titanic acid tests indicated that hydrolyses by these methods were incomplete.[7] Using the method of Bailey as a model, oxidative hydrolysis with formic acid and hydrogen peroxide was attempted.[8] The ozonide of *cis*-1,4-polybutadiene (1.00 g. prepared as described above) was first heated with 5 ml. of aqueous hydrogen peroxide (30%) and 5 ml. of formic acid (90%) for 2 hr. on the steam bath. An additional 5 ml. of hydrogen peroxide was added, and the mixture was heated for 12 hr. Only water-soluble products were obtained. A repetition of this procedure with unozonized polymer indicated that the *cis*-1,4-polybutadiene rubber was degraded to succinic acid by the treatment. Similar results were obtained by using 15% hydrogen peroxide and 50% aqueous formic acid. The best results were obtained by using the ozonide in chloroform with formic acid and 4% hydrogen peroxide. The ozonization was done with 5 g. of *cis*-1,4-polybutadiene in chloroform (300 ml.) as described above. Formic acid (25 ml., 90%) and hydrogen peroxide (75 ml., 4% aqueous hydrogen peroxide) were added and the mixture was heated under reflux for 30 hr. The chloroform layer was then separated, washed with water to neutrality, dried, and evaporated under reduced pressure. A pale yellow fluid polymer was obtained (4.5 g.). Analysis for per cent of unsaturation by the method of Lee et al.[9] indicated that the product contained only about 33% of theoretical unsaturation, which can be accounted for by the presence of succinic acid. A standard base titration showed the carboxylic acid content to be 0.0266 eq. acid/100 g. In one instance, after similar hydrolysis for 24 hr., the acid content was 0.0227 equivalents per 100 grams. After an additional period of 16 hr. under identical hydrolytic conditions, the acid content was 0.0218 eq. acid/100 g. Thus, additional hydrolysis probably only served to dissolve some of the low molecular weight acids.

Infrared analysis of the hydrolyzed ozonide showed strong absorption peaks at 3400, 2900, 1725, 1450, 1185, 1050, and 750 cm.$^{-1}$; medium or weak peaks at 1770, 1650, 1375, 1260, 950, and 800 cm.$^{-1}$.

Saponification of Hydrolyzed *cis*-1,4-Polybutadiene Ozonide

cis-1,4-Polybutadiene ozonide (1.00 g.) which had been hydrolyzed with 4% hydrogen peroxide and formic acid as described above was refluxed 24 hr. with alcoholic potassium hydroxide (100 ml. ethanol, 2.5 g. potassium hydroxide). An orange solution resulted, with a small amount of solid present. The mixture was filtered and the alcohol was removed under vacuum. Water was added and the mixture was extracted with benzene. The benzene solution was dried, and the solvent evaporated under vacuum. Infrared analysis of the yellow saponification product showed strong absorption peaks at 3350, 2900, 1700, 1450, 1265, 1050, and 800 cm.$^{-1}$; medium or weak absorption peaks occurred at 1725, 875, 725, and 675 cm.$^{-1}$.

Reduction of *cis*-1,4-Polybutadiene Ozonide

A preliminary fractionation of the ozonide described above was effected by triturating with ethyl ether, and the mixture was filtered. The procedure used for the reduction of the ozonide was essentially that described by Greenwood.[10] The ether solution of the ozonide (27 g.) was cooled to −10°C., and an ether solution of lithium aluminum hydride was added dropwise during 1.5 hr. at −5 to −10°C. until the reducing agent was present in excess. The reaction mixture was allowed to warm to 25°C. and then was heated at the reflux temperature for several hours. The reaction mixture was cooled, and the excess lithium aluminum hydride was decomposed by cautious addition of water. The ether layer was washed with water and dried by azeotroping with benzene. The solvent was evaporated to dryness and the residue dissolved in benzene. The hydroxy-terminated *cis*-1,4-polybutadiene was obtained by precipitation from benzene with petroleum ether. The light yellow fluid polymer obtained (5.8 g.) has a molecular weight of 300 (Rast), and a hydroxyl content of 0.66 eq./100 g.; it was shown to be 69% unsaturated (95% unsaturated after correction for the effects of the endgroups). The functionality of the polymer was 2.18, and intrinsic viscosity was 0.019 (measured in benzene at 30°C.). The olefinic bonds of the polymers were found to be 95% *cis*-1,4-, 1.3% *trans*-1,4-, and 3.4% vinyl by the method of Silas et al.[11]

Attempts to Control the Molecular Weight of Hydroxyl-Terminated *cis*-1,4-Polybutadiene

By Limiting the Amount of Ozone Used. In general, a 5 g. sample of *cis*-1,4-polybutadiene was dissolved in chloroform and a stream of ozonized oxygen was bubbled through the solution for 1 hr. If the time of ozonization was 45 min., very small amounts of liquid polymers were obtained. When the time of ozonization was reduced to 30 min., only intractable solids were obtained from the reduction of the ozonides. Reduction of the ozonization time did not affect the molecular weights significantly (as shown in Table I), but rather served only to decrease the yield of hydroxy-terminated polymer.

By Dissolving Higher Molecular Weight Ozonides. In addition to diethyl ether, several other solvents were used in the reduction of the ozonides in an effort to dissolve the higher molecular weight ozonides and obtain a product with a higher average molecular weight. When dibutyl ether was substituted for diethyl ether as solvent in the reduction, a brown viscous product was obtained, which had the following analysis: equivalents of hydroxyl per 100 g., 0.129; unsaturation, 60% (uncorrected); molecular weight determinations (Rast) were not reproducible. Use of pyridine as solvent in the reduction step gave dark, insoluble semisolids. Tetrahydrofuran did not yield enough material for characterization. With ethylene glycol dimethyl ether, a yellow liquid product was obtained with the following analysis: equivalents of hydroxyl per 100 g., 0.352; equivalents of carboxylic acid per 100 g., 0.016; unsaturation, 51% (70% corrected); molecular weight, 357 (Rast).

Preparation of the Isocyanate Curing Agent

A trifunctional isocyanate was prepared by reaction of 1,6-hexamethylene diisocyanate with trimethylolpropane by a method similar to that used in the preparation of Desmodur HH[6] except that the reaction was run in a manner which yielded primarily the trifunctional product.

Trimethylolpropane (6.70 g., 0.05 mole) was dissolved in dry monoglyme (90 ml.) and the solution was added dropwise to a stirred solution of 1,6-hexamethylene diisocyanate (47.40 g., 0.3 mole) in dry benzene. Time of addition was 3 hr., and the reaction mixture was heated at 75–80°C. during this time. The mixture was stirred 3 days at 25°C. and then heated at 125°C. under 1 mm. pressure overnight to remove solvent and excess 1,6-hexamethylene diisocyanate. The product was a viscous liquid which was assayed at 21.65% isocyanate. Calculations based on the assumption that the curing agent is a mixture of only di- and trifunctional isocyanates showed the material to be 94% trifunctional and 6% difunctional.

Preparation of Cured Rubber from the Liquid Polymer

Hydroxy-terminated *cis*-1,4-polybutadiene (13.32 g., 0.617 eq. —OH per 100 g., prepared as described above) was mixed with the isocyanate curing agent (12.91 g., 0.637 eq. —N=C=O per 100 g., 77% trifunctional and 23% difunctional, prepared as described above) and cured at 57°C. for 3 days. The product was a tough yellow rubber.

Dogbone specimens were cut from a $^1/_8$ in. sheet and tensile properties were determined by use of an Instron Model TM tensile tester (Instron Engineering Company, Quincy, Massachusetts). The tests were carried out at 77°F. with a crosshead separation rate of 0.5 in./min. The average value of tensile strength was 311 psi, and the average elongation was 59%, as measured from benchmarks on the specimens.

CONCLUSIONS

High molecular weight *cis*-1,4-polybutadiene rubber can be ozonized to yield low molecular weight, functionally modified liquid polymers with the *cis*-1,4-configuration. The oxidative hydrolysis of the ozonides to produce carboxy-terminated *cis*-1,4-polybutadiene is only partially successful. Although control of the molecular weight proved difficult, difunctional, hydroxy-terminated *cis*-1,4-poly-butadiene was synthesized by lithium aluminum hydride reduction of the ozonides The liquid polymer can be cured by isocyanates to give a soft, tough rubber which may be useful where castable rubbers are required.

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WILLIAM D. STEPHENS
CHARLES R. MCINTOSH
CURTIS O. TAYLOR

Thiokol Chemical Corporation
Huntsville Division
Huntsville, Alabama

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Cyclic Oligomer of Diethyleneglycol Terephthalate

Recently great interest has been shown in the mechanism of formation and the structure of cyclic oligomers contained in poly(ethylene terephthalate).[1,2] Cyclic tris-(ethylene terephthalate) is found to be the most abundant oligomer. Ross et al.[3] first isolated cyclic tris(ethylene terephthalate) from trichloroethylene extracts of poly(ethylene terephthalate) films. Hashimoto and Jinnai[4] obtained it by degradation of poly-(ethylene terephthalate) in benzene solution. Meraskentis and Zahn[5] succeeded in synthesizing the cyclic trimer under dilution conditions.

