Polymerization and Copolymerization of Methacrylic Esters Derived from Glycidyl Methacrylate

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Synopsis

Copolymerization of methacrylic esters derived from glycidyl methacrylate and nucleophiles with styrene was carried out. The monomer reactivity ratios of these methacrylic esters were varied with the alkoxy groups of the esters and the solvent used.

INTRODUCTION

The effect of the alkyl group on the reactivity of alkyl methacrylate monomers in radical polymerizations has been studied by many workers.¹⁻⁴ Otsu et al. studied the effect of alkyl group on the rates of polymerization of alkyl methacrylates and concluded that the steric interaction is involved in the propagation process in the radical polymerization of isobornyl (*exo* bornyl) methacrylate. However, there are very few descriptions that copolymerization of alkyl methacrylates varies with alkyl groups and solvents used.

The present paper reports the copolymerizability of methacrylic esters derived from glycidyl methacrylate (GMA) by its ring-opening reaction with nucleophilic reagents such as aniline, naphthylamine, and phenol. The copolymerizability of such methacrylic esters varied with the kind of nucleophiles used and further with the type of polymerization solvent.

RESULTS AND DISCUSSION

Homopolymerization

The methacrylic esters⁵ used in the present study are shown in Table I. Compounds I, II, and IV gave homopolymers in bulk or solution polymerization with azobisisobutyronitrile (AIBN) as an initiator. Compound III polymerized in benzene and compounds V and VI gave homopolymers in dioxane.

Homopolymers of I, II, III, and IV were white powders soluble in organic solvents such as acetone, benzene, and dioxane. The homopolymer

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No.	Melting point, °C.	Boiling point, °C./mm.
$1 CH_2 = CCOOCH_2CHCH_2NH \longrightarrow OH$	42	_
$\begin{array}{c} CH_{3} \\ \\ H_{2} = CCOOCH_{2}CHCH_{2}N \\ \\ OH \end{array}$	—	163-165/2
III CH ₂ =CCOOCH ₂ CHCH ₂ NH	85-85.5	
$ \begin{array}{c} CH_3 \\ \downarrow \\ IV \\ CH_2 = CCOOCH_2CHCH_2O \\ \downarrow \\ OH \end{array} $	-	185-186/5
$V CH_2 = CCOOCH_2CHCH_2NH - N = N - N$	111-112	
VI CH ₂ =CCOOCH ₂ CHCH ₂ NH	157–158	_

 TABLE I

 Methacrylic Esters Derived from GMA

of V was yellow and the homopolymer of VI was a red powder, and both these homopolymers were also soluble in the organic solvents listed above. All of the homopolymers were insoluble in methanol and hydrocarbons such as petroleum ether and hexane.

Copolymerization

Compounds I, II, and IV were copolymerized with styrene in bulk. Solution copolymerizations of I, II, III, IV, and methyl methacrylate (MMA) with styrene were carried out in benzene. The copolymerization of compounds V and VI was examined in dioxane. The monomer reactivity ratios of these compounds were estimated by the Fineman-Ross equation from contents of each component in the monomer feeds and compositions of the copolymers obtained by elemental analysis. The compositions of the monomer feeds and the copolymers obtained are summarized in Tables II–XI. The monomer reactivity ratios estimated are shown in Table XII.

Monomer, mole-%		N in copolymer	Copolymer composition		
M_1	M_2	%	m_1	m_2	
90.26	9.74	2.46	76.22	23.78	
80.95	19.05	3.32	64.16	35.84	
71.14	28.86	3.76	56.83	43.17	
60.17	39.83	4.12	50.09	49.91	
50.57	49.43	4.39	49.54	55.46	
38.80	61.20	4.59	40.11	59.89	
20.45	79.55	5.12	26.82	73.18	

TABLE IICopolymerization of Styrene (M_1) and I (M_2) in Bulk

TABLE III

Copolymerization of Styrene $\left(\mathbf{M}_{1}\right)$ and 1 $\left(\mathbf{M}_{2}\right)$ in Benzene

Monomers, mole-%		N in copolymer	Copolymer, composition, mole-%		
M1	M_2	%	m_1	m_2	
77.15	22.85	3.87	54.8	45.2	
69.65	30.35	4.10	50.5	49.5	
36.75	63.25	4.98	30.7	69.3	
34.90	65.10	4.98	30.7	69.3	

TABLE IV

Copolymerization of Styrene $\left(M_{1}\right)$ and I $\left(M_{2}\right)$ in Dioxane

Monomers, mole-%		Monomers, mole-% N in copolymer.		Copolymer composition, mole-%		
M_1	M_2		m_1	m_2		
80.0	20.0	2.89	70.4	29.6		
68.1	31.9	3.62	59.2	40.8		
59.8	40.2	4.01	52.2	47.8		
50.0	50.9	4.19	48.9	51.1		
42.0	58.9	4.06	50.9	49.1		

 $\begin{array}{c} {\bf TABLE} \ V \\ {\bf Copolymerization \ of \ Styrene \ } (M_1) \ and \ \Pi \ (M_2) \ in \ Bulk \end{array}$

Monomers, mole-%		N in copolymer.	Copolymer composition, mole-%	
M_1	\mathbf{M}_2	%	m_1	\mathbf{n}_{1_2}
78.95	21.05	3.09	66.18	33.82
71.99	28.01	3.43	60.90	39.10
62.53	37.47	3.81	53.15	46.85
31.82	68.18	4.51	36.98	63.02
21.03	78.97	4.81	28.62	71.38

Monomers, mole- c_{c}		Ionomers, mole-% N in conclymer		Copolymer composition, mole- \mathbb{S}_0^{\times}		
Mt	M_2	%	$\mathbf{m}_{\mathbf{I}}$	\mathbf{m}_2		
90.1	9.9	2.30	77.5	22.5		
81.1	18.9	3.14	65.5	34.5		
72.4	27.6	3.78	53.8	46.2		
61.3	38.7	4.05	48.1	51.9		
50.9	49.1	4,30	42.3	57.7		
41.7	58.3	4.52	36.8	63.2		
32.9	67.1	4.71	31.6	68.4		
21.9	78.1	4.97	23.8	76.2		

TABLE VI Copolymerization of Styrene (M₁) and H (M₂) in Benzene

TABLE VII

Copolymerization of Styrene (M_1) and III (M_2) in Benzene

Monomers, mole-%		N in copolymer	Copolymer composition, mole-%		
M_1	M_2		m_l	m_2	
80.32	19.68	3.14	62.41	37.59	
70.29	29.71	3.22	58.87	41.13	
60.28	39.72	3.57	50.72	49.28	
50.05	49.95	4.68	47.75	52.25	
40.58	59.42	3.81	44.21	55.79	
20.71	79.29	4.26	29.43	70.57	

TABLE VIII

Copolymerization of	Styrene	(M_1) and	IV	$\left(M_{2}\right)$	in	Bulk

Monomer	Monomers, mole-%		Copolymer composition, mole-%		
\mathbf{M}_{t}	M_2	copory mer,	\mathbf{m}_1	\mathbf{m}_2	
89.10	10.90	82.26	78.59	21.41	
80.74	19.26	79.67	71.01	28.99	
74.11	25.89	77.94	65.26	34.74	
64.62	35.38	75.84	57.37	42.63	
61.95	38.05	75.50	56.04	43.96	
44.75	55.25	73.48	47.20	52.80	
40.02	59.98	72.60	42.93	57.07	
20.23	79.77	70.19	29.66	70.34	
20.25	19.11	70.19	20.00	10.04	

The methacrylate (M₂) content in the monomer feeds is plotted against the content of the monomer unit in the copolymer in Figures 1-5. The lines in the figures are calculated from the monomer reactivity ratios and the plots are from the experimental data.

The amino (NR₁R₂) or phenoxy group of the monomer is located on the third carbon atom from the ester oxygen (I). Therefore, the possibil-



Fig. 1. Composition curves for copolymerization of styrene (M_1) and $I(M_2)$: $(--- \bigcirc)$ in bulk; $(--- \bigcirc)$ in benzene; $(- \bigcirc)$ in dioxane.



Fig. 2. Composition curves for copolymerization of styrene (M_1) and $H(M_2)$: (----O) in bulk; $(--\Delta)$ in benzene.

	T	'ABI	E IX			
Copolymerization	of Sty	rene	(M_1) and	IV	(M_2) in	Benzene

Monomers, mole- $\frac{C_{c}}{C_{c}}$		Monomers, mole-% C in copolymer.		Copolymer composition, mole- \mathbb{C}_e		
M_1	M_2	Copying man,	m_1	m_2		
91.03	8.97	84.82	85.09	14.91		
79.27	20.73	80.52	73.62	26.38		
38.47	31.53	76.67	60.62	39.38		
59.83	40.17	73.01	44.89	55.11		



Fig. 3. Composition curve for copolymerization of styrene (M_1) and III (M_2) in benzene.



Fig. 4. Composition curves for copolymerization of styrene (M_1) and IV (M_2) : (---O) in bulk; $(--\Delta)$ in benzene.

	TA	BLE X			
Copolymerization	of Styrene	(\mathbf{M}_1) and	id MMA	(\mathbf{M}_2) in	Benzene

Monomers, mole-%		C in conclymer	Copo compositio	lymer on, mole-%
M_1	M_2		\mathbf{m}_1	m_2
90.63	9.37	64.82	85.52	14.48
76.23	23.77	70.18	69.25	30.75
55.33	44.67	74.83	54.98	45.02
36.13	63.87	79.92	39.17	60.83
16.80	83.20	84.69	24.16	75.84



Fig. 5. Composition curves for copolymerization of styrene (M_1) and MMA (M_2) : $(--\Delta)$ in benzene; $(- \cdot -\Box)$ in dioxane.

TABLE XI										
Copolymerization of Styrene (M_1) and MMA ((M_2) in	Dioxane								

Monomer	s, mole-%	C in copolymer.	Copo compositio	lymer on, mole-%
M_1	${ m M}_2$	Se	n_1	m_2
81.85	18.15	83.62	72.45	27.55
47.40	52.60	75.31	46.56	53.44
27.19	72.81	70.43	31.51	68.49
10.49	89.51	65.36	16.12	7 mer 1, mole-% m_2 27.55 53.44 68.49 83.88

TA	ABLE XII	
Monomer	Reactivity	Ratios

			erization				
		Bulk copol	ymerization	In be	enzene	In di	oxane
M_1	M_2	r_1	12	r_1	r_2	r_1	7 . 2
St	I	0.23	0.46	0.19	0.75	0.41	0.58
\mathbf{St}	II	0.30	0.44	0.26	0.74		_
\mathbf{St}	III	_		0.21	0.37		_
St	IV	0.39	0.40	0.58	0.82		
\mathbf{St}	V			~~		0.39	0.28
\mathbf{St}	VI		<u> </u>	_		0.45	0.20
\mathbf{St}	MMA	0.52^{a}	0.46ª	0.51	0.57	0.43	0.54
\mathbf{St}	GMA	$0.44^{\rm h}$	0.53^{b}				

^a Data of Lewis et al.⁶

^b Data of Iwakura and Matsuzaki.⁷



ity of any electronic influence of these groups on the copolymerizability through the carbon chain appears to be absurd. If the electronic effect of the terminal group were the cause of the variation of copolymerizability, the values of $1/\mathbb{P}_1$ should be in the order, $\Pi > I > \Pi I$, V, VI, IV, according to the basicity of the terminal groups; however the actual values did not follow this order.



Fig. 6. Infrared spectra of compound I in CHCl₃: (I) concentration = 25%; (II) concentration = 0.5%.

If the bulkiness of these groups were the cause of the variation of the copolymerizability, r_1 would become larger compared with that of MMA. However, the actual values of r_1 of the monomers were smaller than that of MMA when the copolymerization was carried out in bulk or in benzene.



Fig. 7. Infrared spectra of the homopolymer of I in CHCl₃: (I) concentration = 25%; (II) concentration = 0.5%.

This would indicate that the steric hindrance of these groups is not significant for the addition of these monomers to the styryl radical.

The results obtained here may be interpreted by the following considerations. The ester groups of the monomers used have a hydroxy group, and further, compounds I, III, V, and VI have an NH group. Therefore, intermolecular or intramolecular interaction by hydrogen bonding should occur. This interaction was demonstrated by the infrared absorption spectra of compound I (Figs. 6 and 7). The infrared absorption of compound I in bulk indicates that almost all of the hydroxy groups appear participate in hydrogen bonding; however, the infrared absorption spectrum of a diluted solution of compound I in chloroform showed free hydroxy and NH absorptions at 3590 and 3410 cm.⁻¹, respectively, in addition to the bonded OH and NH absorptions. This interaction may affect the copolymerizability of the monomer.

If the monomer which has OH and NH groups was taken up into the polymer chain by hydrogen bonding between the polymer molecule and the monomer, the concentration of the monomer around the polymer molecule should become larger than the average concentration of the monomer. Consequently, the reactivity ratio r_1 would become smaller than that of MMA. When dioxane was used as a solvent, the hydrogen atom of the OH or NH group would be bonded to the oxygen atom of dioxane. This would break down the interaction among acrylic ester molecules and their units in the polymer, and the r_1 value would then approach the value of MMA.

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The steric effect of the monomer in the addition reaction of it to the styryl radical has been considered to be little significant as described above, but the smaller values of r_2 for the monomers V and VI seem to indicate the steric interaction between these monomers and the terminal ester group in the growing polymer chain according to eq. (1).

$$\begin{array}{ccc} CH_{3} & CH_{3} \\ \bullet CH_{2} - C \cdot \\ \downarrow \\ COOCH_{2}CHCH_{2} - R & COOCH_{2}CHCH_{2} - R \\ \downarrow \\ OH & OH \end{array}$$
(1)

EXPERIMENTAL

Monomer

The monomers used here are shown in Table 1; their preparation has been presented previously.⁵

Solvent

Benzene and dioxane used for homopolymerization and copolymerization were purified by ordinal method.

Polymerization

Bulk Polymerization. The polymerization of monomers I, II, and IV was carried out under nitrogen atmosphere in a sealed tube with AIBN as an initiator at 60° C. The reaction product was poured into methanol, and the precipitates were purified by reprecipitation from benzene with methanol.

Solution Polymerization. The polymerization of monomers I, II, III, and IV was carried out in benzene under nitrogen with AIBN at 60°C.

The polymerization of monomers V and VI was carried out in dioxane. The polymers obtained were purified by reprecipitation from benzene with methanol.

Copolymerization

Bulk Copolymerization. A mixture of both monomers totalling 5 g, and 15 mg, of AIBN were sealed in a glass tube under nitrogen and heated at 60°C, for some time. The copolymer obtained was purified by reprecipitation from benzene and petroleum ether. The conversion of the copolymer was less than 5%.

Copolymerization in Benzene or Dioxane. A mixture of both monomers totalling 5 g. and 15 mg. of AIBN were dissolved in 10 ml. of benzene or dioxane in a sealed tube at 60°C. The purification of the copolymer was carried out in the same way as for the bulk copolymer.

The copolymer purified was dried at 60° C. *in vacuo* and submitted to elemental analysis.

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Lewis Acid-Catalyzed Reactions on Polystyrene

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Synopsis

The action of aluminum halides upon polystyrene was studied as a function of the nature of the reaction medium and of the concentration of catalyst. It was demonstrated that polystyrene undergoes crosslinking, the extent of which is particularly important in chlorinated aliphatic solvents and at high catalyst concentrations. In addition, phenyl rings of the polymer are alkylated and halogenated by the solvent or catalyst. Infrared spectroscopic investigation of the structure of the products indicated that in most cases crosslinking was connected with the formation of 1,4-disubstituted, and eventually 1,2,4-trisubstituted benzenes. In carbon tetrachloride medium, *meta* substitution was also detected. In products obtained when polystyrene was treated with high amounts of the Lewis acid in CCl₄ medium degrees of substitution even higher than three were probable.

INTRODUCTION

Cationically induced reactions on preformed polymers have been the subject of many investigations. According to Smets¹ these reactions can be divided into two principal groups: (a) reactions leading to the chemical transformations of the original polymer, such as degradation, cyclization, crosslinking, etc., and (b) grafting of monomers onto the original polymer, To the first class belong, for example, the Friedel-Crafts-catalyzed reactions of poly(vinyl chloride),^{2,3} in which the abstraction of the chlorine is assumed as the first step with the formation of carbonium ions along the chain. Another reaction of this type is the well-known cyclization of natural rubber or other diene polymers. A survey of various cationically catalyzed reactions on polymers appeared recently.¹

Reactions on polystyrene induced by Lewis acids have not been reported in the literature, although several papers deal with ionic grafting or branching of substituted polystyrenes.⁴⁻⁶ In this investigation, an attempt was made to show that a direct interaction of polystyrene with Friedel-Crafts catalysts takes place and that it leads to deep changes in the polymer structure.

EXPERIMENTAL

Materials

Two types of polystyrene were used, a low molecular weight sample prepared by cationic polymerization in *n*-heptane with an ethylaluminum dichloride-titanium tetrachloride catalyst system at 5°C. ($[\eta] = 0.07$ dl./g.) and a commercial product, Styron (Dow Chemical Co., $[\eta] = 1.0$ dl./g.).

Ethylaluminum dichloride (Texas Alkyls, Inc.) in the form of a 25% solution in *n*-hexane was used as the catalyst in most experiments. In several experiments ethylaluminum dibromide or aluminum tribromide were used. Both samples were synthesized in the laboratory according to standard methods and purified by distillation or sublimation in vacuum. Solvents were distilled through a column packed with Linde 4A molecular sieves. Before distillation they were stored for several days over Drierite.

Procedure

Reactions were carried out in three-necked flasks equipped with magnetic stirrer, nitrogen inlet, reflux condenser with nitrogen outlet, and a side arm closed by a self-sealing rubber cap through which reaction components were charged by means of hypodermic syringes. The polymerization vessel was flushed with dry nitrogen with simultaneous open flame heating for 1 hr. Then the solution of polystyrene in the solvent under investigation was introduced. Major amounts of oxygen were removed by bubbling nitrogen through the solution for an additional 60 min. Reaction was started by addition of the catalyst. After a preset time interval, reaction was stopped by pouring the reaction mixture into a large excess of methanol. Polymers were repeatedly washed with acidified methanol and finally dried at 50°C. under reduced pressure.