Some diethyleneglycol terephthalate units are incorporated into the polymer chain during polycondensation by several side reactions.[6] In some cases, diethyleneglycol is also added to polymer in order to improve dyeability of poly(ethylene terephthalate) fibers.[7]

While carrying on various investigations of poly(diethyleneglycol terephthalate), we have now found that a cyclic oligomer is formed in this case also. Thus, when poly-(diethyleneglycol terephthalate) was heated for 8 hr. at 300°C. under nitrogen, approximately 0.2% needles were sublimated. This sublimed crystal melted at 221–223°C. after several recrystallizations from benzene or ethyl acetate.

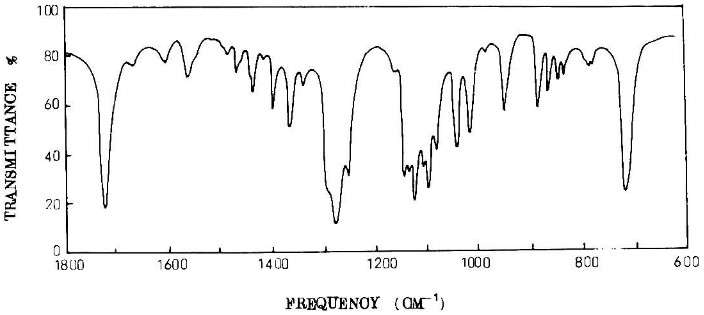

Fig. 1. Infrared absorption spectrum of compound.

The infrared spectrum of this compound, which is shown in Figure 1, includes absorption bands of diagnostic significance at 1719 cm.$^{-1}$, (C=O stretching), 1125 and 1099 cm.$^{-1}$ (C—O—C ether stretching), 1614, 1575, and 1500 cm.$^{-1}$ (C=C benzene ring stretching), 1406 cm.$^{-1}$ (C—C terephthaloyl stretching), 1479 and 1442 cm.$^{-1}$ (CH_2 bending), and 1371 and 1355 cm.$^{-1}$ (CH_2 wagging). However, absorption bands assigned to a hydroxyl group are absent.

This compound was hydrolyzed by boiling with 0.1*N* aqueous potassium hydroxide. When the resultant solution was acidified with hydrochloric acid, it was confirmed by the infrared spectrum that terephthalic acid is formed, and gas chromatographic analysis showed that diethyleneglycol is included in the filtrate.

Relevant analytical data are summarized in Table I, which shows the formula of this compound to the cyclic dimer of diethyleneglycol terephthalate, $(C_{12}H_{12}O_5)_2$.

In regard to the infrared spectrum of this compound, we estimate, from the results of Grime and Ward,[8] that the bands at 1479 and 1355 cm.$^{-1}$ are assigned to vibrations of the *trans* configuration of the $—OCH_2CH_2O—$ group and the bands at 1442 and 1371 cm.$^{-1}$ to the corresponding vibrations of the *gauche* configuration. For these reasons, we believe that the form of this cyclic dimer contains two *trans* ethylenic groups and two *gauche*.

It was also confirmed that the cyclic dimer is formed during polycondensation of poly-(diethyleneglycol terephthalate). When esterified products of terephthalic acid with diethyleneglycol were polymerized with antimony trioxide as catalyst at 285°C. for 3 hr.

under 0.5 mm. Hg, cyclic dimer sublimes as needles on the wall of the reaction vessel. Various analytical data and the infrared spectrum were the same as those of the product from degradation at a high temperature.

However, our attempts to extract the cyclic dimer from high molecular weight poly-(diethyleneglycol terephthalate) with various solvents failed, because of the difficulty of isolating it from very soluble polymer.

We have succeeded in synthesizing the cyclic dimer by reacting terephthalyl chloride with diethyleneglycol under high dilution conditions.

TABLE I
Analytical Data for This Compound

Mean value	Exptl. for compound	Calcd. for $(C_{12}H_{12}O_5)_n$
C, %	60.60	61.01
H, %	5.05	5.12
Saponification equivalent	120	118
Molecular weight[a]	457	236*n*
Molecularity	1.94	

[a] Measured by Rast method.

Chlorobenzene was used as solvent and tri-*n*-propylamine as base. After removing the solvent from the resulting reaction mixture, small amounts of acetone were added to the viscous, oily residue. The precipitated cyclic dimer was filtered off. The thus synthesized cyclic dimer melted at 220–223°C., after recrystallization from benzene or ethyl acetate. The mixed melting point with the dimer obtained from degradation of poly(diethyleneglycol terephthalate) was not depressed, and the infrared spectra are identical.

EXPERIMENTAL

In a flask fitted with a reflux condenser were placed 1700 ml. of chlorobenzene, 2.03 g. (0.01 mole) of terephthalyl chloride, and 3.58 g. (0.025 mole) of tri-*n*-propylamine. The mixture was heated to reflux, and a solution of 1.06 g. (0.01 mole) of diethyleneglycol in 150 ml. of chlorobenzene was added dropwise for 1 hr. After all the reactant had been added, the solution was refluxed for 3 hr. The reaction mixture was evaporated under vacuum, and to the remaining viscous, oily residue was added 30 ml. of acetone. The solid material (0.48 g.) was filtered off, washed with acetone several times, and dried. After recrystallization from benzene or ethyl acetate, the cyclic dimer was obtained as a colorless solid, m.p. 220–223°C.

ANAL. Calcd. for $(C_{12}H_{12}O_5)_n$: C, 61.01%; H, 5.12%; molecular weight ($n = 2$) 472. Found: C, 60.70%, 60.91%; H, 5.20%, 5.37%; molecular weight, 462, 459, 470 (average 464).

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Teijiro Morimoto
Yasuhiro Fujita
Akira Takeda

Research Center
Mitsui Petrochemical Industries, Ltd.
Iwakuni, Japan

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Polymerization of 4-Vinylpyridine by Sodium in Liquid Ammonia

Addition of 4-vinylpyridine monomers to a solution of Na metal in liquid NH_3 at -50°C. produced high molecular weight linear poly-4-vinylpyridine. Conversion of monomer to polymer was essentially complete in less than 1 min. The original dark blue color of the $Na–NH_3$ solution disappeared instantly when monomer was added, with simultaneous precipitation of red-orange solid. The color of the precipitate remained unchanged several hours in the reaction mixture and was apparently indefinitely stable, but the color was rapidly bleached to white upon introducing O_2, N_4HCl, or CH_3OH. Polymerizations were stopped by adding a small amount of NH_4Cl to the reaction vessels.

The solubilities, softening temperatures, and infrared spectra of the solid were similar to those of poly-4-vinylpyridine (P4VP) prepared by other anionic or free-radical polymerization methods.[1–4]

Polymerizations were carried out in all-glass equipment with rubber septum stoppers for injection of monomer. Glass-coated magnets provided agitation in the flasks. The assembled vessels and stirrers were baked at 250°C. at 10^{-5} torr several hours before adding freshly cut Na metal under vacuum from a side-arm. High purity NH_3 was distilled from Na through a glass filter into the reaction vessels. Monomer was purified by distilling from CaH_2 under reduced N_2 pressure, followed by several freeze-thaw degassing cycles at 10^{-4} torr.

Polymer was recovered by boiling off the NH_3, dissolving the crude polymer in CH_3OH to about 5% concentration, then precipitating the polymer by slowly adding the solution into a well agitated excess of aqueous NH_4OH. The precipitate was washed and vacuum-dried to constant weight at 60°C. and 0.1 torr.

Polymer molecular weights were determined by dilute solution viscometry of CH_3OH solutions in suspended-level viscometers. Polymer softening temperatures were measured with a modified Fisher-Johns apparatus. Infrared absorption spectra were obtained from polymer films cast from CH_3OH solutions onto NaCl crystals and vacuum dried. Typical experimental conditions and results are given in Table I.

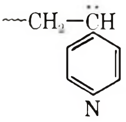
TABLE I
Polymerization of 4-Vinylpyridine with Na in Liquid NH_3 at -50°C.

[Na], mole/l.	[4VP], mole/l.	P4VP, g.	Yield, %	$\bar{M}_v \times 10^{-3}$, g./mole	Moles Na/mole polymer	$\frac{[4VP]}{[M_{Na}]}$
0.0165	1.04	4.87	97.0	235	37.3	63.0
0.0145	1.02	4.71	96.2	225	31.2	70.4

The values of the efficiency of the initiator are reported in the last column of Table I. They are comparable to reported values of 1–40 for styrene in liquid NH_3 with $NaNH_2$[5] and of 6–30 for methacrylonitrile in liquid NH_3 with Li metal.[6]

Purified and freeze-dried white poly-4-vinylpyridine exposed to $Na-NH_3$ solutions at -50°C. for several hours changed to yellow color. Addition of NH_4Cl rapidly restored the polymer to the original white, and the resulting polymer properties and infrared spectrum were the same as those of the original sample.

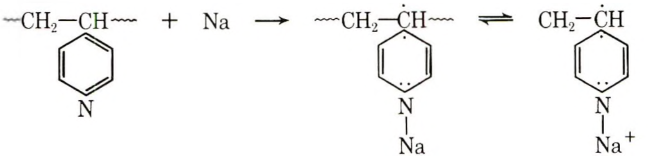
The red color observed during these polymerizations is probably due to the presence of the polyvinylpyridyl carbanion (I)



I

Formation of dipyridyl ions did not probably occur, since the polymer formed had physical and chemical properties similar to those of the polymer prepared by other methods. The presence of dipyridine linkage along the chain is expected to introduce stiffness with higher polymer melting points and lower solubility. In contrast to the case of methacrylonitrile,[6] no hydrodimerization products resulting from the possible presence of hydrodimers were found.

The yellow color developed during exposure of the polymer to Na is presumably due to the adduct formed between Na and the pyridine rings of the polymer. This adduct may dissociate to form a radical anion [eq. (1)].



(1)

The yellow color could not be due to reaction with reduction products formed during polymerization, as would probably occur with 4-ethylpyridine in Na–liquid NH_3. In fact, the color formation reaction occurred by introducing purified polymer in the presence of Na metal in liquid NH_3 in a clean vessel, different from that in which the polymerization occurred.

The formation of the adduct is probably a contributing factor to the large Na to polymer ratios reported in Table I. Termination with NH_4Cl might have hydrogenated the adduct.

The maximum possible extent of hydrogenation, based on the ratio of Na to polymer produced (Table I), corresponds to the addition of 1.4 wt.-% of H_2. Assuming that four hydrogens per ring reduced are involved, this value corresponds to $^1/_{260}$ of monomer units reduced. However, no hydrogenation could be detected by infrared spectra, softening temperatures, solubility, or reaction with phosgene.

The present observations suggest that a nonterminating polymerization occurred. It should be noted that previous reports on similar liquid NH_3 systems (methacrylonitrile with Li[6] or K[7] initiation; methacrylonitrile, styrene, methyl methacrylate, vinyl acetate with Na[8]) have shown that considerable termination by hydrogen abstraction took place. The observed red orange color, probably due to the polyvinylpyridyl anion, was similar to that developed during the electrochemical polymerization of vinylpyridine in liquid NH_3.[9] In this latter system, the presence of nonterminating polymer chains was clearly established.[4,10]

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D. LAURIN
G. PARRAVANO

Department of Chemical and Metallurgical Engineering
University of Michigan
Ann Arbor, Michigan 48104

Received June 28, 1967

Polymers from the Vinyl Esters of Different Samples of Hydrogenated Rosins

Two vinyl esters were prepared from Hercules hydrogenated rosins, Foral AX and Resin S1036 (an experimental resin), and furnished us by G. W. Hedrick[1] of the Naval Stores Laboratory. These vinyl esters were homopolymerized in emulsion and copolymerized with vinyl acetate, vinyl chloride, and butadiene and thus compared to vinyl tetrahydroabietate (VTA)[2] and vinyl dehydroabietate (VDA).[3] Resin S1036 (VRS) was more completely hydrogenated than Foral AX (VFAX) and had a bromine number of 10. Foral AX was a hydrogenated rosin having a bromine number of 50 which contained about 10% of dehydroabietic acid. These vinyl ester monomers were distilled under reduced pressure over a trace of copper resinate. The center cuts of redistilled monomer were used for polymerizations. The physical constants were b.p. 129°C./0.05 mm., n_D^{30} 1.5052 for VRS and b.p. 128°C./0.05 mm., n_D^{30} 1.5091 for VFAX. There was very little difference in their infrared spectra and the infrared spectrum of VTA. Thin-layer chromatography of both monomers showed two continuous spots.

Homopolymerization

VRS and VFAX were polymerized in emulsion by using three initiators. The experimental procedures were similar to the ones described in the polymerization of VTA.[2] The data for the homopolymerization of these monomers and of VTA and of VDA are given in Table I.

All of the polymers were obtained as white powders soluble in THF and could be molded into clear but very brittle films. Lower conversions in the polymerizations and lower inherent viscosities of the polymers obtained were noted as compared to VTA

TABLE I

Homopolymers of Vinyl Esters[a]

Monomer	Catalyst[b]	Conversion, %	Anal. C, %	Anal. H, %	η_{inh}[c]
VTA[d]	$K_2S_2O_8$	71	79.15	10.78	0.125
	AIBN	74	79.16	10.87	0.164
	DEABIB	73	79.37	11.03	0.179
VRS[e]	$K_2S_2O_8$	25	79.26	10.72	0.092
	AIBN	62	79.66	10.62	0.101
	DEABIB	61	79.36	10.77	0.119
VFAX[f]	$K_2S_2O_8$	13	79.44	10.43	0.064
	AIBN	35	80.04	10.52	0.083
	DEABIB	31	79.53	10.60	0.083
VDA[g]	$K_2S_2O_8$	46	80.50	9.37	0.057
	AIBN	51	80.78	9.25	0.056
	DEABIB	44	80.43	9.36	0.065

[a] All of the polymerizations were conducted at 60 ± 2°C. with tumbling of the tubes end-over-end for 48 hr. and with the use of 1% of Siponate DS-10 as emulsifier, and 5% of catalyst.

[b] AIBN = azobisisobutyronitrile; DEABIB = diethyl azobisisobutyrate.

[c] Determined on solutions of 0.400–0.410 g./100 ml. tetrahydrofuran at 30°C.

[d] Anal.: C, 79.46%; H, 10.91%.

[e] Anal.: C, 80.16%; H, 10.86%.

[f] Anal.: C, 79.97%; H, 10.71%.

[g] Anal.: C, 80.93%; H, 9.26%.

TABLE II
Copolymers of Vinyl Esters[a]

Charged composition		Polymerization time, hr.	Conversion, %	Vinyl ester, wt.-%[b]	η_{inh}[c]	Analysis						Comonomer in polymer, %
						Found			Calcd.			
Comonomer, wt.-%	Vinyl ester, wt.-%					C, %	H, %	Cl, %	C, %	H, %	Cl, %	
VAc 50	VTA 50	3	94	49	0.95	67.37	8.89		67.40	8.88		51
VAc 50	VRS 50	3	82	54	0.45	69.03	9.13		68.95	9.10		46
VAc 50	VFAX 50	3	64	68	0.12	72.22	9.45		72.23	9.53		32
VAc 50	VDA 50	48	58	62	0.16	71.24	8.51		71.38	8.40		38
												VCl %
VCl 80	VTA 20	48	88	10	0.85	42.74	5.40	50.70	42.94	5.50	50.50	90
VCl 80	VRS 20	48	75	10	0.65	42.08	5.32	51.42	42.60	5.43	51.07	90
VCl 80	VFAX 20	48	43	12	0.37	43.84	5.55	50.02	43.41	5.53	49.93	88
VCl 78	VDA 22	48	79	27	0.53	50.16	6.13	42.55	50.39	6.09	41.83	73

[a] All of the polymerizations were conducted at 60 ± 2°C. with tumbling of the tubes end-over-end and with the use of Siponate DS-10 as an emulsifier and $K_2S_2O_8$ as an initiator.

[b] Based on analysis for C, H, and Cl in the copolymer.

[c] Determined on solutions of 0.314–0.416 g./100 ml. tetrahydrofuran at 30°C.

TABLE III
Vinyl Ester Copolymer Films

Composition		
Comonomer, wt.-%	Vinyl ester, wt.-%	Properties of films
VAc 51	VTA 49	Soft, tough, transparent
VAc 46	VRS 54	Soft, elastic, transparent
VAc 32	VFAX 68	Very soft, weak, transparent
VAc 38	VDA 62	Very brittle
VCl 90	VTA 10	Tough, brown
VCl 90	VRS 10	Tough, brown
VCl 88	VFAX 12	Brittle, brown
VCl 73	VDA 27	Brittle, brown

polymer. In all of the polymerizations, the inherent viscosity of the polymer prepared with DEABIB as the initiator was found to be the highest. Analytical data (Table I) and infrared spectra for both polymers showed no significant difference in comparison to the VTA polymer. The VRS polymers were similar to the VTA polymer. The VFAX seemed to indicate similar homopolymerizability to the VDA.