Alternatively, polymerizations were performed in evacuated vessels and polymer as well as catalyst were charged by breaking vacuum sealed ampules containing the corresponding solution. The solution of polymer was degassed by repeated evacuation of the frozen mixture. Polymers were characterized by the infrared spectra, melting properties, and solubility in benzene at 25° C.; in addition, soluble products were characterized by ultraviolet spectra and limiting viscosity numbers in benzene at 25° C.

Infrared spectra were taken on the UR-10 (Ziess-Jena) spectrometer by use of KBr pellet technique. Within the region 400–600 cm.⁻¹ potassium bromide, in the 600–1900 cm.⁻¹ range sodium chloride, and in the region 2700–3200 cm.⁻¹ lithium fluoride prisms were used. Ultraviolet spectra were recorded on the CF-4NI spectrometer (Optica Milano) with the use of either rectangular or cylindrical silica cells with 10-mm. path length.

RESULTS

The influence of ethylaluminum dichloride, ethylaluminum dibromide, and aluminum tribromide upon both types of polystyrene was investigated



Fig. 1. Evolution of HCl during the reaction of polystyrene with aluminum tribromide in earbon tetrachloride: (1) 0.31 mmole AlBr₃; (2) 0.46 mmole AlBr₅. Polystyrene, 1 g; CCl₄, 30 ml.; 20°C.

as a function of the amount of catalyst and the nature of the solvent. Addition of these catalysts to the solution of polystyrene resulted in the coloration of the reaction mixture, the intensity and color depending on the nature of the solvents. The coloration did not occur in solvents especially dried and degassed in vacuum, or its intensity was much lower. In all cases there was gas evolution during the reaction, which was very weak in hydrocarbons but extraordinarily strong in chlorinated solvents such as carbon tetrachloride, methylene chloride, or tetrachloroethane. In three experiments carried out in the vacuum apparatus with CCl_4 as the solvent, gaseous products were collected in special ampules attached to the polymerization vessel, scaled off, and analyzed by mass spectrometer

		Culur of	Weight	Solubility		Ana	lysis
Expt. no.	Solvent	reaction mixture	after 60 min., %	at 20°C.,	$[\eta],$ dl./g.	Chlo- rine, %	Ash, %
1	Cyclo- hexanc	Yellow, turbid	+10	100	1.10	1.2	0
2	Benzene	Red-orange, clear	0	100	0.80	0.15	0.3
3	<i>p</i> -Xylene	Yellow, clear	+4	100	1.4	0.2	
4	C ₆ H₅Cl	Red-orange, cl e ar	+15	95(gel)	0.9	0.9	0.32
5	$o\text{-}\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{Cl}_{2}$	Red-brown, clear	+20	100	1.04	4.17	0.8
6	$1,2,4-C_6H_3Cl_3$	Yellow- orange	+35	95(gel)	0.84	1.13	
7	CH_2Cl_2	Bright red	+5	38(gel)		2.6	0.51
8	CCl_4	Deep red	+25	7(gel)		7.85	

TABLE I Influence of Nature of the Solvent on Crosslinking of Polystyrene^a

* Conditions: solvent, 50 ml.; polystyrene Styron $[\eta] = 0.9, 2$ g.; time, 60 min.; catalyst, 2 mmole AlEtCl₂.

	Catal	yst	Polv-		Change of	Solubility	Color of		Analy	ysis
Expt. no.	Nature	Amount, mmole	styrene, g.	Solvent	weight, ζ_{ℓ}	in benzene, 20°C., %	reaction mixture	$[\eta]$, dl./g.	Chlorine, ζ_c	$\overset{\mathrm{Ash}}{\%}$
6	AlBr ₃	0.15	-	CCI4	6-	9.5	Yellow-	1.4	1.7	0.2
10	AlD.	0	-		a	ł	orange	1 10	0	0
11	AID.	0.40		P100			Orange-reu	0.T	0.5	7.0
1	AIDI3	U.40	T	CU14	0	0.1	Deep red		5.0	
12	$C_2H_5AlBr_2$	5.0	0.5	Cyclohexane + CCl ₄	06+	Ι	Deep red	1	2.3	0
				(5:1)						
13	C ₂ H ₅ AlBr ₂	10.0	0.5	Cyclohexane + CCl ₄	+70	21	Deep red]	2.1	0
				(5:1)						
14	$C_2H_5AlBr_2$	10.0	0.5	Cyclohexane	-40	100	Yellow	0.085	1	
15	$C_2H_5AlBr_2$	10.0	0.5	CCI ₄	+35	32	Deep red		7.1	0.3
						no gel				
16	$C_2H_5AlBr_2$	10.0	0.5	$C_2H_5CI_4$	+29	1	Brown-red		10.5	0

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within the range of masses 1-70. The main constituent of the gaseous mixture was hydrogen chloride, but in all cases considerable amounts of molecular hydrogen and methane were also detected. The amount of hydrogen chloride, however, was higher by two orders of magnitude than that of the other two gases and increased with increasing concentration of the catalyst. Two illustrative curves of the hydrogen chloride evolution during the action of $AlBr_3$ on the commercial polystyrene in carbon tetrachloride medium are shown in Figure 1. The amount of HCl evolved in CCl₄ medium was in most cases higher than that corresponding to the amount of aluminum halide used. Thus, for example, in experiment 12 (Table II) 47 mmole of HCl was liberated in 2 hr. from a reaction mixture containing 5 mmole of AlBr₃ and 0.5 g. of polystyrene in a 1:5 carbon tetrachloride-cyclohexane mixture. Among the acid gases, a small percentage of hydrogen bromide was always found when aluminum bromides were used as catalysts.

In hydrocarbon solvents or in chlorinated benzenes the interaction of the catalyst with polystyrene was not accompanied by any apparent change of the viscosity of the reaction mixture. In carbon tetrachloride, methylene chloride, or tetrachloroethane, however, addition of polystyrene to the catalyst solution was followed immediately by thickening of the reaction mixture which resulted, depending on the concentration of the catalyst, in the formation of gel or, at still higher catalyst concentrations, in precipitation of a powdery material. Changes in the properties of polystyrenes treated with $C_2H_5AlCl_2$ in various solvents are shown in Table I. The influence of catalyst concentration is seen from Table II. The products from the reactions carried out in chlorinated aliphatic solvents were almost insoluble in benzene and formed gels. The amount of the insoluble fraction increased with increasing concentration of the catalyst (Table II, Nos. 9–11).

The intrinsic viscosities of the soluble polymers were slightly higher than that of the original polymer. There was also a slight increase of the slope in the reduced viscosity-concentration dependence plot. Soluble portions isolated from polymers treated in halogenated solvents showed very low limiting viscosity numbers, evidently as a consequence of simultaneous chain degradation.

Electrical Conductivity

Strong interaction of aluminum halides with polystyrene in CCl₄ medium was also evident from the measurements of the electrical conductivity of the solution during the reaction. In this case reaction was carried out in a conductivity cell in which two platinum electrodes were placed, forming one arm of a conductivity bridge fed with an alternating current, 38 cps. The cell resistance constant was 0.1. Charging of the reaction components was performed by means of hypodermic syringes in a flow of nitrogen. With carefully dried carbon tetrachloride only a minor increase of the electrical conductivity of the aluminum bromide alone

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Fig. 2. Changes of the specific resistance of the AlBr₃ solution in CCl₄ after addition of polystyrene (polystyrene added at the beginning and at times marked by arrows): (a) 0.07 mmole in 1 ml. of cyclohexane, (b) 0.2 mmole in 2 ml. of cyclohexane, (c) 0.2 mmole in 2 ml. of cyclohexane. Cationic polystyrene, $[\eta] = 0.076$ dl./g.; CCl₄, 30 ml.; AlBr₃, 0.15 mmole; 21 °C.

with time was observed. Addition of polystyrene to that solution led immediately to a drop of the specific resistance to a minimum after a slow increase took place. Introduction of further amounts of polystyrene was, however, accompanied first by an increase followed by a slow decrease of the resistance. An example of such behavior in the system upon three successive additions of polystyrene is shown in Figure 2. It is clear that interaction of polymer with the carbon tetrachloridealuminum bromide mixture results in the formation of ionic species which, however, gradually disappear from the solution, probably due to the precipitation of crosslinked polymer. The initial drop of the conductivity after the second and third additions is due to the dilution of the reaction mixture and the subsequent increase may be connected with the formation of HCl. In benzene medium there are no significant changes of the electrical conductivity when polystyrene is added to the catalyst solution.

Ultraviolet Spectra of the Reaction Mixture

Interaction of ethylaluminum dichloride with carbon tetrachloride and polystyrene was also followed spectroscopically by the use of cylindrical cells which were attached directly to the vacuum manifold, filled with reaction components under vacuum, and sealed off. Comparison of the reaction rates determined from the spectroscopic measurements with those performed under the previously described conditions is not possible because the concentrations of the reaction components in the latter cases are very low, and thus the influence of traces of moisture or oxygen is relatively high. In most cases, induction periods of different lengths were observed.

All reactions were carried out in cyclohexane solutions at the following concentrations of reaction components: ethylaluminum dichloride, 0.075



Fig. 3. Ultraviolet spectra of the reaction mixture AlEtCl₂-CCl₄-polystyrene in cyclohexane medium: (A) immediately after mixing, (B) 200 min. after mixing, (C) 240 min. after mixing; (D) 360 min. after mixing. [EtAlCl₂], 7.5×10^{-2} mole/l.; [CCl₄], 0.2 mole/l.; [polystyrene], 3.5×10^{-3} mole/l.; 21°C.

mole/l.; polystyrene (cationic), 0.36 g./l.; carbon tetrachloride, 0.1-1.0 mole/l.

A solution of ethylaluminum dichloride in cyclohexane did not show any absorption bands at wavelengths longer than 210 m μ . This compound, however, reacted with carbon tetrachloride in the presence of moisture forming a red oil with the liberation of HCl. The ultraviolet spectrum of this oil showed a strong band at 300 m μ and two additional bands at 340 and 390 m μ , all of which increased with time (Fig. 4*B*). The addition of ethanol gave rise to a colored solution showing strong bands at 460 and 540 m μ and a weaker one at 605 m μ .

Polystyrene in cyclohexane exhibited the well-known spectrum typical of a monosubstituted benzene ring with a maximum intensity band at 261 m μ with the benzenoid fine structure. In carbon tetrachloride solution, the spectrum of polystyrene was completely overlapped by the absorption of the solvent up to 280 m μ . In the region of longer wavelengths no further absorption bands occurred. The spectrum of polystyrene in cyclohexane in the presence of smaller amounts of CCl₄ (Fig. 3A) showed absorption bands of polystyrene as shoulders on the absorption of CCl₄ at 253, 258.5, 264, and 268 m μ . The doublet at 258.5 and 261 m μ in the spectrum of polystyrene in cyclohexane disappeared. The intensities of the remaining bands were in ratios slightly differing from those in pure cyclohexane, indicating a weak polymer-solvent interaction.

The spectrum of polystyrene did not undergo any changes in the presence of $EtAlCl_2$ in dry cyclohexane under conditions examined over a period of 100 hr.

Interaction of ethylaluminum dichloride with polystyrene in carbon tetrachloride-cyclohexane mixture could be observed only at higher con-



Fig. 4. Ultraviolet spectra of reaction products: (A) spectrum of the red oil formed from the reaction mixture given in Fig. 3 after 1 week, (B) spectrum of the red oil formed from AlEtCl₂ + CCl₄, concentrations given in Fig. 3, (C) reaction mixture containing EtAlCl₂-CCl₄-polystyrene (concentration of polystyrene, 3.5×10^{-2} mole/l., EtAlCl₂ 3 × 10⁻² mole/l.; CCl₄, 0.6 mole/l.); (D) reaction mixture containing p-xylene-EtAlCl₂-CCl₄ (concentrations the same as given for curve C).

centrations of the halogenated solvent. There was, however, always a long induction period. At the concentrations mentioned above, i.e., a molar excess of $EtAlCl_2$ over polystyrene and 0.2 mole/l. of CCl_4 , the initial spectrum of polystyrene in this reaction mixture did not change over a period of 3 hr. (Fig. 3A). After this time the solution became successively vellow, orange, and finally red colored and turbid. Simultaneously, polystyrene bands disappeared and a new band at 300 m μ began to grow (Fig. 3B). Further reaction led to a rapid increase of the band at 300 m μ and three additional bands at 350 (shoulder), 395, and a very broad band at 460 m μ appeared. All bands increased rapidly with time, and finally there was a continuous absorption up to 350 m μ and in the spectrum only the two long-wave bands at 395 and 460 m μ remained distinct (Fig. 3C and 3D). Bands at 300, 350, and 395 m μ coincided with the band characteristic of the red oil from the EtAlCl₂-CCl₄ reaction mixture. They are evidently connected with the formation of ionic species from both compounds which is facilitated by the presence of an aromatic medium. During the reaction of ethylaluminum dichloride with the CCl₄-polystyrene system a heterogeneous system was formed, consisting of a red oil, which however, was partly converted to a solid. After standing 1 week in the sealed cell, all the solid and oil precipitated, and the clear supernatant solution did not show any absorption at wavelengths longer than $240 \text{ m}\mu$. Thus, the red oil and the solid phase contained not only all the polystyrene but also all the carbon tetrachloride originally charged. The spectrum of the red oil (as a thin film on the cell window) showed all absorption bands present in the original reaction mixture, i.e., 300, 350, 390, and 450 m μ (Fig. 4A).

When the reaction was carried out with a mixture containing an excess of polystyrene over ethylaluminum dichloride, the reaction proceeded faster, and the spectrum of the reaction mixture contained only two bands at 300 and 460 m μ . A similar shape of the spectrum was also obtained when an equimolar amount of *p*-xylene was charged instead of polystyrene (Fig. 4*C* and 4*D*).

The red oil reacted slowly with ethanol, yielding a yellow solution with continuous absorption diminishing from 290 to 500 m μ with no distinct peaks. Addition of concentrated sulfuric acid led to the regeneration of the bands at 300, 390, and 460 m μ , indicating that they could all be assigned most probably to ionic species.

Analysis of the Reaction Products

Infrared Spectra. The nature and the extent of structural change in polystyrenes treated with Lewis acids depended critically upon the nature of the solvent and upon the concentration of the catalyst. Infrared spectra



Fig. 5. Infrared spectra of polystyrenes treated with ethylaluminum dihalide in various solvents: (a) sample 2, Table I; (b) sample 14, Table I; (c) sample 8, Table I; (d) sample 11, Table II; (e) sample 12, Table II; (f) sample 13, Table II.

of a few samples treated with ethylaluminum dichloride are shown in Figure 5. Polymer treated with EtAlCl₂ in benzene at a styrene unit: EtAlCl₂ molar ratio of 10 (Fig. 5a) did not show any structural changes, and its spectrum was identical with that of the original untreated polymer within the range 600-1900 and 2700-3200 cm.⁻¹. A sample treated under the same conditions in cyclohexane gave only a very slight indication of para substitution of the phenyl ring evidenced by the appearance of new weak bands at 815 and 1515 cm.⁻¹. An increase of the catalyst concentration (styrene: $EtAlCl_2$ molar ratio of 0.5) resulted in an increase of the extent of the *para* substitution (Fig. 5b) and, in addition, new bands were noted at 1095, 1265, 1640, and 1670 cm.⁻¹. The appearance of the two weak bands in the region of the C=C stretching vibrations shows that the main reaction leading to the substitution of the ring is accompanied by side reactions in which two kinds of double bonds are formed. The bands at 1095 and 1265 cm.⁻¹ are not characteristic enough to be used for any identification of a structural type. Both, however, may be connected with the influence of a polar substituent such as halogen upon a C--H deformation vibration or with a stretching C—O vibration.

Similar changes of structure also occur in polystyrenes treated with $EtAlCl_2$ of the same concentration in *p*-xylene, monochlorobenzene, o-dichlorobenzene, 1,2,4-trichlorobenzene, or methylene dichloride medium (Table I, Nos. 3–7). Polystyrene retained its basic structure fully with only minor amounts of para substitution, which is evident from the appearance of new bands at 815 cm.⁻¹ belonging to the C—H out-of-plane bending vibration of two adjacent hydrogen atoms on the ring and from a small shift of the 1495 cm.⁻¹ band of the C—C ring stretching vibration towards higher frequency (1515 cm.⁻¹). At higher degrees of para substitution, the intensity increase of the 1900 cm^{-1} band is also indicative of the p-substitution. In some cases, for example, in the sample treated in p-xylene, a band also appeared at 870 cm. $^{-1}$. Its presence in the infrared spectrum might indicate meta substitution, or more probably 1,2,4-trisubstitution, because it always appears together with the 815 cm^{-1} band Assignment of the former band to the C-H out-ofmentioned above. plane bending vibration of a lone hydrogen atom on the ring is rather unambiguous. However, it should be noted that in the excess of unchanged polystyrene it is rather difficult to differentiate between the 1,2,4 trisubstitution and higher degrees of substitution of benzene rings and the 1,3,6 trisubstitution of indane rings.

Most pronounced structural changes occurred when the reaction was carried out in carbon tetrachloride medium. When a relatively low concentration of aluminum halide was used, the infrared spectrum of the product did not lose the aromatic character (Fig. 5c, 5d). Several new bands, however, indicate deeper changes in the polymer molecule. A further increase of the catalyst concentration led to a successive diminution of the bands characteristic of polystyrene and new bands appeared at 790, 930, 1090, 1180, 1285, 1310, 1420, 1640, and 1670 cm.⁻¹. At still lower



Fig. 6. Ultraviolet spectra of various polymers treated with aluminum halide: (A) sample 2, Table I: (B) sample 6, Table I; (C) sample 7, Table I: (D) sample 12, Table II; (E) sample 11, Table II. In cyclohexane, polystyrene concentration, 0.3 g./l.

styrene unit: catalyst ratios (below 2) the character of polystyrene structure disappeared completely (Fig. 5e, 5f) and also many bands which appeared at low catalyst concentrations were no longer distinct.