Copolymerization

Copolymers of the vinyl esters with vinyl acetate (VAc) and vinyl chloride (VCl) have been prepared at the same monomer compositions. The experimental data are given in Table II along with those for the VTA copolymer and the VDA copolymer.

The copolymer of VAc and VRS was obtained as transparent, soft material soluble in THF, chloroform, and toluene and partially soluble in methanol. The copolymer of VAc with VFAX was obtained as light tan-colored, soft material soluble in THF, toluene, and chloroform. Analytical data on copolymers are given in Table II. It is surprising that the copolymers having higher inherent viscosity were obtained with higher conversion, considering the poor homopolymerizability of VRS and VFAX. This specific feature was observed in the copolymerization of VAc with VTA.[2] The chain-transfer activity of monomer in the copolymerization with VAc was shown to increase in the order VTA < VRS < VFAX < VDA and seemed to be proportional to the unsaturation in the acid.

The copolymers of VCl with VRS and VFAX were obtained as white powders soluble in THF which could be molded into transparent films at about 160°C. Both conversion and inherent viscosity of the copolymer decreased in the order VTA, VRS, VDA, and VFAX, so that the chain transfer activity seemed to increase in the order VTA < VRS < VDA < VFAX. This result was similar to the copolymerization with VAc. The properties of films molded from these copolymers at about 140°C. are given in Table III.

Vinyl Ester–Butadiene Copolymers

Copolymers of butadiene (BD) with VRS and VFAX were prepared for a comparison with VTA. The experimental data are given in Table IV.

All of the copolymers were obtained as white or light tan-colored rubbery materials. It was noted that increasing pH increased the conversion but decreased the butadiene content in the copolymer. It is also noted that the copolymers of BD and VRS and VFAX obtained in buffered emulsion were not all soluble in hot THF, benzene, or a mixture of both, while the copolymer of BD with VTA was soluble. Considering the conversion and inherent viscosity, the chain-transfer activity of VRS and VFAX

TABLE IV
Copolymers of Vinyl Esters with Butadiene[a]

Charged composition		Conversion, %			Soluble part		Analysis			
							Found		Calcd.	
BD, wt.-%	Vinyl ester, wt.-%	Buffered[b]	Unbuffered	BD, wt.-%[c]	Wt.-%[d]	η_{inh}[e]	C, %	H, %	C, %	H, %
42	VTA 58	32	—	43	100	0.28	83.53	10.50	83.48	11.09
40	VRS 60	38	—	22	13	0.51	82.07	10.96	82.06	10.93
40	VRS 60	—	5	68	100	0.77	86.09	10.95	86.04	11.09
40	VFAX 60	36	—	89	56	0.63	87.81	11.15	87.84	11.13
32	VFAX 68	—	21	93	100	0.91	88.22	11.23	88.20	11.16
41	VDA 59	42	—	75	17	0.36	86.83	10.81	86.84	10.69

[a] All of the polymerizations were conducted at 60 ± 2°C. with tumbling of the tubes end-over-end for 48 hr. and with the use of Siponate DS-10 as an emulsifier and $K_2S_2O_8$ as an initiator.

[b] pH = 7.00.

[c] Based on analysis for C and H in the copolymer.

[d] Soluble in hot tetrahydrofuran

[e] Determined on solutions of 0.051–0.344 g./100 ml. THF.

appeared to be lower than that of VTA. VRS and VFAX were similar to VDA in copolymerization with butadiene.

This is a partial report of work done under contract with the Western and Southern Utilization Research and Development Divisions, Agricultural Research Service, U.S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is supervised by Dr. Glen Fuller of the Western Division.

We are indebted to G. W. Hedrick and J. B. Lewis of The Naval Stores Research Laboratory, Southern Utilization Research and Development Division Agricultural Research Service, U.S.D.A., Olustee, Florida for the monomeric vinyl esters used in this work.

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WAKICHI FUKUDA
C. S. MARVEL

Department of Chemistry
The University of Arizona
Tucson, Arizona 85721

Received August 22, 1967

Crystals of Polymers Derived from Divinyl Compounds by Photoradiation in the Solid State

We have reported that 2,5-distyrylpyrazine (DSP) (I) polymerizes by photoirradiation in the solid state, resulting in a linear polymer (II) containing a cyclobutane ring in the main chain.[1] This reaction has been attempted with various divinyl compounds, and *trans,trans*-1,4-bis[β-pyridyl-(2)-vinyl]benzene (P2VB) (III) has been found to give a polymer (IV) just the same as that obtained with *trans,trans*-DSP; the details of the polymerization will be described elsewhere.

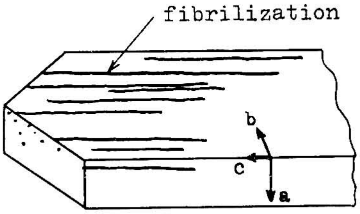


Fig. 1. Sketch of a fibrilar striation observed in the course of polymerization. Arrows indicate the crystallographic axes of the monomer crystal (Orthorhombic; $a = 20.9$, $b = 9.6$, $c = 7.3$ A.).

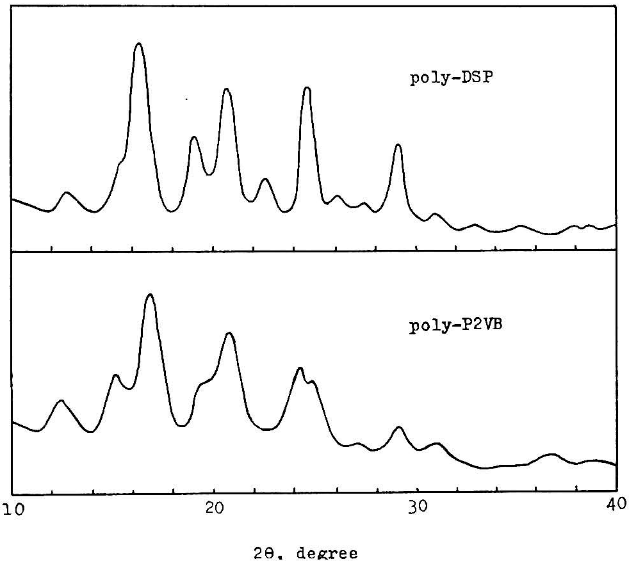
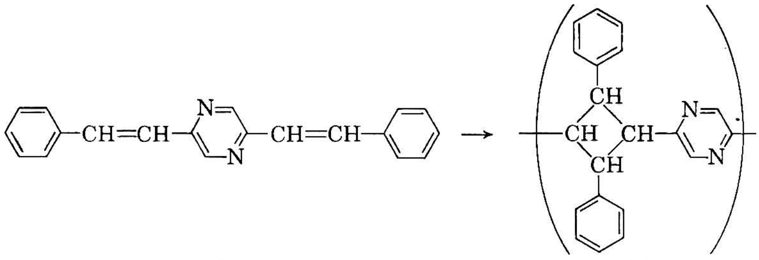


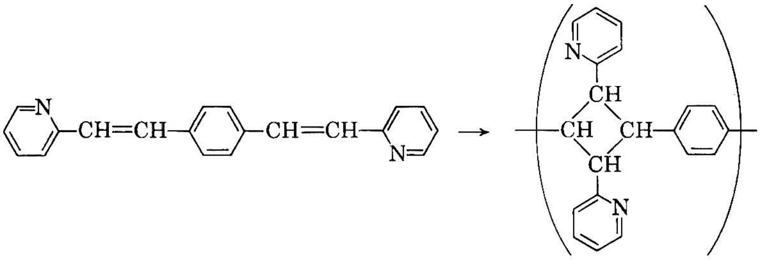
Fig. 2. X-ray diffraction diagrams of filbrilar poly-DSP and poly-P2VB as polymerized. Powder diagram.

Some crystallographic studies have also been carried out for both the polymers of DSP and P2VB. An observation of the crystal in the course of polymerization shows a fibrilar striation of the polymerized fraction aligned in a direction of the mother crystal as shown schematically in Figure 1 in the case of swordlike crystals obtained by sublimation. As the polymerization proceeds, the polymer tends to separate into a needlelike material, 1–5 mm. in length, which shows a clear birefringence under a polarizing microscope. Formation of the needlelike substance is quite common in the above two monomer crystals (DSP and P2VB) and does not depend on the conditions of preparation of the monomer crystals, i.e., a scalelike crystal of the monomer obtained from a solution shows the same fibrillation.



I

II

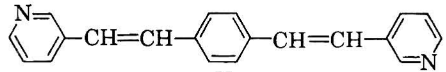


III

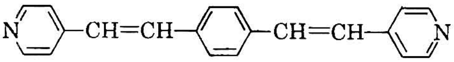
IV

The x-ray diffraction of the two polymers as polymerized is indicative of quite a high crystallinity, as seen in Figure 2, in contrast with the amorphous nature of the film when cast from a solution of polymer in trifluoroacetic acid followed by an extraction with triethylamine. In Figure 2 it is also seen that the main peaks of the two curves are at the same angles for poly-DSP and poly-P2VB, although they differ in their intensities. This suggests that crystals of the two polymers have the same unit cell and symmetry.