The most obvious changes are connected with the almost complete disappearance of the C—H stretching vibrations of the aromatic ring in the region 3000–3100 cm.⁻¹ and with the successive diminution and finally absence of the aromatic C—C stretching vibration band at 1500 cm.⁻¹ as well. The characteristic polystyrene band at 700 cm.⁻¹ of the out-of-plane ring bending vibration was also completely absent in the spectrum of the products. Very weak residues of the bands above 3000 cm.⁻¹ together with the weak bands at 710, 760, 810, and 870 cm.⁻¹ and a shoulder at 1510 cm.⁻¹ indicate the presence of at least trisubstituted or even of higher substituted benzine rings. Their content in the product, however, was rather low. Among the higher substituted rings the occurrence of the 1,2,4-substitution type also seems to be important as supported by the presence of the indicated bands, together with a band at 1890 cm.⁻¹ in the region of overtone and combination bands.

On the other hand, there was a considerable increase in the bands at 1458 cm.⁻¹ of the CH₂ scissoring vibration in alkanes or cycloalkanes, 2850 and 2920 cm.⁻¹ bands of the symmetrical and asymmetrical C—H stretching vibrations in the aliphatic CH₂ group, and bands characteristic for methyl groups (1380, 2865, and 2960 cm.⁻¹), also. In some cases, polymers showed the presence of methoxy groups or they were slightly oxidized, as indicated by the appearance of new bands at 1090 (C—O—C stretching). The band at 1640 cm.⁻¹, always present in treated polymers, may indicate the formation of double bonds conjugated with the aromatic ring, and the band at 1670 cm.⁻¹ can most probably be assigned to some type of isolated double bond (possibly in the cyclohexene ring).

Ultraviolet Spectra. Ultraviolet spectra of the soluble portions isolated from essentially insoluble products confirm structural changes similar to those indicated by the infrared spectra. The absorption spectrum of polystyrene shows a broad absorption band in the ultraviolet region be-

	Cat	alyst	Polv-						
Sample		Amount.	styrene			Analysis (of polymers		Atomic C/I
nu.ª	Nature	mmole	B.	Solvent	c, %	H, 7_0	CI, 76	Total, %	ratio
م	I	I	I	1	91.82	7.59	0	99.41	1.005
7	EtAICl ₂	cı	0	CH ₂ Cl ₂	81.69	7.95	2.60	92.24	0.855
s	EtAlCl ₂	ମ	5	CCI4	76.97	7.45	7.85	91.87	0.848
6	AlBra	0.15	1	CCI	19.06	9.92	trace	100.53	0.766
12	EtAlBr ₂	5	0.5	$CCI_4 +$	S4.2S	8,71	2 2	95.29	0.807
61	E. AID	ç		C_6H_{12} (1:5)	66 30 66		01.0	5	918 0
6	aldivia.	OT	0.0	C ₆ H ₁₂	07 00	11.0	01	10.00	
15	EtAlBr.	10	0.5	(c:1) CCI4	78.74	6.50	10.7	92.34	966.0
16	EtAlBr ₂	10	0.5	$C_2H_2OI_4$	79.61	6.03	10.50	96.14	1,100

TABLE III Elementary Analysis of Polystyrenes Treated with Lewis Acids

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Sample no. ^b	Solvent	Appear- ance change, °C.	Droplet forma- tion, °C.	Flow, °C.	Com- pletely molten, °C.	Appearance in molten state
С	Heptane	94	105	115	130	Clear, colorless
S		145		150	185	Clear, colorless
S1	Cyclohexane	160	175	190	270	Clear, yellow
82	Benzene	150	160	220		Clear, colorless
54	C ₆ H ₅ Cl	160	210		e	Clear, yellow
S5	o-C6H4Cl2		180	260	290	Clear, yellow
87	CH_2Cl_2	300	320	330	e	Brown-red
58	CCl ₄	290	320		c	
89	CCI_4	190	230	250	e	Yellow
S10	CCl_4	170	180	240	340	Yellow-black
SIL	CCl_4	250	290	310	e.	Yellow
C12	C <u>yc</u> lohexane + CCl₄				ત	
C13	Cyclohexane + CCl₄			_	đ	
C14	Cyclohexane	115	120	130	е	

TABLE IV Melting Properties of Crosslinked Polystyrenes^a

* Koffler block heating rate 5°C./min.

 b C = cationic polystyrene; S = commercial polystyrene (Styron).

^o Not completely molten at 360°C.

^d No melting up to 360°C.

^e Not completely molten at 200°C.

tween 240-270 mµ with 7 peaks at 243, 248, 253.8, 258.5, 261, 264, and 268 mµ. The maximum of the band is formed by the doublet 258.5 + 261m μ assigned to the vibrationally split lowest $\pi \rightarrow \pi^*$ transition in the monosubstituted benzene ring. Ultraviolet spectra of five products treated with ethylaluminum dichloride in different solvents are shown in Figure 6. It is seen that in this case also the spectrum of polystyrene treated in benzene does not show any change when compared with the spectrum of the original polymer (Fig. 6A). No changes in the ultraviolet spectra were observed with polymers treated in monochlorobenzene, dichlorobenzene, and cyclohexane at styrene: EtAlCl₂ ratios higher than 10. At lower ratios, however, the spectra of products from cyclohexane, p-xylene, dichlorobenzene, and trichlorobenzene showed the basic character of the polystyrene spectrum with additional bands at 277.8 and 286.3 m μ , the intensity of which increased with increasing catalyst concentration. Both bands were rather weak in polymers treated in cyclohexane or o-dichlorobenzene, but were relatively strong in products from 1,2,4-trichlorobenzene (Fig. 6B). As seen from Figure 6B, intensity ratios of the remaining polystyrene bands changed substantially. The fine structure of the 260 m μ band in soluble products from the treatment of polystyrene in methylene dichloride (Fig. 6C) or in carbon tetrachloride (Fig. 6D) disappeared, most probably as a consequence of higher degree of substitution. Finally, in products treated

Mass of the peak	Summary formula	Structure
55	C_4H_7	
67	C_5H_7	+
69	$\mathrm{C}_{5}\mathrm{H}_{9}$	+
81	$C_6 H_9$	$\overset{+}{\frown}$ $\overset{+}{\frown}$ $\overset{-}{\frown}$ $\overset{-}$
82	$\mathrm{C}_{6}\mathrm{H}_{10}$	
83	C_6H_{11}	\leftarrow + \leftarrow CH ₃
95	C_7H_{11}	\bigcirc $-CH_2^+$ \checkmark $-CH_3$
109	$\mathrm{C_8H_{13}}$	\leftarrow + C_2H_5 \leftarrow $CH_2-CH_2^+$
151	$C_{11}H_{19}$	
195	$\mathrm{C}_{14}\mathrm{H}_{27}$	

TABLE V Mass-Spectrometric Analysis of Liquid Reaction Products^a

* Reaction in CCl₄-cyclohexane medium, 0.5 g, of polystyrene, 5 mmole EtAlBr₂, 20°C.

with higher amounts of the catalyst in CCl_4 medium, the aromatic character disappeared almost completely (Fig. 6E).

Chemical Analysis. Several samples of polystyrene treated by aluminum halides were analyzed chemically. Results of the elementary analyses are summarized in Table III. Results of the analyses of chlorine content are included in Tables I–III. It is seen that at lower concentrations of catalyst, i.e., when the spectra showed only higher degrees of substitution of the benzene rings but the basic polystyrene structure was retained, the chlorine contents in the polymers ranged from 0 to 2%. The chlorine content was rather high in products treated in carbon tetrachloride or tetrachloroethane solution with the use of relatively high amounts of aluminum halide (Nos. 8, 15, 16 in Tables I and II). It is interesting that the treatment of polystyrene by aluminum halides was also accompanied by changes in the C/H atomic ratios of the products (Table III), indicating the formation of hydrogen-rich compounds. Some samples contained considerable amounts of oxygen (content not included in Table III). All treated polystyrenes showed marked changes in their melting properties (Table IV). Even polymers whose infrared spectra showed no difference in structure melted at higher temperatures than the original polystyrene. Polymers treated in carbon tetrachloride at higher catalyst concentrations showed only partial melting at temperatures below 360°C. At higher temperatures partial decomposition always took place. It should also be noted that the melts were never clear due to crosslinking.

Mass-Spectrometric Analysis of Low Molecular Weight Products. In two cases 0.5 g, of polystyrene was treated in a 1:5 mixture of carbon tetrachloride and cyclohexane with 5 mmole of ethylaluminum dibromide. The liquid remaining after precipitation of all polymeric material with methanol was analyzed by mass spectrometry. A blank experiment without polystyrene was also evaluated. A very complicated mixture of various low molecular weight compounds was found, evidently as a consequence of a variety of side reactions taking place in the system. The following compounds were detected among low molecular weight products: bromoform (CHBr₃), dicyclohexyl or methylcyclopentylcyclohexyl ($C_{12}H_{22}$), monochlorodibromomethane (CHClBr₂), and cyclohexene. In addition, various radicals or ions formed by the splitting of molecules in the spectrometer were clearly identified such as CBr₃⁺, CHBr₂⁺, CCl₂Br⁺, CHClBr⁺. Assignment of other peaks is given in Table V, although under no circumstances can these be taken as the single possibility as they are of rather speculative nature. It is interesting to note that no products from a profound destruction of the polystyrene, such as substituted benzene derivatives, were detected among the products contained in the reaction liquid.

DISCUSSION

From the results given above it is seen that polystyrene interacts with Friedel-Crafts catalysts with the formation of crosslinked and branched products. The crosslinking density depends on the reaction conditions and can be varied within wide limits. Reactions taking place in such systems are very complex and in many cases direct participation of the solvent molecules plays a decisive role in the reaction course.

Interpretation of the structural changes in polystyrene by the action of aluminum halides is rather difficult due to the complex nature of the infrared spectrum of polystyrene itself which causes serious overlapping of the absorption bands of the products with those of unchanged polystyrene. There are, however, several distinct new bands in the infrared spectra of aluminum halide-treated polymers, the assignment of which can be made rather accurately. Thus, polymers treated in hydrocarbon solvents do not show any deep changes of structure. In most cases, however, *para* substitution could be identified quite safely. On the other hand, *ortho* substitution cannot be traced by the infrared spectra in the presence of high amounts of unreacted polystyrene because all bands characteristic of that type of aromatic substitution might be indicated by the band at 870 cm.⁻¹

of the C—H out-of-plane bending vibration of a lone hydrogen on the ring. This band, however, always appears together with bands characteristic of *para* substitution. Other bands characteristic of *meta* substitution (near 700 and 780 cm.⁻¹) are overlapped by the bands of polystyrene, so that it is rather difficult to decide whether the presence of these bands is an indication of 1,2,4 trisubstitution or of a mixture of 1,3- and 1,4-disubstituted benzene rings. All bands increase in polymers treated with higher amounts of catalyst.

A completely different course of the interaction of aluminum halides with polystyrene takes place in carbon tetrachloride medium. At low catalyst concentrations (Table I, No. 8, and Table II, Nos. 9–11; Fig. 5c, d), the structural changes detectable by the infrared spectra are not too significant. Substitution in the *para* position is almost undetectable and, in its place, *meta* substitution is more distinct, as indicated by the appearance of the 870 cm.⁻¹ band of the lone hydrogen-bending vibration and of a shoulder at 790 cm.⁻¹ which could be attributed to the bending vibration of three adjacent ring hydrogen atoms. Bands at 1285 and 1310 cm.⁻¹ might arise from some OH deformation or C—O stretching vibrations in alcohols, the presence of which is strongly supported by a broad band at 3400 cm.⁻¹ in the spectra of practically all products.

The great diminution of all bands characteristic of polystyrene in polymers treated with higher amounts of the catalyst in CCl₄ medium, i.e., the almost complete disappearance of the bands exhibited by the vibrations of hydrogen atoms of the aromatic nucleus in the regions 650–900 and 3000-3100 cm.⁻¹ and also the absence of the band of the skeletal C—C vibration at 1500 cm. $^{-1}$ can be explained either by the formation of products with degrees of substitution higher than three or by the assumption that the action of the catalyst upon the polystyrene led to the destruction of the rings. This latter possibility does not seem to be probable for energetic reasons, and also because there is no indication of the presence of highly unsaturated compounds among the products. Thus, the former explanation of the shape of the infrared spectra of treated products should be taken into account. It is also supported by the presence of weak residues of bands characteristic of lower degrees of substitution (705, 760, 810, and 870 cm^{-1}). The disappearance or strong diminution of the 1500 cm $^{-1}$ band can be readily explained by its shift to a lower frequency where it coincides with the CH₂-scissoring vibration band and contributes to its intensity. Indeed, the short wave flank of this band is deformed. The 1610 cm.⁻¹ band can be assigned to the shifted 1600 cm.⁻¹ band of the original polystyrene. The formation of some aliphatic double bonds conjugated with rings cannot be excluded (band at 1640 cm. $^{-1}$).

Similar results have also been obtained by ultraviolet spectroscopy (Fig. 6). The extent of *para* substitution is indicated by the band at 277.8 m μ which increases when the reaction medium is changed from cyclohexane to *o*-dichlorobenzene or trichlorobenzene (Fig. 6B). It should be noted, however, that this band is not characteristic for the simple *para*

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substitution of the benzene ring only because it also appears in higher substituted benzenes or even in substituted indanes.⁷ The other long wave band at 286 m μ probably indicates the presence of double bonds conjugated with the ring. Spectra of the products treated in CCl₄ again point to the progressively increasing degree of substitution (Fig. 6*C*, *D*). The spectrum of the soluble part of the polymer treated with AlBr₃ in CCl₄ (Fig. 6*E*; Table II, No. 11) is very diffuse and typical of higher substituted polyphenyls.

It is apparent that all polymers treated with ethylaluminum dihalides show a slight weight increase which is more significant in the presence of carbon tetrachloride. Highly crosslinked insoluble polymers usually contain a considerable amount of bound chlorine (Tables I and II). Elementary analysis indicates that most polymers treated in the CCl₄ medium also show a marked decrease of the atomic C:H ratio (Table III). Infrared spectra of samples 7, 8, 12, 13, 15, and 16 (Tables I and II) quite distinctly show the presence of methyl groups (1380, 2865, and 2960 cm.⁻¹ bands), together with an increase of the CH₂ absorption bands. In the case of samples 15 and 16 there is only a single explanation of such changes in the infrared spectra, i.e., that alkylation of polystyrene by ethylaluminum dihalide took place. Because there was also a strong HCl evolution, the decrease of the C/H ratio caused by incorporation of the ethyl group was compensated in this case by the loss of hydrogen by HCl liberation. Samples 7, 8, 12, and 13 also contain methyl groups originating in the ethylation of the nucleus by catalyst but, in all these cases, cyclohexane also present in the reaction mixture could be attached to the polymer by a side reaction causing an additional increase of the hydrogen content in the polymer. This is supported by the analysis of a polymer treated with AlBr₃ (Table III, No. 9), the infrared spectrum of which did not indicate any traces of methyl groups. The C/H ratio, however, showed a marked increase of the hydrogen content. In this case AlBr₃ was dissolved in cyclohexane and, as follows from the mass-spectrometric analysis, the assistance of the latter is in many reactions highly probable.

When summarizing the results of the spectroscopic structure investigations it is apparent that the action of aluminum halides on polystyrene leads to crosslinking of the latter at least partially through the phenyl rings. In addition, benzene rings undergo alkylation by the catalyst or solvent as well as halogenation which is particularly important in polymers treated in carbon tetrachloride medium.

It is now the generally accepted view that in the absence of moisture aluminum halides interact with aromatics with the formation of weak π -complexes.⁸⁻¹⁰ Evidently this type of interaction is not accompanied by any changes in the polystyrene structure, as has been demonstrated by the fact that a solution of polystyrene in cyclohexane did not show any changes in the ultraviolet spectra in the presence of EtAlCl₂ over a considerably long period of time.

The action of aluminum halides upon polystyrene in the presence of moisture, leading to crosslinking, may proceed by two mechanisms. By analogy with the well-known chain transfer with polymer during the polymerization of styrene,¹¹ the interaction of Lewis acids with polystyrene in the presence of hydrogen halide (formed by the hydrolysis of aluminum halide) may also involve the formation of cations on the main chain by the abstraction of hydride ion from the tertiary carbon. The second type of interaction may be the formation of σ -complexes¹⁰ of the general type p-ArH· ArH₂+·Al_n x_{3n+1} , through direct interaction of the aluminum halide– hydrogen halide system with the nucleus (x denotes alkyl, halogen, or hydroxyl). The existence of both types of interaction is highly probable.

The former possibility, i.e., the formation of cations on the backbone chain, appears to be supported by the presence of molecular hydrogen among the gaseous reaction products. This reaction can be visualized as shown in eq. (1):

$$\sim CH_2 - CH_2 - CH_2 \sim + AIX_3 + HX \rightarrow CH_2 - CH_2 \sim + AIX_3^{-} (1)$$

The polymeric cation either loses hydrogen and is converted to the carbonium ion or, to some extent, disproportionation connected with the chain rupture may also be possible.

$$\sim CH_2 - CH_2 \sim + H_2 \qquad (2)$$

$$H (H^+) \sim CH_2 - CH_2 \sim - CH_2 \sim - CH_2 \sim (3)$$

Both types of cations react in the absence of chlorinated hydrocarbons with further polystyrene molecules, again partially on the site of the tertiary carbon atom and partially alkylating the ring.

The formation of σ -complexes with aromatic rings is supported by the fact that higher degrees of substitution have been detected, the occurrence of which can be hardly explained by chain transfer for steric reasons. Thus, the formation of higher substituted benzene rings may take place through the electrophilic attack of ethylaluminum dichloride upon the nucleus already twice substituted.

A completely different situation arises when carbon tetrachloride or another chlorinated hydrocarbon is present. It can be assumed that CCl_4 forms complexes with aluminum halides similar to those of alkyl halides with aluminum tribromide. Such complexes are relatively stable in the absence of moisture, as has been shown by electrical conductivity measurements. In the presence of traces of water their stability decreases and they are more ionized. They precipitate from the solution as a red liquid characterized by three absorption bands at 300, 340, and 360 m μ in the ultraviolet spectrum. Inside of these complexes exchange of halogens occurs, as indicated by the appearance of mixed carbon trihalide ions when carbon tetrachloride and ethylaluminum dibromide react in cyclohexane medium. In this case also small amounts of trichloropropane were detected arising from the displacement reaction

$$(C_2H_5)_2Al_2Br_4 + CCl_4 \longrightarrow C_2H_5CCl_3 + C_2H_5Al_2Br_4Cl$$
(4)

The reaction of the CCl₄-aluminum halide complex with polystyrene is rather complicated. In the presence of hydrocarbons such as cyclohexane, many ill defined side reactions involving the latter compound also take place, as follows from the mass spectrometric analysis of reaction products (Table II, No. 12). From the composition of the reaction mixture it is clear that various isomerizations, dehydrogenations, and alkylation reactions, proceeding mostly by an ionic mechanism, may assist in structural changes of the polystyrene. The strong evolution of hydrogen chloride together with the formation of practically insoluble products containing relatively high amounts of bound chloride indicate that one path of the interaction of polystyrene with the CCl₄-aluminum halide complex may be a condensation reaction analogous to that well known from the condensation of substituted benzenes with dichloroethane.¹² Detailed mechanism of that reaction is probably the displacement mechanism now generally accepted in many Friedel-Crafts alkylations of aromatics. Carbon tetrachloride in this case replaces the alkyl halide in the former case.¹⁰

A free cationic mechanism involving the formation of CCl_3^+ ions and their electrophilic attack upon the nucleus cannot be excluded. This type of reaction also explains why the amount of HCl evolved is much higher than the molar amount of aluminum halide used. In some cases there is also some evidence of this reaction arising from the infrared spectra of polymers, because in many cases absorption bands appear at 650 and 740 cm.⁻¹ the origin of which is not fully understood but which, however, could be assigned to a symmetrical and asymmetrical C—Cl vibration in a CCl₂ group situated between two phenyls. The major part of such groups, however, should be removed by hydrolysis during precipitation of the polymer by acidified methanol.

The above-mentioned alkylation reaction of phenyl rings taking place when ethylaluminum dihalides are used as catalysts can be represented by the scheme in eqs. (6) and (7).

$$\operatorname{CCl}_{4} + (C_{2}H_{5})_{2}\operatorname{Al}_{2}\operatorname{Br}_{4} \rightarrow C_{2}H_{5}\operatorname{CCl}_{3}\cdot C_{2}H_{5}\operatorname{Al}_{2}\operatorname{Br}_{4}\operatorname{Cl}$$

$$+ C_{2}H_{5}\operatorname{CCl}_{3}\cdot C_{2}H_{5}\operatorname{Al}_{2}\operatorname{Br}_{4}\operatorname{Cl} \rightarrow$$

$$+ H_{C_{2}H_{5}} - \left[\operatorname{CCl}_{3}\cdot C_{2}H_{5}\operatorname{Al}_{2}\operatorname{Br}_{4}\operatorname{Cl}\right]^{-} \rightarrow$$

$$+ C_{2}H_{5} + \operatorname{CHCl}_{3}\cdot C_{2}H_{5}\operatorname{Al}_{2}\operatorname{Br}_{4}\operatorname{Cl} \qquad (6)$$

In this case it is clear that ethylaluminum dibromide reacts as a dimer (appearance of CBr_3^+ ions in the mass spectra). Cross-halogenation inside of the complex is very fast.

A third reaction path in carbon tetrachloride medium may also be the mechanism shown in eqs. (1) and (3) for the absence of carbon tetrachloride, i.e., the formation of cations on tertiary carbon atoms and subsequent attack of these cations upon another molecule.

The ultraviolet spectra do not give unambiguous evidence of the structure of the intermediate ionic species involved in the crosslinking reactions due to the complexity of the reactions taking place. At low polystyrene concentrations (Fig. 3) the reaction product of the polystyrene–EtAlCl₂– CCl_4 interaction exhibits absorption bands overlapping those of the original complex alone, all increasing with time (bands at 300, 350, 395, and 460 m μ). However, only the long wave band at 460 m μ is conditioned by the presence of polystyrene. An EDA complex of the type assumed in reaction (5) may be responsible for its appearance. This conclusion is also strongly supported by the similarity of the ultraviolet spectra of the reaction mixture containing an excess of polystyrene in carbon tetrachloride (Fig. 4) with the spectra of an identical mixture in which, however, polystyrene was replaced by *p*-xylene (Fig. 4D) and where formation of cations of the diarylmethane or even triaryl methane type could be detected.¹³

CONCLUSIONS

Due to its basic nature, polystyrene interacts under appropriate conditions with strong Lewis acids, undergoing branching, crosslinking, alkylation, and halogenation. The occurrence of the two latter reactions depends upon the nature of the catalyst and the solvent. The extent of all reactions leading to structural changes of the original polymer is rather high in carbon tetrachloride medium and increases with increasing catalyst concentration.

It is obvious that under appropriate conditions crosslinking reactions may also play some role in the cationic polymerization of styrene, especially in the case when the reaction is allowed to proceed to high conversions and when carbon tetrachloride is used as the reaction medium.¹⁴ Crosslinking phenomena, for example, may explain an anomalous volume increase in the AlCl₃-initiated polymerization of styrene in CCl₄.¹⁵

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Morphology of Nascent Polyolefins Prepared by Ziegler-Natta Catalysis

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Synopsis

The morphology of nascent (i.e., as-polymerized) Ziegler-Natta polymers was studied by optical and electron microscopy and x-ray and electron diffraction. Observations were made on six polyolefins: polyethylene, polybutene, polypropylene, polystyrene, poly-4-methylpentene-1, and polyisoprene. These polymers were synthesized by using conventional techniques by polymerizing the undiluted monomer or monomer-diluent mixtures with a preformed heterogeneous catalyst obtained by reacting a titanium halide and aluminum alkyl. After the reactions were terminated the polymers were subjected to suitable purification treatments and stored in the wet state. Observations in the optical microscope revealed that, in most cases, the polymer is formed as discrete hollow particles with a fibrous texture, but in a few instances, depending upon experimental conditions, it could also form as fibrous sheets or webs. More detailed observations in the electron microscope showed that the polymer is composed of a profusion of fibrils 200-1000 A. in width and of indefinite length. The fibrils themselves have a fine structure as indicated by the presence of lamellae running perpendicular to their length. Various interpretations of this apparent structure are discussed. The x-ray and electron diffraction studies show that the molecular chain axis is oriented perpendicular, or nearly so, to the plane of fibril lamellae and suggest that the molecules are folded within the lamellae in a manner analogous to conventional polymer single crystals. As fibril formation is observed under most conditions of polymerization it is considered to be basic to the mechanism of Ziegler-Natta catalysis. It is proposed that the fibrils are formed by the crystallization of polymer chains growing from the active sites on the catalyst surface. The process is likened to root growth in whiskers, new material being added at the base or root. The detailed mechanism of fibril formation and of the organization of the fibrils into larger structural formations are obscure, but several possibilities are discussed.

INTRODUCTION

During the last decade great progress has been made in the understanding of crystallization phenomenon in high polymers. In the main this has been due to two developments which occurred almost simultaneously.

In 1955 Natta¹ announced the discovery of new methods for synthesis of linear polymers with a sterically ordered arrangement of monomer units. Most of these so-called stereoregular polymers are prepared by carrying out the polymerization on the surface of a solid catalyst. The most important of these heterogeneous processes are those involving the Ziegler-Natta coordination complexes formed by the interaction of metal alkyls with transition metal halides. The stereoregular polymers possess many unique properties which are associated with their ability to crystallize.

During the same period the wide application of optical and electron microscopy, as well as x-ray and electron diffraction, to problems of polymer morphology led to the recognition that polymers crystallize from the melt characteristically with a spherulitic habit, and culminated in the discovery of polymer single crystals.² It is now well established that in solution-crystallized polymers the fundamental unit of structure is the thin lamella, in which the molecules are folded regularly back and forth on themselves. There is mounting evidence that this is equally true in melt-crystallized polymers.

In all of the observations leading to the above conclusions the polymers used were essentially regenerated, in the sense that the original morphological structure of the material as polymerized was destroyed by dissolution or melting prior to use. Little attention has been paid to the study of structures formed by the large scale organization of the macromolecules during the process of polymerization. Niegisch^{3,4} reported that dendritic crystals of polyethylene grew during the early stages of the polymerization of linear polyethylene with a soluble aluminum halide-tetraphenyltin-vanadium halide catalyst in cyclohexane. Leese and Baumber⁵ showed that polyoxymethylene single crystals appeared during the polymerization of trioxane catalyzed homogeneously with boron trifluoride. Finally, Kargin et al.⁶ showed that "supermolecular" formations, consisting of an accumulation of fibrils, are formed directly during the polymerization of poly(vinyl chloride) and polyethylene. The morphology of these structures was stated to be similar to that found in films of these polymers obtained from solution.

In the present work we have attempted to obtain information about the morphology of nascent polymers prepared by Ziegler-Natta catalysis. In addition to its intrinsic interest in relation to the study of the morphology and crystallization mechanism in polymers, it was hoped that the work might be helpful in extending our understanding of the mechanism of polymerization with heterogeneous catalysts.

It will be shown that during the course of Ziegler-Natta catalysis, structural entities are obtained which are unique and distinct from those normally formed in solution and melt crystallization.

The observations provide evidence that the catalyst surface, in addition to exerting a strong influence on the geometry of the polymer and its stereoregularity, also plays an important role in organizing the polymer chains into larger structural formations. The work has embraced a wide range of polymers as well as several heterogeneous catalysts, and the phenomena to be described appear to be of general occurrence. This paper deals with observations on the morphology of nascent polyethylene, isotactic polypropylene, isotactic polybutene-1, isotactic poly-4-methylpentene-1, isotactic polystyrene, and 1,4-trans- β -polyisoprene.

EXPERIMENTAL

Materials

Ethylene, propene-1, butene-1, and prepurified nitrogen (all from Matheson) were dried by passing through a Drierite tower and then bubbling through 50% triethylaluminum in tetradecane befor reaching the reaction vessel.

Styrene (Eastman Kodak) was purified by distillation at 50°C./14 mm., the first and final fourths of the charge being discarded.

Isoprene (Eastman Kodak) and 4-methylpentene-1 (Anachemia) were distilled over sodium metal directly into the reactor under a blanket of nitrogen, the first and final fifths of the charge being discarded.

All hydrocarbon solvents and diluents were of C.P. grade and were distilled over sodium metal immediately before use. Acetone and methyl ethyl ketone were redistilled over Drierite while alcohols were used as supplied.

Titanium tetrachloride (Fisher), titanium trichloride (Stauffer), triethylaluminum (Ethyl Corp.), lithium aluminum hydride (Metal Hydrides), metallic sodium, and chromium acetate (Fisher) were used as received.

Apparatus and Methods

Polymer Syntheses. Most polymerizations were conducted in a 1-liter three-necked glass reactor fitted with a large Teflon paddle stirrer, a gas inlet, a thermometer, and an air condenser having two branches, one serumcapped for the injection of catalyst while the other was protected by a mineral oil bubbler and drying tube. In runs where uniform temperature was desired a jacket thermostated the assembly to better than $\pm 0.5^{\circ}$ C. In some instances sealed screw-cap 1-liter bottles, fitted with self-sealing liners, were used either with magnetic bar agitation or placed on a reciprocating shaker.

In all cases the catalysts were prepared in the absence of monomer either *in situ* or in a separate container and subsequently transferred to the diluent-monomer mixture.

Withdrawal of samples during polymerization was effected by using a modified reactor fitted with an oblique side-arm extending below the liquid level. Nitrogen pressure in the reactor was momentarily raised, a stopcock at the end of the side arm was opened, and the required amount of polymer-catalyst slurry forced into a vessel containing 1:1 toluenemethanol.

Two runs were conducted in the absence of a liquid phase. The inside surface of a puncture-top reactor was coated with the preformed catalyst

	Experimental conditions and remarks	Sealed bottle	Std. reactor	11 II	11 II	<i>11</i>	Samples taken during	reaction	Modified reactor	Std. reactor	1)ry catalyst	film on reactor wall	Std. reactor	<i>ti ti</i>	11 11	25 ZZ	97 91	Std. reactor	11 II	11 II	55 55	11 (I	I)ry catalyst film	on reactor wall
	Ref.ª		7	2	I	1	1			x	1		6	I	1]	10	10	10	10	11	П	1	
	Mono- mer/ diluent ratio]	1	ſ	I]	I			Ì	ł		ļ	l	l	ļ	I	ł	Ι]		Į]	
I ples	Polymerization medium (diluent)	Toluene	Tetralin	Benzene	Toluene	n-Hexane	Toluene			Toluene	N_2		Toluene	Benzene	<i>n</i> -Hexane	Toluene	Benzene	Benzene	и	**	<i>n</i> -Hexane	11	N_2	
TABLE List of Sam	Catalyst concn. (Ti), mmole/l.	0.2	0.2	0.2	0.2	0.2	0.2			l	Ι		0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
	Catalyst	/Al(C ₂ H ₅) ₃ , 1:3	11 II	77 TT	11 11	11 11	11 11			sd	$(Al(C_2H_5)_3, 1:3)$		$TiCl_2/Al(CH_3)_2Cl$	$(AI(C_2H_5)_3, 1:3)$	11 11	11 11	11 11	11 II	33 33	<i>11 11</i>	u u	11 II	11 II	
		TiCl4/	22	"	11	11	11			Phillif	TiCl4/		(C_2H_5)	TiCl4/	77	22	IJ	11	11	**	2	11	11	
	Reac- tion temp., °C.	80	30-40	40 - 50	81-82	12 - 16	51			<u>0</u> %	12		28 - 35	35-42	31	2	35 - 42	17	37	56	19	37-38	37	
	Code	49	51	52, 53	66	71	75A	to	75H	62	81		82	54	67	68	55, 56	61	63	62	6.5	78	80	
	Polymer	PE	PE	PE	PE	PE	PE			PE	PE		PE	ΡΡ	ΡP	ЪР	PB_{II}	PBu	PB_{U}	PBu	PB_{U}	PB_{U}	PB_{II}	

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PIP	57	27 - 28	z	73	77	0.2	n-Hexane	1:7	12^{b}	Std. reactor
\mathbf{PS}	50	27-28	"		U U	0.2	Undiluted	Ι	[Sealed bottle
							styrene			
\mathbf{PS}	11	50	11		11	0.2	11	I	136	Std_reactor
\mathbf{PS}	12, 77	25-28	TiCl4/1	LiAI(C ₁₀	$H_{21})_4$	0.07	Cyclohexane-	1.5	14b	
							tetralin			
PS	19	50 - 60	a-TiCl	$_3/Al(C_2l)$	$(1_5)_3, 1:3$	0.05	Benzene	1.5	1.5	77 FT
\mathbf{PS}	72	51	$TiCl_4/_2$	Al(C ₂ H ₅)) ₃ , 1:3	0.2	Toluene	1:12	16	12 27
\mathbf{PS}	73	25	"	"	77	0.2	Undiluted	1	1	Sealed bottle
	8						styrene			
FS S	74	52	3	,,	ti ti	0.2	Toluene	1:1	16	Std. reactor
PS	22	50	"	3	77	0.2	Undiluted			Sealed bottle
							styrene			no agitation
\mathbf{PS}	8	25 - 26	"	"	,,	0.2	Xvlene	111	I	Sealed hottle
\mathbf{PS}	86	11	11	11	"	0.2	Mesitylene	-	İ	
PS	87	53	"	11	,,	0.2	Tetralin	1.1		, i î î
PS	XX XX	<i></i>	n	11		0.2	<i>m</i> -Hexane	 	1.6b	55 55
PS	06	51	n	11	5	0.005	Toluene	9.3 2.6		Standard monte-
PS	96A	50	11	11	11	0.2	Toluene	5 - F 5 - F		Somular leadur
	to							6. T		during takel
	96G									
P4MP	69, 70	31	TiCl ₄ //	M(C ₂ H ₅)) ₃ , 3:1	0.2	Benzene	1.4	17	(modified reactor)
P4MP	76	30-32	**	"	77	0.2	Undiluted	1	1	Sealed bottle
							monomer			
^a Unless ot ^b Literatur	herwise not e procedure	ted, proced	lures mod. exactly	ified to a	some extent.				an a	
			· Cronnero							

MORPHOLOGY OF NASCENT POLYOLEFINS

suspension and heated to the polymerization temperature, while a current of nitrogen was passed in order to sweep out the *n*-hexane used as a diluent during the catalyst preparation. Purified monomer was then substituted for nitrogen.

The usual precautions were taken to ensure anaerobic and anhydrous conditions throughout all polymerizations.

A summary of the polymerizations carried out is given in Table I. The usual abbreviations, such as PE for polyethylene, PP for polypropylene, PBu for polybutene-1, PIP for polyisoprene, PS for polystyrene, and P4MP for poly-4-methylpentene-1 are used. Although some preparative methods were followed exactly from the cited references most were more or less modified. Preparation of the most frequently used catalyst, TiCl₄-Al(C₂H₅)₃ at a ratio of 1:3, has been described in detail by Kern and Hurst.¹⁸ It was found that this preformed catalyst could polymerize all the six listed olefins at a conversion efficiency adequate for our purpose.

A superficial examination was made of polymers produced by other catalytic systems. Among these were: (a) a Phillips catalyst⁸ made by pyrolyzing chips of alundum impregnated with chromium acetate in the presence of air at 625°C. for 20 hr. and subsequently "promoted" by adding Al(C₂H₅)₃ (1:1 chromium to aluminium alkyl) in toluene before allowing ethylene into the system; (b) a homogeneous Ziegler-Natta system described by Karapinka and Carrick⁹ with dicyclopentadienyltitanium dichloride-dimethylaluminum chloride for the polymerization of ethylene; (c) a Natta catalyst¹⁵ where α -TiCl₃ is used instead of TiCl₄; and (d) the system of Campbell and Haven¹⁴ which consists of TiCl₄-LiAl(C₁₀H₁₁)₄. Both of these last catalysts were used for the preparation of isotactic PS.