In order to investigate the mechanisms of polymerization, x-ray analysis has also been carried out on the two monomers and similar divinyl compounds. The powder diagrams of DSP and P2VB are nearly identical in both of their diffraction angles and intensities. They are, however, different from the curves of 1,4-bis[β-pyridyl-(3)vinyl]benzene (P3VB) (V) and 1,4-bis[β-pyridyl-(4)-vinyl]benzene (P4VB) (VI) which do not polymerize under the same radiation conditions (Fig. 3).



V



VI

Thus it may be assumed that the molecules of DSP and P2VB are favorably arranged for polymerization in the crystalline state and differ from those which do not polymerize. The unit cell of P2VB is orthorhombic with $a = 20.9$, $b = 9.6$ and $c = 7.3$ A., with the axes oriented as indicated in Figure 1 by arrows. The details of the arrangement of the

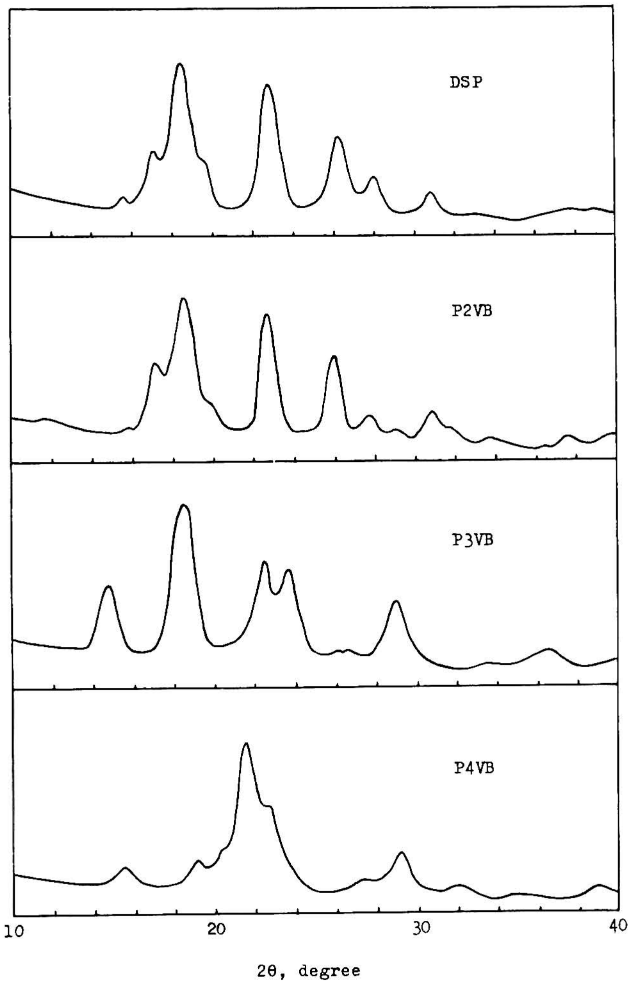


Fig. 3. X-ray diffraction diagrams of monomeric DSP and P2VB and similar divinyl compounds. Powder diagram.

molecules in the unit cell will be discussed elsewhere, but the direction of the polymer axis is nearly parallel with the *c* axis of the monomer, which may give rise to a specific growth of polymer into an extended-chain crystal with an extremely high crystallinity.

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Masatoshi Iguchi
Hachiro Nakanishi
Masaki Hasegawa

The Textile Research Institute of Japanese Government
Yokohama, Japan

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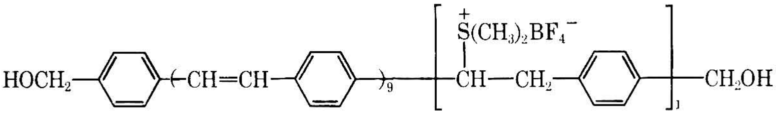
*Synthesis of Poly-*p*-xylylidene from* p*-Xylylenebis(dimethylsulfonium) Tetrafluoroborate*

There have been some papers on the synthesis of poly-*p*-xylylidene (I). McDonald and Cambell[1] obtained I by the Wittig condensation of terephthalaldehyde and *p*-xylylenebis(triphenylphosphonium) chloride. Smith[2] and Hoeg[3] prepared the same polymer by treating *p*-xylylene dichloride with sodium amide. Furthermore, Moritani et al.[4] have reported the formation of I through *p*-phenylene dicarbene which may be produced by the reaction of $\alpha,\alpha,\alpha,\alpha$-tetrabromo-*p*-xylylene with methyl lithium.

In this paper, we wish to describe a new method to obtain I from *p*-xylylenebis(dimethylsulfonium) tetrafluoroborate(II).

In a typical reaction, the following recipe was used: *p*-Xylylene dibromide (26.4 g., 0.10 mole) was dissolved in 200 ml. of dimethylformamide together with 24.8 g. (0.40 mole) of dimethyl sulfide and the solution was left overnight at room temperature to precipitate colorless crystals. Hygroscopic *p*-xylylenebis(dimethylsulfonium) bromide thus obtained was converted to the tetrafluoroborate, II (m.p. 220°C., decomp.) by mixing with $NaBF_4$ in the solution, in a yield of 72% (29 g.). To 80 ml. of a stirred aqueous solution of II (8.04 g., 0.02 mole), 120 ml. of 0.5*N* aqueous solution of sodium hydroxide was added slowly at 80°C. The reaction proceeded with vigorous evolution of dimethyl sulfide and produce a white precipitate, which then turned bright lemon-yellow. After 1.5 hr., the precipitate was separated and then treated with 10% alcoholic sodium hydroxide solution under reflux for 4.5 hr. to complete the reaction.

The greenish-brown polymer thus obtained (2.0 g., 98% yield based on pure xylylidene) was infusible and also insoluble in common solvents at their boiling points. The infrared spectrum (Fig. 1) exhibited characteristic absorption bands at 825 cm.$^{-1}$ (*p*-substituted benzene), 958 cm.$^{-1}$ (*trans*-ethylenic unsaturation), and 3450 cm.$^{-1}$ (hydroxy group). Elemental analysis gave the following results: C, 82.00%; H, 6.37%; S, 2.49%. The structure which gave the best fit to these data was:



for which calculated values are: C, 82.65%; H, 5.93%; S, 2.44%).

Furthermore, the following bromination and oxidation experiments supported the *p*-xylylidene structure. The polymer was brominated with excess bromine in carbon tetrachloride (0°C., 12 hr.) to give a colorless product (Calcd.: C, 39.37%; H, 2.83%;

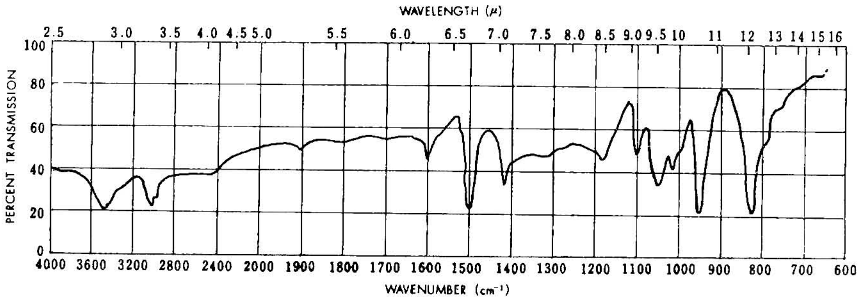
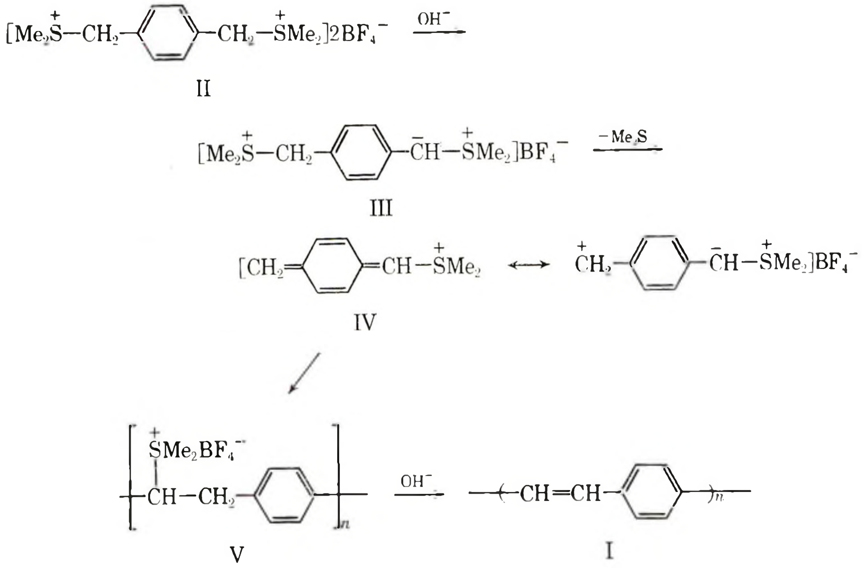


Fig. 1. Infrared absorption spectrum of poly-*p*-xylylidene (KBr pellet).