Specimen Recovery and Purification. Polymerizations were sometimes terminated by poisoning the catalyst with a large excess of methanol or isopropanol added directly into the stirred reaction flask. This was followed by filtration of the solids, washing twice with methanol (or isopropanol), then with acetone containing 1% concentrated hydrochloric acid, and finally with distilled water. The polymer obtained was then dried at room temperature under reduced pressure. Further treatment was required in order to separate low molecular weight material, atactic and stereoblock polymers. This was achieved by refluxing the products in fresh portions of toluene or benzene until no more polymer could be extracted. This method of specimen recovery, although satisfactory for some preparations, had several disadvantages. The most objectionable was that some polymer soluble in the polymerization medium was precipitated at the end of the reaction with the stereoregular high polymer, and its subsequent removal required treatments which were generally deleterious to the nascent structure of the isotactic component. Accordingly, in many preparations, an alternative procedure which obviated these difficulties, was also used. At the end of the reaction the catalyst was deactivated with 10 ml. of methanol added dropwise with vigorous stirring. The solids were sedimented and the highly swollen, catalyst-laden polymer

was washed three times with fresh portions of the same diluent as used during the synthesis (benzene or toluene, if undiluted monomer had been used). Solvent exchange to methanol with overnight immersion, followed by methanol containing 3% concentrated hydrochloric acid, removed most of the catalyst. The polymer was then solvent exchanged in three steps to toluene, benzene, or *n*-hexane and stored in this condition.

The two polymerizations conducted over dry catalyst, PBu 80 and PE 81, were treated in the same way, except that a toluene wash preceded catalyst deactivation and the continuous polymer film obtained was cut into pieces, about 1 cm.², to facilitate handling.

Microscopy. Direct viewing of whole "as-polymerized" polymer, in its original uncollapsed state, was carried out by optical microscopy. Diluent-swollen polymer was deposited on a glass slide, covered gently with a cover slip, and examined in transmitted, polarized or phase-contrast illumination. Optical observations were also made under steep oblique illumination after drying down the specimen on a microscope slide and coating it with an evaporated layer of aluminum.

Observations of "as-polymerized" material by direct transmission in the electron microscope was seldom possible because of excessive sample It was therefore necessary to resort to replication techniques. thickness. For this purpose a shadow transfer replica method was adopted. Solventladen polymer was pressed between two microscope slides and the occluded liquid expelled. The specimen then consisted of a thin laminated web, which after drying was shadowed with platinum or platinum-palladium. A moderately thick layer of carbon was then evaporated onto the specimen. Finally, the carbon-metal layer was backed with gelatin and mechanically stripped from the polymer, or the polymer was dissolved in boiling ochlorotoluene for the strongly adhering samples. By floating the composite film on aqueous hydrochloric acid solution (2-20%) the gelatin was dissolved, and the replica was ready for mounting on copper grids for examination in the electron microscope.

In some cases the polymer could be disintegrated mechanically under toluene or benzene. The suspension thus obtained was sedimented and washed with fresh portions of diluent. Drops of the suspension were then dried down on copper grids previously coated with a film of evaporated carbon, and shadowed with platinum or platinum-palladium.

The replicas and specimens for observation by direct transmission were viewed in a J.E.M. 6A electron microscope, in which selected area diffraction experiments were also performed. Some electron diffraction patterns, with the plane of the specimen in an oblique position with respect to the electron beam, were obtained in an AEI-EM-6 electron microscope.

In a few cases whole specimens were examined by a scanning electron microscope as described by Smith.¹⁹ The advantages of this instrument are that it has a great depth of field and permits direct observation of thick material.

X-Ray Diffraction. All x-ray diagrams were obtained with Ni-filtered

CuK α radiation. Wide-angle patterns were registered on a flat-film camera, while low-angle measurements were made in a Kiessig vacuum camera²⁰ giving a resolution of about 300 A.

OBSERVATIONS

General Remarks

To set in perspective the findings to be reported in the sequel, it will be useful here to describe certain relevant observations made during the preparation of the polymers.

Most of the specimens were synthesized by adding a preformed catalyst to pure monomer or monomer-diluent mixtures. Initially, the reaction mixture is a uniformly dispersed and free-flowing suspension of finely divided catalyst particles. This suspension thickens as polymer begins to form, and after the reaction has proceeded for some time, the mixture takes on a curdled aspect, becomes considerably more viscous, and discrete gellike particles can be discerned by visual inspection. Microscopic examination of the mixture then reveals that most of the catalyst has become concentrated within the gellike particles, as can be seen in Figure 1.

In all cases, the polymer separates immediately during synthesis, as a solid phase even in reaction media which would, *a priori*, be expected to dissolve it; for example, PS in styrene–benzene and PBu in benzene.

The precipitated solids are highly crystalline, giving x-ray diagrams



Figure 1.

with well-defined reflections characteristic of the particular stereoregular polymer, and in some cases are insoluble in hydrocarbons even under prolonged reflux.

In the synthesis of crystalline polyolefins by Ziegler-Natta catalysis, atactic and stereoblock polymers are also formed. However, in the present investigation only the stereoregular polymer is of interest; the other polymeric species are generally soluble in the reaction medium and do not precipitate unless deliberately brought out of solution by the addition of large amounts of nonsolvent. In this event a separation of the amorphous and crystalline polymers can be achieved by selective solvent extraction as outlined by Natta.²¹ While such treatments leave the crystalline precipitated solids undisturbed, they were avoided in the present work whenever samples were intended for microscopy.

From the foregoing it may be concluded that the discrete gellike particles which separate directly during synthesis are the morphological expression of the stereoregular polymer. These precipitated solids were characterized by x-ray diffraction studies. The samples of PE, PP, P4MP, and PS were in their usual crystal form, i.e., orthorhombic,²² monoclinic,²³ tetragonal,²⁴ and rhombohedral,²⁵ respectively. Although isotactic PBu is polymorphic,²⁶ all samples prepared (see Table I) were principally of modification I which, according to Natta et al.,²⁷ is rhombohedral. However, the specimens prepared at higher temperatures also appeared to contain small amounts of modification III, in keeping with the findings of Boor and Youngman.²⁸

The preparation of polyisoprene (PIP 57) closely followed the procedure of Adams et al.¹² which gives mainly *cis*-1,4-PIP; it appears, however, that this polymer is soluble in the reaction mixture. The small amount of solids precipitated during synthesis were identified as *trans*-1,4-PIP on the basis of the x-ray reflections which correlate partly with the orthorhombic structure of Bunn²⁹ and Storks³⁰ for β -gutta-percha. In addition, an authentic sample of *trans*-1,4-PIP (Polymer Corp. of Canada PIP 388) gave an identical diagram.

Gross Morphology of Nascent Polymer

When the particles of stereospecific polymer are examined in the optical microscope they are found to be well-defined structural entities which will be referred to hereafter as globules. In size and shape they vary with the polymer and reaction conditions.

Representative examples of globules of the various polymers are shown in Figures 2–5. In any given preparation all the globules were more or less of the same shape and showed a fairly narrow distribution in size with mean dimensions ranging from about 0.1 mm. in some samples to nearly 2 cm. in others (Table II). In general, the globules of PS, PBu, PIP, PE, and P4MP were spherical or spheroidal, while those of PP might be described as shaped like a catenoid.



Figure 2.



Figure 3.



Figure 4.



Specimen	Polymerization particulars	Globule size, mm.ª	Fibril width, A.			
PE 66	85°C.	1.0-20.0	700-10,000			
PE 51–53	30–50°C.	0.5 - 1.0	400			
PP 68	84°C.	0.4 - 0.6	300-600			
PBu 61	17°C.	0.3 - 0.7	300-600			
PIP 57	_	0.7 - 1.2	200-300			
PS 96	Toluene	0.1 - 0.3				
PS 88	<i>n</i> -Hexane	0.07 - 0.15				
PS 86	Mesitylene	0.5 - 0.7	200 - 300			
PS 85	Xylene	0.5 - 0.7				
PS 11	Undiluted styrene	0.1-0.3				
PS 77	$TiCl_4$ -LiAl(C ₁₀ H ₂₁) ₄	1.0 - 3.0				
PS 19	lpha-TiCl ₃ -Al(C ₂ H ₅) ₃	0.2 - 0.3	300-600			
P4MP 69		0.5 - 1.0	200 - 300			

TABLE II Globule Size and Fibril Width in Nascent Polyolefins

 $^{\rm a}$ The stated dimensions refer to a hypothetical sphere which encloses the globule exclusive of any appendages present.

A less common but still frequently encountered type of globule is shown in Figure 6. It consists of two interconnected spheroidal structures. These were often found in preparations of PBu and PIP where they occurred along with the more common single spheroids. There were no preparations consisting of the interconnected type exclusively.



Figure 6.



Figure 7a.





Figure 8.



Figure 9.



Figure 10.

Perhaps the most remarkable type of globule is that shown in Figure 3. These were seen only in preparations of PS and P4MP and are characterized by the presence of conical appendages (hereafter to be referred to as "spikes") protruding from the globule surface. For PS the size and appearance of the spikes may vary with the conditions of polymer synthesis but was approximately the same from one globule to another in a given preparation. When seen in the optical microscope between crossed nicols the spikes show a peculiar banded extinction pattern which is not present in the remainder of the globule (Figs. 3 and 7). This indicates that the architecture of the spike differs from that of the globule itself, an inference which is supported by two other observations, viz., (a) whereas globule collapse is an inevitable consequence of drying, the spike frequently remains erect, (b) ultrasonic treatment of a suspension of globules causes their disruption in such a manner that only the spikes remain intact after a short time; a considerably longer treatment is needed to disintegrate the spike itself.

In many cases the extinction pattern of the spike is highly suggestive of a spiral structure (Fig. 7), and further indications of this are found in specimens which have been dried on a flat surface and examined in the optical microscope with steep oblique illumination (Fig. 8).

From all these observations the morphology of the spikes emerges, clear in broad outline if not in detail. They seem to be composed of a membrane surrounding a spiral framework. The possible significance of these structures will be discussed later.



Figure 11.

Closer observation of the globules in the polarizing microscope reveals other important aspects of their morphology. In the first place, it is noteworthy that they fail to exhibit the characteristic Maltese cross between crossed nicols and consequently are not spherulitic in structure. Secondly, with a suitable adjustment of the focus the globules are seen to be surrounded by what appears to be a thin birefringent skin (Fig. 9). This suggests that the globules may in fact be hollow and there is strong further evidence in support of this proposition: (a) when the globules are allowed to dry on a glass slide they collapse to flat sheets (Fig. 10); -(b)large specimens obtained in some preparations can be manually punctured to reveal a hollow interior under the stereo microscope; (c) when suspensions of the globules are freeze-dried from benzene they do not collapse completely and many take on the appearance of partially deflated balloons. A particularly striking example of this effect is shown in the photomicrograph of Figure 11, which was taken with the scanning electron microscope.

The conclusion that the globules are hollow thus appears to be firmly based and applies to all the polymers with the exception of PP. In this case the globules neither alter their shape nor collapse on drying, and no birefringent skin is evident on optical examination. One gains the impression that these particles, if not entirely solid, at least have a wall which is densely packed and thick in comparison with the overall dimensions of the particle itself.

Factors Affecting Gross Morphology

As already mentioned, the overall appearance and mean size of the globules in a given preparation was largely determined by the monomer. However, the type of catalyst and the reaction conditions were not without influence. An effort was therefore made to ascertain the effect of some of the reaction variables independently. Those investigated include the type of catalyst and its concentration, the diluent and its concentration, the reaction temperature, and the mode of agitation. The results of all these experiments will not be detailed here. Suffice it to say that changes in any of the variables mentioned caused changes in the size and appearance of the globules. In many cases, changes in different reaction variables produced equivalent morphological effects. Consequently it was difficult to assess the significance of the observed morphological changes. It is nevertheless interesting to note that many of these reaction variables influence the polymerization rate. Accordingly it may be suspected that the reaction rate is the vehicle by which each of the variables affects the morphology.

The most important observations were the following. A striking demonstration of the influence of the catalyst was obtained when a soluble catalyst was used for the polymerization of ethylene (PE 82). This preparation gave a suspension of lamellar crystals, as distinct from the globules obtained in a heterogeneously catalyzed preparation of the same polymer. This, however, is a special case and will be considered later.

In a series of experiments various methods of stirring the reaction mixture were used, and in some cases the polymerization was carried out in an unstirred system. It was found that the mode of agitation (slow rotating paddle, rapidly spinning magnetic bar, or gently reciprocating shaker) had no significant effect, but if stirring was suppressed altogether, discrete globules were not formed. Instead, one obtains an apparently coherent mass, which, when carefully torn apart, is found to consist of long convulated strands of fibrous polymer as shown in Figure 12. This may be compared with Figure 3, which shows the product obtained under identical conditions with stirring. It thus seems clear that at least minimal agitation is necessary for the formation of the globules.

Genesis and Growth of Globules

There would appear to be few ways by which the genesis and rate of growth of the globules can be studied. The best approach is undoubtedly the direct microscopic observation of the same group of globules from birth to maturity in the reaction mixture. However, the necessity for continuous stirring in order to achieve adequate mixing, and strict adherence to anhydrous and anaerobic conditions, presented technical difficulties



Figure 12a.





Figure 13.

of such magnitude that efforts along these lines were not fruitful. The alternative is to sample the reaction mixture at intervals, and examine the products *in vitro* after deactivating the catalyst. The chief difficulty with this method arises from the existence of a distribution of particle sizes in any preparation; consequently definitive results can only be obtained by an elaborate statistical analysis. Nevertheless, as will now be shown, useful information could be obtained without going to this length.

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Figure 13 shows photomicrographs of specimens withdrawn from a polystyrene preparation (PS 96) at various times. At the start of the reaction, the catalyst particles are uniformly distributed in the reaction medium. Shortly thereafter, there appear isolated clusters of fibrous material in which most of the catalyst is entrapped. A portion of such a cluster is shown in the first plate. For a period of about 30 min, there is scarcely any observable change in the appearance of the system. Abruptly, after this induction period, the faint outline of the globules becomes visible under polarized illumination, and subsequently they increase somewhat in size. There is, also, a gradual improvement in contrast which may presumably be ascribed to wall thickening. In the final



Figure 14.

stages the protruding spikes make their appearance. The foregoing observations suggest that the globules do not develop by a process involving conventional nucleation and growth. There remains, however, the remote possibility that the globules, perhaps of smaller size, were already present from the very earliest stages of the reaction, but went undetected because of low optical contrast due to extreme wall thinness. In order to check on this possibility specimens from polymerizations interrupted at various low degrees of conversion were examined in the electron microscope. No globules were observed. It was found, however, that in the earliest stages of the reaction lamellar crystals and short fibrils which elongate with time, are formed. More will be said later about these lamellar crystals and fibrils.

Structure of the Globule Wall

In the optical microscope the wall of the globules in many cases exhibited a distinctly fibrous texture. Appreciation of this feature is facilitated by reference to Figure 2. In some instances, where the wall was inadvertently damaged, fibrils could be clearly seen protruding outward into the suspending medium. The fibrous character also appears prominently on the collapsed wall when the globules are dried on a flat surface and viewed with steep oblique illumination (Fig. 10).

In some samples, fibrosity was so marked as to be easily discernible even with the naked eye. Figure 14 shows a section of wall dissected



Figure 15.



Figure 16.

from a large PE globule; it appears to consist of a coplanar array of fibrils. Details of the surface of the globule wall, as seen by the scanning electron microscope (Fig. 15) suggests that it may consist of superposed lamellae of fibrils.

The optical evidence so far presented suggests that the globules consist entirely of long fibrils. In order to obtain more detailed structural infor-



Figure 17.

mation, transmission electron microscopy was utilized. However, because of their wall thickness, globules are not suited for examination by direct transmission methods, and it is therefore necessary to resort to surface replication techniques. These have been described in the experimental section. In electron photomicrographs of the replicas the fibrillar structure of the wall is clearly visible. Examples are shown in Figures 16 and 17. For many specimens the fibrils appeared to be randomly oriented, while in other cases portions of the walls exhibit a high degree of fibril orientation. Such well-ordered regions are often contiguous to less-ordered areas, as can be seen in Figure 16. In general, most samples possessed at least some portions showing orderly fibril arrangement.

Examination of the replicas at higher magnification reveals that the fibrils themselves have a fine structure (Fig. 17). They are conspicuously notched and give the impression of being composed of stacks of platelets. Further details of the fibril structure are given in the next section.

Attempts were made to locate areas on the replicas corresponding to spikes similar to those seen in the optical micrographs, (e.g., Fig. 8). Regions bearing impressions suggestive of spikes were often seen, but they were badly damaged and could not be unambiguously identified and interpreted with confidence. The detailed fibrillar arrangement of the wall of the spikes therefore remains uncertain.

Morphology of Fibrils

In order to obtain further information on the details of fibril structure, the nascent polymer was disrupted mechanically and the fibrils so obtained examined by direct transmission in the electron microscope. Fibrils were separated either singly or in clusters by subjecting a suspension of the polymer to the action of ultrasonic waves or a high speed stirrer. In some cases (e.g., PP, PE) vigorous manual agitation of a suspension sufficed. In shadowed preparations (Fig. 18) one gets the distinct impression that the fibrils are composed of platelets about 100 A. in thickness, stacked like a skewed deck of cards along the fibril axis. The effect is illustrated schematically in Figure 19a. It is possible, however, that the "inclined platelet" structure may be illusory and that the fibrils are in fact helicoids as shown schematically in Figure 19b.

There is yet another type of fibril which is found frequently in PE, rarely in PP but is absent from PS and P4MP. These structures appear to be sequences of thin platelets mounted on one or more central filaments (Fig. 20); they will be designated as "shish-kebabs." There is, however, reason to suspect that this latter morphology is not representative of the polymer in its nascent state. The "shish-kebab" could conceivably be a helicoidal fibril which has been deformed as a consequence of stirring during synthesis or during specimen preparation for microscopy. These and other related questions will be amplified in the Discussion.