Br, 52.36%. Found: C, 42.94%; H, 3.36%; Br, 49.04%). The infrared absorption spectrum of this showed complete disappearance of the peak at 958 cm.$^{-1}$ In the permanganate oxidation of the polymer, terephthalic acid was produced.

We propose a mechanism for the formation of the polymer I in which sulfur ylid III formed from II with equimolecular amounts of base eliminates one mole of dimethylsulfide to yield an intermediate (IV) of *p*-quinodimethane type. The intermediate IV polymerizes to V (colorless), and then V may produce polymer I by β-elimination with excess base.

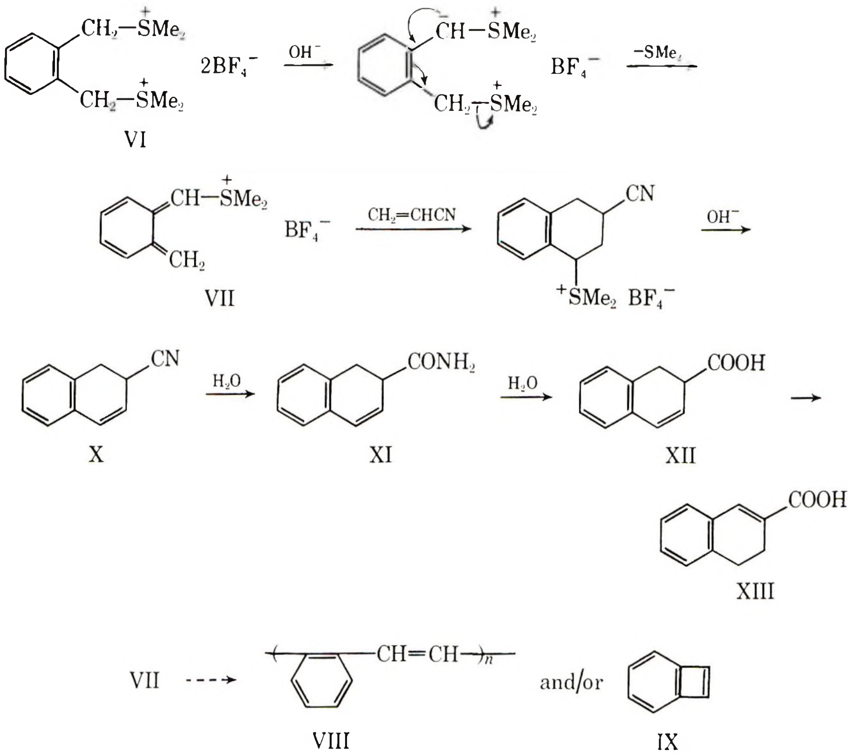


The above method would be superior for obtaining I to the phosphorylid method using, instead of II, *p*-xylylenebis(triphenylphosphonium) bromide which produces only triphenylphosphine oxide and water-soluble products.

In the case of *o*-xylylenebis(dimethylsulfonium) tetrafluoroborate (VI) (m.p. 206–207°C., decomp.), the formation of the corresponding poly-*o*-xylylidene (VIII) or the products derived from benzocyclobutadiene (IX) might be expected.

On treating the aqueous solution of the sulfonium salt VI with excess sodium hydroxide, a benzene-soluble, yellow polymer (molecular weight by cryoscopic method, 1700) was obtained. However, no infrared absorption band due to *trans*-ethylenic unsaturation was detected in this polymer. Analysis of the polymer showed C, 86.31%; H, 6.58%; S, 2.57%. No further attempts were made to determine the structure of this polymer.

On the other hand, the formation of an intermediate (VII) of *o*-quinodimethane type corresponding to IV was proved by the reaction carried out in the presence of acrylonitrile. Thus, reaction of the aqueous solution of the sulfonium salt VI and excess acrylonitrile with sodium hydroxide gave 1,2-dihydro-2-naphthonitrile (X) (m.p. 55.5–56.5°C.) and 1,2-dihydro-2-naphthoamide (XI) (m.p. 153°C.) in yields of 26 and 4%, respectively. When X was treated with 25% aqueous sodium hydroxide solution at 150°C., 3,4-dihydro-2-naphthoic acid (XIII) (m.p. 118°C., lit.[5] m.p. 118°C.) was produced quantitatively. The formation of XIII from X might be ascribed to the double bond migration[5] of 1,2-dihydro-2-naphthoic acid (XII) produced by the hydrolysis of X.



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MASARU KANBE*
MAKOTO OKAWARA

Research Laboratory of Resources Utilization
Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo, Japan

Received September 25, 1967
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* Present address: Konishiroku Photo Industry Co., Ltd. Niphonbashi Muromachi, Chuo-ku, Tokyo, Japan

Identification of Cellulose Phenylpropionylphenylpropionate as a Side Product in the Reaction of Cotton Cellulose with Phenylpropionyl Chloride

INTRODUCTION

In the course of our studies on the esterification reaction of cotton cellulose with propionyl chloride[1] in a medium of pyridine and dimethylformamide (DMF), it was found that a side reaction occurs. The product was a mixed ester of cellulose propionate and cellulose propionylpropionate (see below). The latter arises from the substitution of the α-hydrogen atom of the primary ester with another propionyl moiety. It was of interest to know whether such a side reaction in cellulose esterification is peculiar to propionyl chloride only or would take place with other acid chlorides of similar nature under identical conditions. The present report shows that the side reaction does take place with another acid chloride, β-phenylpropionyl chloride, and describes how the side product was identified and quantitatively determined.

EXPERIMENTAL

Chemicals

β-Phenylpropionyl chloride and dimethylformamide (DMF) were Eastman reagent grade and were used as such. Pyridine and methanol were Baker analyzed reagent grade.

β-Phenylpropionic acid was prepared by hydrolysis of phenylpropionyl chloride and recrystallization from water. The melting point was 48–48.5°C. (lit.[2] m.p.: 48.6°C.).

1,5-Diphenyl-3-pentanone was prepared by the method of Dünschmann and Pechmann.[3] The semicarbazone prepared from this ketone had a melting point of 115.5–116.5°C. in a Kofler hot stage (lit.[4] m.p.: 118°C.).

Preparations of the Samples

The ester samples were prepared by the acid chloride-pyridine method[5] at 75°C. The molar quantity of phenylpropionyl chloride used was twice that estimated for the total hydroxyl groups in the sample of cellulose taken (7/2 cotton yarn) for samples 1–5 (Table I). The volume of pyridine was double that of the acid chloride and was diluted with 4.5 times its volume of DMF except for sample 3, in which case the pyridine was diluted with only 1.3 times its volume. After the reaction, each sample was washed successively with pyridine, a solution made from equal volumes of pyridine and methanol, methanol, and finally with water, and then dried.

TABLE I
Estimation of the Side Chain

Sample number	Weight gain (WG), g./mole of cellulose	Apparent DS_β (WG/132)	DS_{sap} ($DS_\beta + DS_{\beta\beta}$)	DS_β (calculated)	$DS_{\beta\beta}$ (calculated)
1	17	0.13	0.07	0.01	0.06
2	66	0.50	0.37	0.24	0.13
3	106	0.80	0.58	0.36	0.22
4	167	1.27	0.92	0.57	0.35
5	226	1.71	1.23	0.75	0.48

Degree of Substitution

The apparent degree of substitution as phenylpropionate was determined from the weight gain. The actual degree of substitution was determined by saponification according to Genung and Mallatt.[6]

The degree of substitution as β-phenylpropionate (DS_β) and the degree of substitution as α-(β-phenylpropionyl)-β-phenylpropionate ($DS_{\beta\beta}$) were calculated by using the equations:

$$DS_{sap} = DS_\beta + DS_{\beta\beta}$$

$$WG_{mole} = 132\ DS_\beta + 264\ DS_{\beta\beta}$$

where WG_{mole} is the weight gain per mole of cellulose. These data are shown in Table I.

Chromatography

An F & M Model 500 gas–liquid chromatograph was used with a column containing silicone gum rubber on Chromosorb W. A column temperature of 150°C. was maintained for obtaining the acid peaks and 200°C. was used for the diphenylpentanone since it did not come out below this temperature.

Samples of the mixed ester (4 mg.) were sealed into glass ampules. Each ampule was then introduced into the injection port of the chromatograph, kept for 7 min. at 375°C. and then broken. Peaks were obtained which corresponded to those of the known β-phenylpropionic acid and the known 1,5-diphenyl-3-pentanone.