The fibrils vary in size from one preparation to another. Table II shows the width of fibrils in representative specimens. The values range from about 200 A. for PS to 10,000 A. for PE. The fibrils of some polymers are extremely uniform in width, while others are irregular. The size and unifromity of the fibrils do not correlate with any of the reaction variables studied.



Figure 18.

Fibrils bearing a striking resemblance to the "shish-kebabs" have been observed previously in polymers crystallized by cooling solutions which are mechanically agitated by stirring³¹ or sonication.³² Two questions may then be raised: (a) Could the ultrasonic or mechanical dismembering of the polymer during specimen preparation affect the morphology of the detached fibril? (b) Could the fibrils themselves have originated from the effect of stirring during the preparation of the polymer? Although it is certain that drastic and prolonged mechanical agitation, particularly with ultrasonics, will damage the fibrils, there is no evidence that the brief exposures used in this work caused appreciable alterations, except possibly in polymers vulnerable to microdrawing effects (e.g., PE and other polymers which are known to undergo plastic deformation near ambient temperature). Indeed, as far as can be ascertained, there is no difference between the detached fibrils and those in the wall replicas. It may also be noted that the "shish-kebabs" are very seldom seen in



Figure 19.

the undisturbed globule wall where deformation effects would be at a minimum. The second question concerning the possibility of fibrils being formed solely as a consequence of stirring during the polymerization reaction may also be refuted. That this is not the case is shown by the fact that fibril formation occurs even in the polymers synthesized under quiescent conditions.

"Dry" Polymerizations

In the foregoing, all specimens investigated were prepared under classical Ziegler-Natta conditions, the catalyst being dispersed in an inert diluent or in the pure monomer. As demonstrated, the polymer so formed is fibrillar in structure. In order to ascertain whether fibril formation is a phenomenon associated with the catalyst system, or with the liquid environment during polymerization, it was of interest to study polymers prepared over "dry" catalyst. To this end, gas-phase polymerizations of ethylene and butene-1 (PE 81 and PBu 80, respectively) were conducted on dry catalyst deposited on the wall of a reactor, as described in the experimental section. The polymer obtained in these systems was in



Figure 20.

the form of a continuous coherent sheet of irregular thickness covering the reactor wall.

Because of their thickness, these films were totally unsuited for transmission electron microscopy, and replication methods were therefore used for examining their structure. At low magnification the surface of the polymer film exhibits a blistered appearance, some areas showing spheroidal prominences (Fig. 21*a*) while others look like convoluted ridges (Fig. 21*b*). Fibrils can sometimes be seen traversing these prominences, and at higher magnification (Fig. 21*c*) the fibrillar nature of the polymer becomes clearly apparent. Attempts to break up the films by mechanical agitation were not successful, and therefore the fibrils could not be studied in detail.



Figure 21a.



Figure 21b.



Figure 21c.

Nevertheless, judging from their appearance in the replicas, these fibrils have a similar structure to those described earlier. The conclusion which thus seems to emerge from these observations is that fibril formation is determined predominantly by the catalyst.

Further observations relating to the distribution of the catalyst in the polymer film should be mentioned. It was found that the catalyst particles, which initially were uniformly distributed in a thin layer over the wall of the reactor, are embedded in the polymer film in localized regions. Furthermore these pockets of catalyst usually appear on the side of the polymer film which is not in contact with the reactor wall. This is clear evidence for extensive catalyst migration, an effect which suggests that the growing polymer fibrils are able to displace the catalyst particles over considerable distances. In addition, when polymer formation takes place from catalyst particles in a compact aggregate, the mechanical action of the growing polymer is able to disrupt and disperse the aggregate. This phenomenon was predicted by Natta and Pasquon³³ on the basis of kinetic data, and, as will be shown in the Discussion, it may possibly be related to the mechanism of globule formation.

Nonfibrillar Crystals

The evidence presented so far suggests that the fibril is the dominant structure element in nascent Ziegler-Natta polymers. There are, however, indications that tabular single crystals also occur in these products. Very rarely, they have been observed in replicas of globule walls, but are clearly apparent in preparations interrupted at very low degrees of conversion where, as shown earlier, few fibrils are yet formed. Electron diffraction experiments revealed that they are single crystals of PE, and further observation showed that they are formed in the initial stages of all preparations, regardless of the polymer. Accordingly it was presumed that they arise mostly from the catalyst itself. This is confirmed by the observation that they are formed when the titanium halide is reacted with the aluminum alkyl. This result is in fact expected, for it is known that small amounts of ethylene and other olefins are evolved in preparing the catalyst complex.¹⁸



Figure 22.

There were two preparations which did not yield fibrillar crystals. These were a polyethylene (PE 82) synthesized with the homogeneous catalyst dicyclopentadienyltitanium dichloride-dimethylaluminum chloride and all polypropylene samples prepared at or near ambient temperature. The former, strictly speaking, does not fall within the purview of the present work, but the experiments were conducted to check the surmise that fibril formation requires the presence of a solid catalyst surface. This point will be elaborated later. The polyethylene sample in question consisted of tabular single crystals as illustrated in Figure 22. They have the conventional orthorhombic structure and a step height of 85 A. (x-ray).



Figure 23.

Figure 23 shows a typical example of the low-temperature polypropylene preparations. They consist of lathlike crystals of approximately uniform size. Direct measurements on photomicrographs gave a thickness of about 100 A., a length of 2000–4000 A., and a width of 300–600 A. It was noted that benzene suspensions of these particles have a characteristic purple color due to light scattering from the regular particles. At high magnifications many of these crystals exhibit striations spaced about 100 A. apart throughout their length, thus suggesting that they may be related to the long fibrils which occur in other preparations.

Low-Angle X-Ray Scattering

These experiments were carried out in an attempt to uncover long spacings which might be related to the platelet thickness in the fibrils. The specimens were usually investigated in the form of a laminate, consisting of collapsed globules which had been constrained to dry from the solvent-swollen state between two glass plates, and were examined with the plane of the laminate oriented parallel to the incident beam. Alternate methods consist of drying a single large globule while applying a

	Fundamental long period, A.	123		123		84	95	94				100	121	ŝ		11	94	138
IIIS	d spacings, A.	123 ± 3	123 ± 3	60 ± 5 2nd order	43 ± 5 3rd order	84 ± 3	9.5 ± 3	94 ± 3	50 ± 15 (Diffuse)	2nd order	9.5 ± 3	100 ± 3	121 ± 5	80 ± 3	41 ± 5 2nd order	71 ± 5	94 ± 5	135 ± 5
TABLE III Long Periods in Nascent Polyolefi	Remarks	Tetralin	Benzene			Homogeneous	Benzene	Benzene			Benzene	$n ext{-Hexane}$	"Dry" reaction	<i>n</i> -Hexane		${ m TiCl_4/Al(C_2H_5)_3}$	$TiCl_4/LiAl(C_{10}H_{21})_4$	Benzene
	Polymerization temperature, °C.	3()-4()	40-50			28-35	56	37			17	37-38	37	27-28		50	25-28	31
	Specimen	PE 31	PE 53			PE 82	P.B.u 62	P13u 63			PBu 61	PBu 78	PBu 80	PIP 57		PS 50	PS 77	P4MP 69

gentle tension along two poles, or dissecting the walls under a stereomicroscope and selecting a ropelike bundle of fibers; the former results in a ligament whose component fibrils are oriented more or less parallel to the direction of the applied tension, while the latter is a special technique used only with certain PE samples. Specimens in the form of ligaments of fibers were examined with the beam perpendicular to the fiber direction.

Although the majority of samples gave only a strong diffuse central scattering, there were several cases in which clearly resolved maxima were obtained as meridional arcs. The results, as calculated from the Bragg equation, are set forth in Table III. Reproducibility was checked by carrying out measurements on specimens from duplicate polymerizations and on samples from the same batch.

The spacings are of the same order of magnitude as the thickness of the fibril platelets, and accordingly it seems beyond reasonable doubt, that they represent the periodicity observed along the fibril axis in the electron microscope. As more than two orders are seldom found it may be supposed that the periodic arrangement is somewhat less regular than that in solution-grown single crystals where up to four orders have been recorded.³⁴

For comparison, the spacing derived from the homogeneously catalyzed PE 82 is also included in Table III. As already indicated, this preparation gave tabular single crystals, and the long spacing observed is that which would be expected for polyethylene single crystals grown at the same temperature. The wide divergence between the values obtained from the homogeneous and heterogeneously catalyzed polyethylene samples suggests that fibrils and conventional single crystals grow by different mechanisms. This point is also illustrated by the following observation. Within the limited range that is experimentally accessible, the polymerization temperature appears to have no effect on the long spacing. This is surprising, by comparison with experience on solution-grown polymer crystals, and suggests that the growth of the fibrils is not nucleationcontrolled, or that the catalyst itself is able to act as a nucleator.

Molecular Orientation

In order to obtain information on the orientation of the chain molecules within the fibrils, wide-angle x-ray and electron diffraction experiments were performed. The x-ray diffraction photographs obtained on laminates or fiber bundles prepared and examined as described in the preceding section, were essentially fiber patterns. However, they showed considerable deviation from perfect fibering, the diffraction maxima being arcs several degrees in length or nearly continuous rings. A typical example of these patterns is shown in Figure 24, along with a line drawing defining the positions of the principal reflections and the corresponding indices.

In all cases the (hk0) reflections were intensified on or near the equator. This in itself implies that the significant zone axis, i.e., the molecular chain direction, must be more nearly parallel to the fiber axis as distinct from perpendicular. For a more quantitative interpretation the patterns





Figure 24.

were analyzed as follows. Let ρ be the angle between the normal to a given set of planes and the fiber axis. The relation between ρ and the angular position of the corresponding reflection along the Debye-Scherrer ring is given by the equation:

$\cos \rho = \cos \beta \cos \theta$

where β is the angle measured on the photograph from the meridian, and θ is the Bragg angle. First ρ was calculated, then knowing the geometrical relation between the (hk0) plane in question and the crystallographic c axis or (001) plane, the angle between the fiber axis and the c axis could be estimated. The largest tilts found in this way were about 30°.

The results of the electron diffraction experiments are consistent with the x-ray evidence. As with conventional polymer single crystals, the



Figure 25.

diffracting power of the fibrils deteriorates rapidly at normal beam intensities, and it was therefore necessary to work at very low beam currents. The experiments were carried out on preparations similar in appearance to that in Figure 18, the fibrils being oriented at random in the plane of the substrate.

With the beam normal to the specimen plane, the patterns showed the expected reflections as continuous Debye-Scherrer rings. When the plane of the specimen was tiled in an oblique position around an axis normal to the beam, the isotropic rings split into arcs whose position along the corresponding Debye-Scherrer circle depends on the angle of tilt. By way of illustration, the results with P4MP are described. The patterns obtained with the specimen plane perpendicular to the beam and tilted through 45° are shown in Figures 25a and 25b, respectively. In the line drawing of Figure 25c the indices of some of the reflections are shown.

The continuous rings in Figure 25a indicate that the crystallites are randomly oriented around the normal to the specimen plane which is perpendicular to the beam direction. However, the occurrence of arcing in the tilted pattern (Figure 25b) shows the presence of preferred molecular orientation within the fibrils. The presence of reflections other than (hk0) rules out the possibility that the molecular axis is perpendicular to the plane of the specimen support which is parallel to the fibril axis. The reflections (200) (210) (220) are arced around the axis of tilt and consequently must arise from planes having their normal situated in the plane of the specimen and hence almost parallel to the fiber axis. The (311) reflection appears prominently perpendicular to the tilt axis. This implies that the angle between these planes and the fiber axis is about 45° . It then follows that the c axis or molecular helix direction must be inclined to the fiber axis by an angle which is less than 45° .

A quantitative estimate of the molecular inclination could be obtained by using the more general method described by Keller and Engleman.³⁵ In this approach the molecular orientation is determined from two suitably chosed reflections $(h_1k_1l_1)$ $(h_2k_2l_2)$ in a single pattern obtained from a tilted sample. The analysis is based upon the relationship

$$\sin \phi = \left[\sin^2 \eta + 2 \cos \rho_1 \cos \rho_2 \cos \eta - (\cos^2 \rho_1 + \cos^2 \rho_2) \right]^{1/2} \sin \eta$$

where

$$\cos \rho = \sin \delta \sin \omega$$

Here δ is the angle between the normal to the plane of the specimen and the beam direction, ω is the angle between the tilt axis on the photograph and the arcs of a given reflection, ρ is the angle between the normal of a given (hk_1) plane and the fiber axis, and η is the angle between the normals of the two planes in question.

The calculations carried out in this way indicated, in agreement with the x-ray evidence, that the molecular chain axis is inclined to the fibril axis by an angle which is less than 45° . In terms of the observed morphology of the fibrils this is physically reasonable. Such an orientation would be realized if the molecules are normal, or nearly so, to the plane of the fibril platelets which are also tilted with respect to the fibril axis (see Fig. 19). These deductions appear generally applicable to the fibrils of all the nascent polymers examined in the present work.

DISCUSSION

Fine Structure of the Fibrils

The observations described above clearly demonstrate that nascent Ziegler-Natta polymers are fibrillar in structure. So far as can be judged from the present work, this appears to be a general feature of heterogeneous Ziegler-Natta catalysis. Before proceeding to consider the significance of these observations, it seems appropriate to examine the structure of the

fibrils in somewhat more detail. The fibrils have been shown to have a fine structure consisting, apparently, of platelets or lamellae obliquely arranged with respect to the long axis. Three possible models may be proposed to account for this morphology. The fibrils may consist of stacks of thin lamellae growing epitaxially on one another and possibly held together by tie molecules (Fig. 19a). Alternatively, the fibrils may arise from lamellar platelets strung at more or less regular intervals along thin central filaments ("shish-kebabs"). Evidence for the latter morphology is well illustrated in Figure 20 where many fibrils show this appearance over major portions of their length. It has already been proposed above that these are structures which suffered local deformation subsequent to their synthesis. In this context, the central filaments are regarded as the result of deformation and the fibrils or portions thereof, which do not show the filaments, are assumed to be in their natural or nascent state. This proposal is supported by the observation that only polymers which can undergo plastic deformation near ambient temperature (those with a low glass transition temperature, e.g., PE, PP) give the "shish-kebabs" while brittle polymers such as PS and P4MP, with high glass transitions, do not. Such an effect is predictable from the work of Geil,³⁶ who has shown that when PE single crystals are deformed, microfibrils of polymer are drawn across the torn portions. By analogy, one may visualize the fibrils in Figure 20 as helical crystals which tore at more or less regular intervals, leaving a structure consisting of segments of original crystal held together by microfibrils or micronecks whose number could vary from segment to segment.

The third possibility, implicitly suggested above, is that the fibrils are formed as helicoidal crystals which might arise from a single screw dislocation having a Burgers vector parallel to the fibril axis. This model is illustrated schematically in Figure 19b.

There are thus two models to be considered, the stacked platelet and the helicoidal crystal. It is difficult to establish unequivocally which of these is correct. However, intuitively, the helicoidal model is most appealing, if for no other reason than that plausible fibril growth mechanisms can be more readily visualized if a continuous, rather than a discontinuous or segmented structure is postulated. In the next section the growth of the fibrils will be considered.

It has been established that the molecular chain axis is inclined to the fibril axis direction by an angle which is less than 45° . This has been interpreted to mean that the molecules are oriented predominantly perpendicular to the plane of the fibril lamellae. Investigation of the small-angle scattering by bundles of fibrils leads to the observation of meridional reflections corresponding to a repeat distance along the axis of about 100 A., which is also the observed thickness of the fibril lamellae. For all the polymers studied, the molecular chain length greatly exceeds the observed lamellar thickness, and, accordingly, the molecules must be folded within the lamellae. This is a phenomenon familiar from experience

with conventional single crystals and, in the light of the observed fibril morphology, it is not unexpected. The observed long spacings can thus be tentatively identified with the molecular fold period in the fibril lamellae.

Mechanism of Fibril Growth

In single crystals grown from solution, the fold period is known to increase strongly with crystallization temperature, as predicted on thermodynamic and kinetic grounds.³⁷ On the other hand, as indicated already, the fold period in the fibrillar crystals of the nascent polymers appears to be invariant with polymerization temperature. This is surprising and suggests that crystal growth in these polymerizations is not nucleation-controlled, and thus cannot be accounted for in terms of current theories of crystallization.

There is another factor which suggests that crystallization in these systems has unusual features. Many of the polymers studied will not crystallize from solution in a time interval commensurate with the duration of the polymerization reaction. For example, polyisoprene will not crystallize from hydrocarbons at room temperature. Similarly, when isotactic polystyrene is dissolved in xylene or toluene and the solutions are supercooled, crystallization will not occur for many weeks.³⁸ Finally, polybutene-1 forms stable solutions when dissolved in benzene and other good solvents.

It therefore seems singular that during these polymerizations crystallization takes place with remarkable facility. The fibrils form with equal ease in reaction media which do not dissolve the polymer (e.g., PE in benzene near room temperature), in media which would be expected to retain the polymer in solution indefinitely (PBu in benzene), and even in gas-phase polymerizations.

These observations may indicate that crystallization takes place concurrently with synthesis, and that the catalyst surface, besides exerting a strong influence on the stereoregularity of the polymer, also acts as a nucleator by fixing the conformation of the molecules as they are formed at the surface. On this view, the growth of the fibril may be regarded as related to the growth of chain molecules which it contains. The rate of fibril growth would be mainly controlled by the kinetics of polymer formation, while the crystallization kinetics would have little or no influence. The question as to what determines the fold period remains unanswered at present.

The dominant role of the catalyst surface in fibril formation was demonstrated by comparing the morphology of nascent polyethylenes prepared by homogeneous and heterogeneous Ziegler-Natta catalysis. Whereas the heterogeneously catalyzed samples were fibrillar, the homogeneously catalyzed material consisted of tabular single crystals, essentially similar to those obtained in normal crystallization from dilute solution. In view of the close chemical relationship between these two classes of ZieglerNatta catalysts, it appears that the difference in the morphology of the polymers formed may be attributed to the presence and possibly also the character of the catalyst surface.

Recently Rodriguez and Van Looy³⁹ have observed large platelike crystals of activated TiCl₃, on the surface of which traces of nascent polymer appear as dots along the growth spirals. This implies that the active sites are localized along the growth spirals on the catalyst surface. According to their published photographs the dots of polymer have about the same width (200–300 A.) as fibrils of nascent polymer obtained at comparable temperatures. It is thus reasonable to suppose that the fibrils are formed directly at the catalyst surface through the crystallization of polymer chains growing from the active sites. The molecules may be envisaged as undergoing synthesis at one end and crystallization at the other. One end of the fibril is fixed to the catalyst surface, and the process of fibril growth may then be likened to root growth in whiskers; that is to say, the fibril may lengthen by adding new material at the root or base which is in contact with the catalytic surface.

In seeking to understand further the mechanism of fibril growth it is thus logical to focus attention on the catalytic site. In this connection it seems relevant to speculate about the number of active sites involved in the formation of a fibril. A given fibril may arise entirely from one active site or, alternatively, from several active sites in close proximity to one another. In the latter case the theory of $Boor^{40}$ and Arlman and Cossee⁴¹ may be applicable. Briefly, and in the simplest terms, the chains are propagated from equivalent chlorine vacancies which are postulated to be located at the edges of a TiCl₃ crystal. For simple monomers, such as ethylene and propylene, the theory allows the simultaneous synthesis of chain molecules on adjacent sites. For monomers with bulky side groups, such as styrene, the use of contiguous sites may be sterically forbidden, but chains could select the sites of best fit such as every second or third colinear vacancy. In either case it is not difficult to visualize conceptually how these growing chains could interact and crystallize to form fibrils.

The other possibility whereby a given fibril arises from one active site has interesting implications. It might be supposed that as long as monomer is available and the catalyst site remains active, a single polymer chain would continue to be generated. This molecule could then crystallize intramolecularly by aggregating with itself or folding to form a fibril. It follows that such a fibril would contain one molecule only and the molecular weight of the nascent polymer would then be enormous, certainly of the order of many millions. In this regard the following may be relevant. It has been observed that nascent isotactic polystyrene is insoluble in xylene or toluene even under conditions of prolonged reflux. However, the polymer can be dissolved in boiling chlorotoluene, and after regeneration from this solution it is found to be readily soluble in hot xylene or toluene. Similar observations have been made with some of the other



(a)

(b)

nascent polyolefins. The observed difference in solubility might be attributed to the fact that considerable chain scission may have occurred in the initial dissolution process. It would also imply that the molecular weight in regenerated stereoregular polymers may not be representative of the nascent material.

These ideas may seem perhaps more intriguing than plausible, for it is known that stereoregular polymers have a molecular weight distribution which depends on the polymerization variables. This could hardly be so if infinitely long chains were formed during polymerization. Nevertheless, these considerations do not rule out the possibility that a given fibril
may originate from a single active site. Chain transfer could take place at or near the catalyst site with the formation of additional polymer molecules. Thus a fibril could contain large numbers of molecules although it arose from a single active site.

At this point it is appropriate to consider how the fibrils may grow. The details are not understood and we restrict our remarks to the model in which the fibril is regarded as a helicoidal structure. By analogy with normal polymer single crystals, it may be presumed that the molecules fold in planes which are parallel to the growth faces. As the surfaces which contain the folds are more or less perpendicular to the fibril axis, it may be supposed that growth occurs by the coupling of monomer units to molecules which are laid down on the lateral bounding faces of the fibril lamellae.

In Figure 26 a portion of the helicoidal crystal is shown. Growth may take place on either a radial face or a lateral face. The corresponding disposition of fold planes is shown in the figure. It is interesting to note that, each of these schemes, oversimplified though they may be, suggests a unique mode of growth. In Figure 26a the fibril would be expected to form either from a single molecule or from many molecules emerging from a single catalytic site. On the other hand, growth on a lateral face (Fig. 26b) would require a multitude of sites contributing simultaneously to the formation of the fibril. In either case fibril growth would be envisaged as a continuous process in which polymer chains synthesized by the catalyst are immediately incorporated into a solid polymer strip of uniform thickness. Intuitively, we can envisage how such a strip could develop into a helicoidal crystal through the action of a screw dislocation or as a consequence of uneven surface stresses. These qualitative speculations obviously do not exhaust all the possibilities, and it is clear that only further experiments can yield answers to the riddle of fibril growth.

Mechanism of Globule Formation

It has been shown that the fibrils are organized into larger structural entities, the globules. However, the development of these structures appears to be a secondary phenomenon which can be suppressed by proper choice of experimental conditions. As already indicated, it does not occur under quiescent conditions or in gas-phase polymerizations. Thus while the appearance of these structures, in all their manifest forms, is certainly one of the more intriguing aspects of the present observations, the effect may be considered as subordinate to fibril formation.

The mechanism by which globulation occurs is not obvious, but certain conceptual possibilities may be suggested. The genesis of the globules may be envisaged in terms of the chance collision of catalyst particles under the influence of mechanical agitation. Each particle may have a multitude of active sites, at many of which fibrils grow. After the fibrils have attained a certain length, collision of the catalyst particles may result in the formation of loose, three-dimensional aggregates in which the catalyst particles are held together by enmeshed fibrils. These aggregates will tend to expand in size as the fibrils grow and push the catalyst particles apart. On this expanding framework other catalyst particles may be trapped through further collisions. As synthesis continues the deposition of fibrillar material around the aggregate leads to globule formation. It may be supposed that the shape of the initial aggregate, and therefore of the final globule, would be determined by the rate of fibril growth which may vary with the monomer used and the reaction conditions. Although this suggested mechanism may have elements of plausibility it does not account for the hollow globule interior; it does, however, seem consistent with the observation that globules are formed only in stirred systems and appear after the reaction has proceeded for some time.

A possible, if less likely, alternative mode of globule "nucleation" is through the entrapment of catalyst particles at the interface of gas bubbles present in the reaction medium. The entanglement of the growing fibrils may cause catalyst aggregation similar to that described above.

It remains to consider the origin of the globule appendages or spikes. It would seem possible to attribute this feature to osmotic forces acting on the globule. The surface of the globule may behave as a semipermeable membrane, permitting the passage of certain substances (e.g., solvent, monomer, and low molecular weight atactic polymer) and including or excluding others (e.g., dissolved high molecular weight atactic and stereoblock polymer). The osmotic pressure which is thereby developed could cause the formation of a spike in several ways. For example, if the osmotic pressure is greater outside the globule than it is inside, shrinkage could occur through the removal of fluid from the globule interior. Spikes could then form if the shrinkage in volume is not matched by the contraction in surface area. The structure of the globule wall, in localized regions, may restrain and modify the forces acting on the globule and thereby contribute to the phenomenon. D'Arcy Thompson⁴² describes the formation of spikes by a similar mechanism on certain living cells when they are immersed in saline solutions of varying density.

Alternatively, if the osmotic pressure is greater inside the globule than outside, the wall might rupture at a flaw. Spike growth would then serve as a means of "healing" the rupture.

While these speculations may seem plausible they do not provide an explanation for the spiral structure in the spike. The origin of this feature thus remains obscure at present.

The observation that the fibrils are organized into globules may provide insight into some of the problems in the kinetics of Ziegler-Natta catalysis. For example, the tendency of the catalyst to be shielded in the tightly woven globule wall might contribute to the well-known apparent decrease in catalyst activity at moderately high conversion.¹¹ However, further work would be required to provide answers to these questions.

CONCLUSION

In the preceding sections it has been demonstrated that, in their nascent state, poly-*a*-olefins produced by Ziegler-Natta catalysis exhibit a complex morphology quite unlike that normally obtained when they are crystallized from the melt or from solution. To recapitulate briefly, during polymerization the polymer appears as long, folded-chain fibrillar crystals which, depending upon the reaction conditions, may be organized into larger structural formations. The appearance of the polymer in this form could not have been predicted on *a priori* grounds and came therefore as a surprise.

The natural interpretation of the observations is that the catalyst surface plays a role in the development of morphology. It is proposed that the fibrils are formed directly on the catalyst surface through the crystallization of macromolecules growing from the active centers. The process is likened to root growth in whiskers, new material being added to the fibril at the root or base.

The observed fibril growth occurs under most conditions of polymerization and may therefore be considered as basic to the mechanism of Ziegler-Natta catalysis. It may be anticipated that the control of morphology by a catalytic site or surface which is here proposed may have scientific implications beyond the specific systems studied.

The details of the mechanism of fibril growth are not understood, but it is clear that it must be closely related to the physicochemical processes occurring at the catalyst surface. These processes are evidently somewhat more complex than has hitherto been supposed. Current theories of the action of Ziegler-Natta catalysts do not go beyond the description of the formation of the stereoregular chain. It would seem that any complete theory must incorporate an explanation for the form in which the polymer appears.

Much remains to be done to solve the most outstanding problems connected with fibril growth and the apparent control of morphology by the catalytic site. One can, however, look forward hopefully to the possibilities now opened by these studies for the further clarification of the mechanism of Ziegler-Natta catalysis.

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Polymerization and Copolymerization Studies on Vinyl Fluoride*

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Synopsis

The polymerization of vinyl fluoride has been studied in the temperature range of 0-50°C, with the aid of different types of initiators. Ziegler-Natta systems based on vanadyl acetylacetonate and AlR(OR)Cl compounds showed good activity. Enhanced reaction rates and higher polymerization degrees were achieved with boron alkyls (and, to a lesser degree, Cd, Zn, and Be alkyls) activated by oxygen. With either type of initiator, the main features and the kinetic parameters of the polymerization were determined. In all cases, the polymerization is considered to be of the free-radical type, though some properties (crystallinity, melting temperature) of the polymer. This is chiefly ascribed to an improved degree of chemical regularity of the chains. The copolymerization of vinyl fluoride in the presence of the cited initiators was studied with a number of monomers. The values of the copolymerization parameters allow us to obtain $Q(0.010\pm0.005)$ and $e(-0.8\pm0.2)$ values and to discuss the reactivity of vinyl fluoride in radical chain propagation.

INTRODUCTION

Although vinyl fluoride is a monomer of considerable practical interest, only a few publications have appeared describing its polymerization, and there is still uncertainty as to its behavior in the copolymerization. The lack of knowledge of pertinent reactivity data is even more regrettable in view of the fact that vinvl fluoride would represent the monomer best suited for a direct examination of the effects of fluorine substitution on the polymerization characteristics of the double bond. To a certain extent this situation has arisen because of the experimental difficulties involved in studying these reactions, due to a scarce reactivity of the monomer. It is known, indeed, that vinyl fluoride resembles ethylene rather than vinyl halides and some other halo-substituted ethylenes because it is very difficult to polymerize.^{1,2} The most common free-radical initiators, for example, are generally employable only at temperatures above the critical temperature of vinyl fluoride (54.7°C.), and this implies that extremely high monomer partial pressures must be adopted during polymerization to assure formation of high polymers.³

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With an interest in examining the behavior and evaluating the reactivity of such a fluoromonomer, we investigated alternate methods of catalysis to provide means of polymerizing liquid vinyl fluoride under more practical conditions.

The present work deals with the free-radical polymerization of vinyl fluoride at near room temperatures initiated by either metal alkyls or by some Ziegler-Natta systems. It was of further interest to determine the reactivity of this monomer in copolymerizations with several monomers, most of them bearing vinylic fluorine atoms, and from these results to calculate the Q and e parameters according to the Alfrey-Price scheme. The data thus obtained are used to arrive at some deductions, from which conclusions of a general value are drawn concerning the effects of fluorine substitution on the reactivity of the double bond in free-radical chain reactions.

EXPERIMENTAL

Materials

Vinyl fluoride was produced in this Institute by a process based on the pyrolysis under reduced pressure of 1,1-chlorofluoroethane.⁴ Gas-chromatographic analysis showed the monomer to contain no more than 0.01% impurities, with less than 5 ppm of acetylene. All ethylene, vinyl chloride, tetrafluoroethylene, hexafluoropropene, and vinylidene fluoride used in this study were Montecatini-Edison polymerization grade.

Commercially available acrylonitrile (British Drug House) vinyl acetate (U.C.C.), and chlorotrifluoroethylene (Allied Chemical) were used after purification using known methods.

The *cis*-1,2,3,3,3-pentafluoropropene was obtained by a procedure already described elsewhere.⁵

Hexafluorocyclobutene was prepared via dechlorination of the cyclic dimer of $C_2F_3Cl.^6$

Solvents used in the polymerization studies were purified by rectifying distillation after careful drying.

All trialkylborons were prepared from the reaction of boron trifluoride etherate with the appropriate Grignard reagent, according to known procedures.^{7a}

Ammonia–triethylboron (b.p. 57°C./13 mm. Hg) was obtained according to the method of Brown.⁸

n-Propyl derivatives of Zn, Cd, and Be were obtained from the reaction of C_3H_7MgBr with the anhydrous metal halides. These were purified by redistillation under reduced pressure in the presence of nitrogen.^{7b,9}

All the components of the Ziegler-Natta systems were synthesized, purified and analyzed according to general methods described in the literature.¹⁰

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VINYL FLUORIDE

Polymerization and Copolymerization

Reactions were conducted either in 50-ml. stainless steel bombs or in sealed glass tubes with a calibrated section $(100 \times 5 \text{ mm. I.D.})$. In the latter case, not only was the degree of the final conversion obtained by weighing the polymer, but the polymerization rate was followed by dilatometric measurements. The following procedure was used. The reaction vessels were filled, under dry nitrogen, with measured amounts of solvent and catalyst(s) and, in the case of copolymerizations, of liquid comonomer. At liquid air temperature, the proper amount of vinyl fluoride was then distilled in under high vacuum by regulation of the pressure drop in a constant-volume reservoir. Any other gaseous comonomer was also introduced into the reaction vessel by the same technique. The requirement for the exclusion of any extraneous oxygen was fulfilled by repeated freezing and thawing cycles under vacuum. Known amounts of pure oxygen gas were then admitted to the frozen and evacuated vessel from a small calibrated buret.

Reactions were run in a constant temperature bath and were stopped by freezing at liquid air temperature. After venting the unreacted monomer(s), the solid polymer was repeatedly washed with boiling methanol and dried at 100°C. under reduced pressure. Copolymerizations were always stopped at an early stage, at about 5% monomer conversion.

Polymer Characterization

Intrinsic viscosities were measured in a Ubbelohde viscometer at 110°C. in dimethylformamide solution.

The melting points and heats of melting were determined with a Perkin-Elmer differential scanning calorimeter at a scanning rate of 8°C./min. Copolymers were analyzed for composition by elementary analysis.

RESULTS AND DISCUSSION

Polymerization

With Metal Alkyls as Initiators. Several metal-alkyls, and among them especially alkylboranes, are well known to induce low-temperature polymerization of vinyl monomers;^{11,12} in most cases the presence of oxygen or of some other oxidizing agent proved advantageous for their catalytic activity¹³⁻¹⁵ and copolymerization experiments furnished convincing evidence of the free-radical nature of the process.^{14,16} Recently, even the polymerization of vinyl fluoride (reportedly in the absence of oxygen) with organoboron initiators, has been disclosed.¹⁷

However, we have now established that a variety of metal alkyls are effective initiators of this polymerization, but only in the presence of oxygen. By using metal alkyl-oxygen couples polymerization of liquid vinyl fluoride was readily accomplished at room temperature, either in the

	V	inyl Fluo	oride Polymo	erization	with Differe	ent Metal	Alkyls¤	
	B(<i>n</i> -0	$C_{3}H_{7})_{3}$	Zn(n-C	$({}_{3}H_{7})_{2}$	Cd(n-	$C_3II_7)_2$	Be(n-C	$(_{3}H_{7})_{2}$
${ m O}_2/{ m MeR}_n$	Con- version,	$[\eta],$ dl./g.	Con- version,	[η], dl.∕g.	Con- version,	$[\eta],$ dl./g.	Con- version, %	$[\eta],$ dl./g
0.0	0	_	()		0		0	
0.2	10	0.94	<0.5		$<\!0.5$		<0.5	
0.5	50	2.8	3	1.6	2	0.56	ca. 1	0.2
0.8	35	2.4	10	2.8	.)	1.1	2	0.2
1.0	3	0.5	-1	1.2	:}	0.7	ca. 1	0.15

		TABI	LE I			
'invl	Fluoride	Polymerization	with	Different	Metal	Alkyls

^a Monomer: 15 g.; solvent: ethyl acetate, 2 ml.; MeR₁₀ 0.2×10^{-3} mole; 5 hr. reaction at 30°C.

pure state or in solution in an inert medium; the product was a polymer of rather high molecular weight.

Table I shows the results of comparable experiments in which *n*-propyl derivatives of different metals were used to polymerize vinyl fluoride at 30° C. In all cases, no activity was displayed by the metal alkyl by itself, and each redox system gave a similar variation of the catalytic activity with the metal/oxygen ratio; the data further indicate the sequence B, Zn, Cd, Be, of decreasing effectiveness of the corresponding *n*-propyl derivatives.

We have studied in some detail the polymerization of vinyl fluoride at $0-50^{\circ}$ C. promoted by alkylborons. A set of data in Figure 1 shows the variation in the degree of conversion as the O₂/B ratio is varied, for constant B(C₂H₅)₃, in a series of different solvents. The marked effect on the rate arising from the nature of the solvent is placed in evidence and here again it appears that in the absence of oxygen, triethylboron does not initiate po-



Fig. 1. Variation of the polymerization conversion with the O_2/BR_3 ratio: (a) in the absence of solvent, and in the presence (5 ml.) of (b) dimethyl sulfoxide, (c) ethyl acetate, (d) methylene chloride and (e) cyclohexane. 5 hr. reaction at 30° C.; $B(C_2H_5)_3 = 0.25 \times 10^{-3}$ mole; 11.5 g. monomer.