Large quantities of the diphenylpentanone were obtained from the solutions remaining after saponification of the cellulose esters. The solutions were acidified and then concentrated on a steam bath. The concentrate was extracted with a little benzene and this benzene solution was then injected into the chromatograph and the material producing the ketone peak was collected in carbon tetrachloride.

Infrared

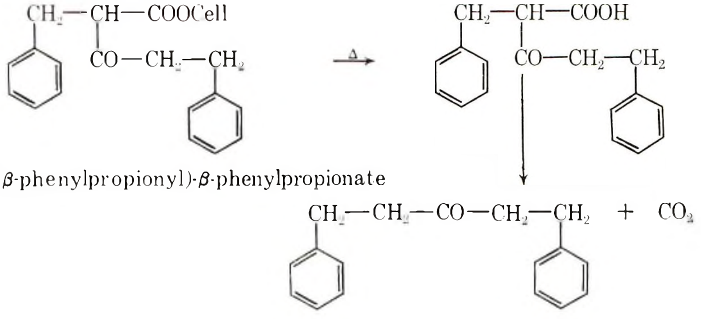
A Perkin-Elmer Model 21 double-beam spectrophotometer was used to obtain the infrared spectra.

Nuclear Magnetic Resonance

A Varian A-60 A NMR spectrometer was used to obtain the spectra with tetramethylsilane as reference.

RESULTS AND DISCUSSION

The presence of side chains was indicated by the lack of agreement in the apparent DS values from weight gain and those from saponification. As with cellulose propionates,[1]



Cellulose α-(β-phenylpropionyl)-β-phenylpropionate

1,5-Diphenyl-3-pentanone

the former were always higher than the latter (Table I). Also an extra peak corresponding to 1,5-diphenyl-3-pentanone was observed in the chromatograms of all the samples. In close analogy to the propionates this may arise from the ester side chain: The recovery of the same component from the liquid left after saponification experiments, as described in the experimental section, lends further support to the above assumptions. As further evidence of this reaction taking place on pyrolysis of the ester, the semicarbazone was prepared from both the synthetic sample and the ketone fraction as recovered from the yarn sample by the method described. The melting point of the semicarbazone was identical in both cases (115.5–116.5°C.) and compared well with the value given in the literature.[4]

In order to confirm the above findings, infrared and NMR spectra of the above samples were recorded. Infrared spectra of both the samples were essentially identical, with sharp absorption for the ketonic group at 1725–1730 cm.$^{-1}$ as well as for $=$C—H stretching of the benzene ring at 3030 cm.$^{-1}$ and at the 1600–1500 cm.$^{-1}$ region for C$=$C vibrations. NMR spectra of the two samples are also identical except for a sharp singlet at 5.93 ppm in both spectra which could not be explained and accounted for from the structure of 1,5-diphenyl-3-pentanone. However, this extra peak varies in intensity in the samples examined and might have come from some unknown adventitious impurities. This may also account for the minor difference in the infrared spectra of the two samples. The ratio of the integrated areas in the NMR spectra for protons from the phenyl group (at 7.2 ppm) and methylene groups (at about 2.8 ppm) conform to the structure of 1,5-diphenyl-3-pentanone in both the samples. This together with the infrared spectra and the identical melting point of the semicarbazones strongly suggest that the ketone recovered from the yarn sample is 1,5-diphenyl-3-pentanone and was formed by the decarboxylation of α-(β-phenylpropionyl)-β-phenylpropionic acid, formed in the side chain in the reaction of the cellulose yarn with β-phenylpropionyl chloride in pyridine-DMF media.

A plot of DS as β-phenylpropionate versus α-(β-phenylpropionyl)-β-phenylpropionate shows that on the average about 40% of the groups attached to the cellulose contain a side chain. This is much higher than with the propionate where the side chain occurs in about 25% of the attached groups.

It is probable that the propionyl chlorides react at the most accessible hydroxyl groups first to produce cellulose ester. Once some ester has been formed, competition between formation of additional ester and side chain takes place. With the less bulky propionyl chloride, penetration of the cellulose is facilitated, and hence a relatively greater amount of unbranched ester is produced with this acid chloride.

The authors wish to express appreciation to E. R. McCall and N. C. Morris for the infrared spectra, and to G. J. Boudreaux for the NMR spectra. Thanks are also due to C. M. Conrad and V. W. Tripp for helpful discussions during the course of this investigation and during the preparation of the manuscript.

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Anil K. Sircar*
David J. Stanonis

Plant Fibers Pioneering Research Laboratory
Southern Utilization Research and Development Division
United States Department of Agriculture
New Orleans, Louisiana 70119

Received October 26, 1967

* Postdoctoral Resident Research Associate, 1965–1967. Present address, J. M. Huber Corporation, Borger, Texas.

Isolation of Pure p-Divinylbenzene from Commercial Divinylbenzene

The use of Werner complexes in the separation of hard to separate mixtures of aromatic compounds has been reported.[1,2] We have investigated the possibility of using this technique to separate *p*-divinylbenzene (*p*-DVB) from commercial DVB, which is a complex mixture of *m*- and *p*-diethylbenzene, *m*- and *p*-ethylvinylbenzene, *m*- and *p*-divinylbenzene, with traces of naphthalene and indene, by complexing with cuprous chloride.[3-5] *p*-DVB was reported to form selectively a solid complex with cuprous chloride at an optimum ratio of 1:1 and at 0–5°C.

In a typical experiment, 100 g. of commercial DVB (supplied by Dow Chemical Co. *p*-DVB content 20.5%) was placed in a 400 ml. beaker and was cooled to 0–5°C. A 30 g. portion of anhydrous cuprous chloride (Baker analyzed reagent) was added in small quantities at a time with continuous stirring. As the slurry became viscous small quantities of toluene were added (total about 50 ml.) to render the slurry mobile. After stirring for 30 min. the yellow, solid complex was collected on a Buchner funnel with suction. The solid was reslurried with 100 ml. of toluene cooled to 0–5°C. and was again collected. The toluene washing was repeated twice more. Finally the solid was suspended in 100 ml. of toluene and was decomposed by heating to 80°C. The grey slurry was filtered hot and the cake of cuprous chloride was washed with hot toluene. The toluene was separated from the combined filtrate and washings by fractionation under vacuum. The residue was distilled to give 12–13 g. (60–65% yield) of *p*-DVB. With 10 g. of commercial DVB, twice complexed, the yield was 40–50%.

p-DVB samples thus obtained were subjected to gas-chromatographic analysis with a Perkin-Elmer vapor fractometer, Model 154D with R [poly(propylene glycol) on Chromosorb-W] column. The purity of the samples as found from relative peak, areas varied from 80–90% in a series of three check runs.

For further purification, a sample was partially crystallized by cooling to 5°C. and the unfrozen liquid was decanted. The remaining solid crystals (5.8 g. from 13.2 g.) were 96.5% pure. Further purification by one preparative gas chromatographic separation on Bentone[4] gave material of 99.9+% purity in 40% yield. If the unrecrystallized 80–90% purity material is chromatographed directly, it must be passed through the column at least twice to get a purity of 99+% with considerably less favorable overall yield.

This work was supported in part by the U.S. Atomic Energy Commission under Contract AT-(30-1)-3644 with Hunter College of the City University of New York.

We are indebted to Mr. J. M. Looney, Cosden Chemical Company, for providing us with the details of such a separation as used in their laboratories.

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Richard H. Wiley[6]
J. I. Jin
Y. Kamath

Department of Chemistry
Graduate Division
Hunter College, The City University of New York
New York, New York 10021

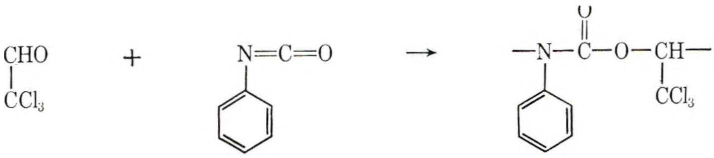
Received October 20, 1967

Copolymers of Chloral and Heterocumulenes

Copolymers of formaldehyde with phenyl or alkyl isocyanates have been described.[1-3] Recently copolymers of acetaldehyde with ethyl isocyanate, of *n*- or isobutyraldehyde with phenyl isocyanate and of chloral with phenyl isocyanate have been reported.[4,5] In most cases low polymerization temperatures with butyllithium as a catalyst were used.

We have found[6] that chloral copolymerized easily with aryl isocyanates and also with *N*-sulfinylaniline at room temperature and in the presence of a tertiary amine. Homo- or copolymerizations of *N*-sulfinylaniline have not been reported. Sulfinylaniline is known to form crystalline adducts with equimolar amounts of aldehydes or ketones, except chloral.[7]

The two copolymers, however, differed widely in structure. The chloral–phenyl isocyanate copolymer can be described as a polymeric methylidene carbanilate (I).

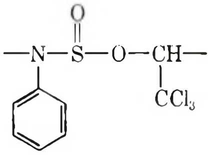


I

The presence of C=O absorption peaks in the infrared spectrum (5.8 μ) of copolymer I showed that polymerization had proceeded through the N=C bond of the isocyanate. The results of elemental analysis agreed well with the structure I. Proof of copolymerization was based on the fact that the copolymers were soluble in common organic solvents and contained 52–66 mole-% of chloral. If a mixture of homopolymers had been present, the polychloral would have been insoluble.

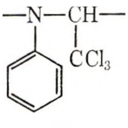
Butyl isocyanate could not be polymerized with chloral.

The copolymerization of chloral and *N*-sulfinylaniline in the presence of 0.6% of water yielded a soluble polymer with a molecular weight of 5000. It does not have the expected methylidene iminosulfinate II structure (II):



II

It was found that sulfur dioxide was evolved during the reaction. The final copolymer contained 5.7% of nitrogen and less than 0.4% of sulfur. The structure suggested for this copolymer is that of a substituted poly(methylidine aniline) (III).



III

Infrared absorptions around 7.4 to 8.5 μ, in addition to the elemental analysis, indicated the presence of small amounts of structure II. Since the oxygen content of the copolymer exceeded the amount calculated from sulfur content for structure II, it is possible that some ring substitution occurred. However, the formation of short polychloral segments in the copolymerization would also account for excess of oxygen. The

TABLE I
Copolymers of Chloral with Isocyanates and N-Sulfinylaniline at 25°C.

Comonomer		Mole ratio mono-mer/cat.	Solvent	Reaction time, days	Yield, %	Chloral in polymer, mole-%[b]	M.W.	M.P., °C.	Solubility
Mole-%	Type[a]								
50	PhI	500/1	Benzene	7	26.7	66.1	13,500	241–251 (dec.)	Benzene, THF
60	PhI	500/1	Benzene	7	59.0	62.3	16,700	237–247 (dec.)	Benzene, THF
70	PhI	500/1	Benzene	7	35.5	63.6	20,400	244–258 (dec.)	Benzene, THF
60	PhI	50/1	Toluene	1[c]	35.9	76.5	—	275–290 (dec.)	Ins.
60	PhI	1900/1	Toluene	1[c]	17.4	52.2	—	275–290 (dec.)	Ins.
50	*m*-ClPhI	28/1	Toluene	6	50.0	55.4	11,200	205–207 (dec.)	Benzene, THF
50	ATI	56/1	Toluene	1	48.0	53.2	7,290	175–180	Benzene, THF
50	SA	500/1	Bulk	2	45.5	61.0	4,900	280 [205 (dec.)]	MEK, THF

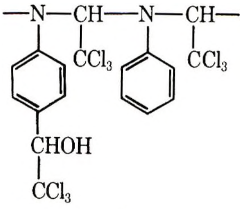
[a] PhI = phenyl isocyanate; *m*-ClPhI = *m*-chlorophenyl isocyanate; ATI = 2-*n* amyloxycarbamoyl 4-toluene isocyanate; SA = *N*-sulfinylaniline.

[b] Based on elemental analysis.

[c] Reaction temperature: −75°C.

elemental analysis corresponded closely to a copolymer of aniline, trichloroethylidene, and chloral in molar ratios of 5.18:3.08:1.78, respectively.

The final structure might be IV:



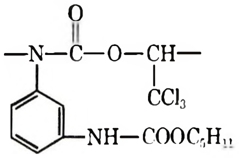
IV

When the monomers were thoroughly dried (<10 ppm H_2O) only polychloral was formed.

Reaction conditions and properties of several copolymers are summarized in Table V. The polymerizations were carried out in bulk, in benzene, or in toluene solution. Tertiary amines were used as catalysts (triethylamine or 1,4-diazabicyclo[2,2,2]octane) at room temperature. Molecular weights were determined in a vapor pressure osmometer (Mechrolab, Inc., Model 302) and ranged from 3,000 to 20,000. The composition of the copolymers was found to vary only slightly when the monomer ratios, the substitution on the benzene ring, or the extent of the reaction was varied.

Fig. 1. X-ray diagrams of chloral–phenyl isocyanate copolymers (CuKα): (left) with triethylamine catalyst, 25°C.; (right) with butyllithium catalyst, −75°C.

When phenyl isocyanate was replaced by 2-*n*-amyloxycarbamoyl 4-toluene isocyanate, obtained by reacting equimolar amounts of amyl alcohol wth 2,4-tolylene diisocyanate, the melting point of the resulting copolymer was low (180°C.) but the molar chloral content was in the same range as for the other copolymers. As expected, this polymer (V) had higher flexibility than the previous ones.



V

The polymer was soluble, confirming the higher reactivity of the *ortho* isocyanate group towards amyl alcohol. As a result, mostly 2-*n*-amyloxycarbamoyl 4-toluene isocyanate was formed and little, if any, unreacted diisocyanate was present during the reaction with chloral.

It is also possible to apply the reaction to urethane prepolymers, formed from two moles of a diisocyanate and one mole of a diol. This resulted in crosslinked polymers with a broad range of elasticity, depending on the amount of chloral and type and molecular weight of the diol used.[6]

The copolymers based on simple aryl isocyanates were colorless, transparent, hard, brittle, and high melting. Copolymers derived from sulfinylaniline were yellow. All copolymers showed discoloration when heated above their melting points (240–275°C.).

When the copolymerization of equimolar amounts of phenyl isocyanate and chloral was conducted with butyllithium as catalyst at -75°C., the copolymer was insoluble in tetrahydrofuran, dimethylformamide, or dimethyl sulfoxide and decomposed in concentrated sulfuric acid only at 100°C. The x-ray diagram (Fig. 1) revealed about 50% crystallinity, while a similar copolymer made at room temperature was amorphous. A stereoregular structure and perfect alternation of the comonomers at least over large chain segments is assumed.

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MAURICE C. RAES
JOSEPH V. KARABINOS
HEINZ J. DIETRICH

Olin Research Center
New Haven, Connecticut 06504

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BOOK REVIEW

Graft Copolymers. H. A. J. BATTAERD and G. W. TREGEAR. Interscience, New York, 1967. 551 + xii pp. $27.50.

The useful feature of this book—a literature survey of block and graft polymers, synthetic techniques, properties, commercial applications, and patents issued—is its collection of some 3000 references, patents, and abstracts of many of the published papers. More than half the book—300 pages—is devoted to the compounds listed in the patents. Inclusion of relatively recent (1964–1965) and significant papers by Benoit, Urwin, Stearne, Krause, and Ende enhance the value of the book. It is well organized and presents sufficient background material to serve as an introduction to the fascinating world of blocks and grafts. For these reasons the book is recommended to workers in the field.

With all these features, this work, nevertheless, is not as complete an account of this area of polymer chemistry as it might be: it falls short of its mark to correlate and unify what is known about blocks and grafts; and indeed, one expects a more profound contribution from a book, even when it is part of a review series. For example: The discussion about the Pluronics, Tetronics, and ABS polymers is dispensed with in a few sentences and the authors miss the opportunity to capitalize on the wealth of structure–property relations reported for these examples of the ingenuity of polymer scientists. In fact, commercial exploitation of all blocks and grafts is taken care of in only 6 pages. And ABS—probably the highest volume graft system produced—is *not,* as the authors state, a low cost engineering plastic and its mechanical properties at high temperatures are *inferior* to nylon, acetal, and polycarbonate. Copolymerization of styrene with unsaturated esters is discussed in terms of references 11 yr. old, while 1965–1966 papers describing kinetics of this radiation-graft have been overlooked.

The presentation is uneven in its balance. A large segment of the Japanese literature is not reviewed because such papers, the authors state, are "hard to translate and... [require much] time and money." Fiber grafts are not reviewed because these are "surface modifications rather than graft copolymers *per se*"–a distinction difficult to reconcile with the 60 pages devoted to radiation grafts which to a large extent are surface changes.

The chapter on synthetic methods devotes 1½ pages of the barest, insufficient summary of chain transfer—a technique that lends itself to rigorous analysis—compared to 60 pages on radiation techniques in which such minutae as pair production and Compton scattering, as well as copolymerization kinetics are described. Extension of the latter material to graft systems is assessed correctly by the authors: "The rate constants derived by most authors... do not apply to the actual... reaction."

The authors frustrate the reader frequently by making tantalizing statements such as, "Detailed melt flow data... are reported," and then not divulging more details. Again, "...evaluate rate constants for the grafting reaction," but, alas, no more information is presented.

While the book is a useful addition to the literature it is not a definitive analysis of the field of blocks and grafts.

W. J. Burlant

Scientific Research Staff
Ford Motor Company
Dearborn, Michigan