Fig. 2. First-order dependence of the initial rate of polymerization on monomer concentration: (a) $B(i-C_4H_9)_3 = 0.25 \times 10^{-3}$ mole, $O_2/B = 0.5$, $30^{\circ}C.$, solvent ethyl acetate, overall volume = 38 ml.; (b) $(C_2H_3)_3B-NH_3 = 0.5 \times 10^{-3}$ mole, $O_2/B = 0$, $25^{\circ}C.$; solvent ethyl acetate, overall volume = 9.2 ml.; (c) same as (a), but with cyclohexane solvent.

lymerization; on the other hand, excess oxygen inhibits the reaction, and a molar ratio O_2/BR_3 of 0.5 appears to be near the optimum for catalyst efficiency.

The last result is in accord with the findings of various authors and the more consistent explanation is that a peroxyborane, ROOBR₂, is formed as intermediates by a fast reaction between molecular oxygen and trialkylborane. The above compound by itself is not a polymerization initiator, but the alkyl radicals which are generated by a redox reaction between the above peroxy compound and unoxidized trialkylborane are.¹⁸⁻²¹

A somewhat different behavior, however, was encountered when the triethylborane-ammonia addition compound was used to initiate the same polymerization. This catalyst exhibited, in fact, a slight but reproducible activity even when oxygen was removed with great care from the polymerization system. For example, in a 15 mole/l. solution of vinyl fluoride in methylene chloride, $(C_2H_5)_3B \cdot NH_3 0.05$ mole/l. gave 11% conversion to a polymer in a 2-hr. period at 20°C. On the other hand, in the same system oxygen was proved to enhance the catalytic activity substantially to a maximum, where the ratio $O_2/(C_2H_5)_3B \cdot NH_3$ was 0.5. Whereas this last result presumably arises from the fact that the ammonia addition compound



Fig. 3. Square-root dependence of the initial rate of polymerization (mole/l.-hr.) on the initiator concentration (mole/l.). (a) $O_2/B(i-C_4H_9)_3 = 0.6$, 2.3 g. monomer, 30°C., solvent ethyl acetate, overall volume = 9.2 ml.; (b) $O_2/B(i-C_4H_9)_3 = 0.5$, 6.0 g. monomer, 30°C.; solvent cyclohexane, overall volume = 38 ml.; (c) (C_2H_3)₃B-NH₃; 2.3 g. monomer, 25°C., solvent ethyl acetate, overall volume 9.2 ml.

is considerably dissociated at room temperature,⁸ it is difficult to explain why, contrary to alkylboranes, the addition compounds with ammonia do initiate polymerization even without oxygen cocatalyst.

The possibility that R₃B-NH₃ can generate radicals more effectively than BR₃ reacting with traces of oxygen present in the reaction system can be ruled out, since these polymerizations were always proved to adhere strictly to 0.5-order kinetics with respect to R₃B–NH₃ concentration. Furthermore, an entirely different mechanism of initiation will be suggested for the ammonia addition compound than that for uncomplexed boronalkyls arising from different values of energies of activation for initiation. The data, which will be discussed later, would suggest a unique role of the complexing agent in lowering the energy of the C-B bond, thus allowing the R₃B-NH₃ compound to generate radicals by itself at relatively low temperature. A study of the various initiators of this class revealed that while initial rates of polymerization were maintained at a reasonably steady value, above a certain degree of conversion (ca. 30%) rates decreased continuously; the maximum conversion reached under conditions used here The same behavior has been revealed by others in the was about 70%. polymerization of different monomers under the action of the alkylboranesoxygen couples and was attributed by them to depletion of catalyst accompanying a very fast initiation.²¹ In the present case, however, even the heterogeneous character of the system, due to polymer insolubility, may play an important role. Kinetic experiments, which are reported in Figures 2 and 3, proved that initial polymerization rates were first-order in respect to monomer concentration and 0.5-order in respect to initiator concentra-



Fig. 4. Arrhenius plot of the initial rates of polymerization (mole/l.-hr.): (a) $(C_2H_5)_{3-}$ B–NH₃ = 0.5 × 10⁻³ mole, O_2/B = 0, 2.3 g. monomer, 6 ml. ethyl acetate; (b) $(C_2H_5)_{3-}$ NH₃ = 0.25 × 10⁻³ mole, O_2/B = 0.8, 11.5 g. monomer, 5 ml. ethyl acetate; (c) B- $(C_2H_5)_3$ = 0.5 × 10⁻³ mole, O_2/B = 0.8, 18.4 g. monomer, 13 ml. cyclohexane; (d) B(*n*-C₄H₉)₃ = 0.25 × 10⁻³ mole, O_2/B = 0.5, 11.5 g. monomer, 5 ml. ethyl acetate; (e) B(*i*-C₄H₉)₃ = 0.25 × 10⁻³ mole, O_2/B = 0.5, 6 g. monomer, 30 ml. ethyl acetate.

tion. The above results hold regardless of the nature of the alkylborane, the solvent, and the ratio O_2/B . This simple kinetic points to a conventional free-radical polymerization mechanism; first order dependence of the rate on the monomer would imply no participation of the monomer or the solvent in the initiation step, and square-root order on the initiator would require no termination process other than bimolecular (such as termination by degradative chain transfer). The Arrhenius plots for the polymerization of vinyl fluoride with the different alkylborane-oxygen couples and with $(C_2H_5)_3B \cdot NH_3$ are shown in Figure 4.

Table II lists the calculated overall energies of activation E in the range $0-50^{\circ}$ C., which are markedly influenced by the nature of the alkylborane.

On the basis of the usual kinetic treatment, the overall energy of activation can be related to the activation energies of the individual steps of the polymerization by the equation:

$$E = \frac{1}{2}E_i + E_p - \frac{1}{2}E_i$$

where subscripts i, p, and t refer to initiation, propagation, and termination, respectively. In Table II there are also reported the values, taken from the

Initiator	${ m O}_2/{ m B}$	E, kcal./mole	E_i , kcal./mole
$B(C_2H_5)_3$	0.8	$6~\pm~1$	-2 ± 2^{a}
$B(n-C_4H_9)_3$	0.5	16 ± 1	16 ^b
$B(i-C_4H_9)_3$	0.5	$15~\pm~2$	16°
$B(C_2H_5)_3 - NH_3$	0.8	$6~\pm~2$	
$B(C_2H_5)_3 - NH_3$	0	25 ± 3	

TABLE II Energies of Activation in the Boronalkyl-Initiated Polymerization of Vinyl Fluoride (0-50°C.)

^a Data of Hansen and Hamann.²⁰

^b Data of Bawn et al.¹⁸ and Welch.¹⁹

^c Data of Talamini and Vidotto.²²

literature¹⁸⁻²² of the activation energies for initiation E_i for the alkylboraneoxygen couples used here. As a first approximation, these values can be assumed as independent from the monomer under examination, and, together with the corresponding E values measured in the present study, the data permit us to arrive at a value of about 7 kcal./mole for the difference $E_p = -\frac{1}{2}E_t$ in the polymerization of vinyl fluoride. This value is only slightly higher than the values (6.5–4.5) accepted for the free-radical polymerization of the most common monomers; considering that bimolecular termination reaction has little or no activation energy this would indicate a relatively high E_p for vinyl fluoride.

It is interesting to compare the E values measured with $(C_2H_5)_3B\cdot NH_3$ initiator in the presence (E = ca. 6 kcal./mole) or in the absence (E = ca. 25) of oxygen. While the former is practically the same value as obtained with uncomplexed triethylboron, the latter is a far higher value and would actually imply E_i of the order of 35 kcal./mole. This would suggest that the free radical generation step is accompanied by the breaking of some rather stable bond.

In the present study, no quantitative relationship has been determined regarding the dependence of the molecular weight of the polymers on the polymerization conditions; qualitatively, the degree of polymerization was found to vary with the concentration of the monomer and of the alkylborane and with the temperature as is usual in free-radical polymerization. As to the general result, polymers of rather high molecular weight, having $[\eta] = 3-6$ dl./g., were obtained by utilization of the most active O₂/BR₃ ratios and in the absence of solvents. Except for dimethyl sulfoxide and ethyl acetate, all of the examined solvents were actually found to cause a marked decrease in the degree of polymerization, due to the occurrence of very active chain transfer processes.

With Ziegler-Natta Systems. Since some binary systems of the Ziegler-Natta type have been proved to be active even for the polymerization of several halo-substituted olefins,²³⁻²⁵ it was considered that their use may give an alternate method of polymerizing vinyl fluoride. It was of further interest to know if the stereospecific activity displayed by several of the



Fig. 5. First-order dependence of the initial rate of polymerization on monomer or on catalyst concentration. Catalyst: $(i-C_4H_9)AlCl(Oi-C_4H_9)/VO(acetylacetonate)_2 = 2; 30^{\circ}C.;$ methylene chloride solvent.

above catalysts, could possibly lead to the synthesis of a new stereoregular poly(vinyl fluoride).

A preliminary investigation showed that heterogeneous catalysts based on aluminum alkyls and either titanium or vanadium halides were ineffective for this polymerization. However, a slow polymerization took place when vinyl fluoride was allowed to react at room temperature with homogeneous catalysts resulting from the combination of a soluble vanadium salt free of halogens with an aluminum mono- or dialkyl. The best results were achieved with vanadyl acetylacetonate, VO (Acac)₂, in a solution of a rather polar solvent, like methylene chloride or dimethylformamide, and the system VO (Acac)₂-AlR(OR)Cl was selected for a brief study of the polymerization. No precipitation occurs on mixing the above components of the catalyst either in the absence or in the presence of monomer and there were no stringent requirements concerning the order of mixing the catalyst components. With the solvent used, the solutions remained homogeneous throughout the formation and aging of the catalyst; however, when the polymerization was started, the reaction systems became heterogeneous due to polymer separation. The activity of this catalyst, measured as initial polymerization rate on a constant $VO(Acac)_2$ basis, was found to increase up to the molar ratio Al/V = 2 and further on to be virtually independent of the concentration of aluminum alkyl.

As shown in Figure 5, at the constant molar ratio, Al/V = 2, the initial rate of polymerization was in direct proportion to the concentration of the vanadium salt and to the concentration of vinyl fluoride. This simple kinetic was, however, complicated, during the course of the polymerization, by the aging of the catalyst. The reaction rate decreased with time, in fact,

according to a decay process of the catalyst activity. It is to be noted that all of the above features are quite usual in the polymerization of different monomers with catalytic systems of the present type.²⁶

Although a careful study of the dependence of the molecular weight of the polymer on catalyst composition and reaction conditions was not carried out, certain qualitative observations have been made. The degree of polymerization was not significantly influenced by Al/V ratio in the range 1–5, increased with increasing monomer concentration, and decreased with increasing VO(Acac)₂ concentration and with temperature. However, all of the polymers thus obtained always had quite low molecular weights and, even under the most suitable conditions, polymers having intrinsic viscosity larger than 0.3 dl./g. were never obtained. These results confirm that the most serious drawback revealed by the Ziegler-Natta systems, when used in the polymerization of halo-substituted olefins, is the low molecular weight of the obtainable polymers.

As reported in the next section, the polymer of vinyl fluoride obtained with the described Ziegler-Natta catalysts, did not reveal any improvement in its stereoregularity when compared with the usual atactic poly(vinyl fluoride).²⁷ The lack of stereospecificity is well in line with our assumption that the present vinyl fluoride polymerization is of the free-radical type; a radical mechanism has already been suggested for the polymerization of vinyl chloride with the same catalysts,²³ and our copolymerization studies further confirmed this assumption.

Properties of the Polymers

All polymers prepared under the conditions described above were examined in order to detect any improvement in their degree of stereoregularity. All samples exhibited the same type of x-ray diffraction spectra, with only minor differences due to differences in the degree of crystallinity in the various samples. Furthermore, the samples did not reveal any significant differences in crystal structure with respect to the randomly oriented poly(vinyl fluoride) produced by the conventional free-radical processes.²⁷

TABLE III

Variation of the Melting Point and Degree of Crystallinity of Poly(vinyl Fluoride) with the Polymerization Temperature (Boron Alkyl Initiators)

Polymerization temperature, °C.	Melting point, °C.	Degree of crystallinity $\% \pm 2^{a}$
85 (at 300 atm.)	197 - 205	37
40	205 - 215	44
30	218-225	45
20	222-230	45
10	220-235	48
0	225-235	50

^a From the heat of fusion (differential scanning calorimeter) and the averaged ΔH_u = 1813 cal./monomer unit.²⁹

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However, as a consequence of lower temperatures of polymerization, the low-pressure polymers obtained here differed in some properties from the high-pressure type previously described.²⁸ The data in Table III refer to polymers of vinyl fluoride prepared with alkylborons and show that the melting points are remarkably higher for the samples prepared at the lower temperatures; a similar trend is observed in the degrees of crystallinity, as estimated by comparison of the relative heats of melting.

The same effect of the temperature of polymerization was revealed on polymers prepared with the Ziegler-Natta systems; due to the low molecular weight, these polymers were easily separable into fractions by solvent extraction. Some properties of the fractions obtained from a typical polymerization at 30°C. are reported in Table IV. Here again the polymer, in spite of its rather low molecular weight, shows melting temperatures which can be as much as 20°C. higher than the melting temperature of the highpressure polymer.^{29,30}

As previously noted, the improvement in properties achieved by the lowtemperature polymerization of vinyl fluoride with both catalysts used

C_4H_9-	Al(OC ₄ H ₉)Cl/V	O(Acae) ₂ Ca	ntalyst	
Solvent	% ex- tracted (at the boiling tempera- ture)	[ŋ], dl./g.	Melting point, °C.	Degree of crystal- linity, C ± 2
Methanol	2	0.03	120-130	20
Acetone	8	0.07	170 - 175	30
Methyl ethyl ketone	4	0.08	180 - 185	40
Dioxane	20	0.14	200-210	45
$\operatorname{Dimethylformamid}{\epsilon}$	66	0.25	215 - 225	55

 TABLE IV

 Solubility Characteristics, and Properties of the Fractions of a Poly-(vinyl Fluoride) Sample Prepared at 30°C, with

 TABLE V

 Reactivity Ratios in the Copolymerization of Vinyl Fluoride (M1) at 30°C. with B(i-C₄H₉)₃-O₂ Initiator

M_2	r_1	r.2	$r_{1}r_{2}$
$CH_2 = CH_2$	0.3 ± 0.03	1.7 ± 0.1	0.51 ± 0.08
CH ₂ =CHCl	0.05 ± 0.005	11.0 ± 1	$0.55~\pm~0.10$
$CH_2 = CF_2$	$5.5~\pm~0.5$	$0.17~\pm~0.03$	$0.93~\pm~0.20$
$CF_2 = CF_2$	0.27 ± 0.03	$0.05~\pm~0.02$	0.013 ± 0.007
$CFCI = CF_2$	$0.18~\pm~0.02$	0.006 ± 0.02	$0.011~\pm~0.005$
$CF_3CF = CF_2$	1.01 ± 0.01	0	0
$CF_3CF = CFH$ (cis)	$0.9~\pm~0.05$	0	0
Cyclo-C ₄ F ₆	3 ± 0.6	0	0
CH2=CHOCOCH3	0.16 ± 0.01	$2.9~\pm~0.2$	$0.46~\pm~0.05$
CH=CHCN	ca. 1 \times 10 ⁻³	$24~\pm~2$	ca. 0.024

should not be ascribed to an improved steric order of the chains; in this connection it is important to consider that a similar improvement was also achieved in the low-temperature polymerization of vinylidene fluoride,³¹ and that obviously in this case no stereoregularity effects can be involved. Hence, it can be deduced that the higher crystallinity and the higher lattice energy of the polymers prepared at the low temperatures, are due to an improved chemical regularity of the chains, with particular regard to the occurrence of head-to-head and tail-to-tail monomer linkages. It is a wellknown fact, indeed, that vinyl fluoride³² and, to a minor extent, vinylidene fluoride,^{33,34} give rise in the chain propagation step to a high proportion of additions inverse to the usual vinylic head-to-tail type. As recently discussed in great detail by Koening and Mannion,³⁵ the lowering of the temperature of polymerization will result in a diminished probability of monomer links added "backwards" to give ---CH2---CHF---CHF---CH2--configurations along the chains.

Only the polymers of vinyl fluoride prepared at the lowest temperatures would be consequently endowed with a high grade of chemical regularity.

Copolymerization

With the use of either $B(i-C_4H_9)_3 + O_2$ or Ziegler-Natta systems, the copolymerization of vinyl fluoride was studied with a series of monomers over the entire composition range. All copolymerizations were carried out at 30°C. in ethyl acetate or methylene chloride solution. Some studies concerning the properties of several of these copolymers have been made and reported elsewhere.³¹ This study is concerned only with reactivity data.

Figure 6 shows the monomer-copolymer composition curves in the boronalkyl-initiated copolymerization of vinyl fluoride with: acrylonitrile (AN), vinyl chloride (VCl), vinyl acetate (VA), ethylene, chlorotrifluoro-



Fig. 6. Monomer-copolymer molar composition in the copolymerization of vinyl fluoride (VF) at 30°C, with $O_2/B(i-C_4H_9)_3 = 0.5$ initiator and ethyl acetate as solvent.



Fig. 7. Monomer-copolymer molar composition in the copolymerization of vinyl fluoride (VF) at 30°C. with Ziegler-Natta catalysts and methylene chloride as solvent.

ethylene, tetrafluoroethylene, cis-1-hydropentafluoropropene (C₃F₅H), hexafluoropropene (C_3F_6) , hexafluorocyclobutene $(c-C_4F_6)$, and vinylidene fluoride (VF_2) . There can be observed that in the copolymerization with $C_{2}F_{4}$ and $C_{2}F_{3}Cl$, vinvl fluoride shows a strong tendency toward alternation; with no homopolymerizable comonomers, i.e., with C₃F₆, C₃F₅H, c-C₄F₆, typical copolymerization systems with $r_2 = 0$ result, while the remaining systems are nonazeotropic and somewhat close to the ideal type.

Figure 7 shows the composition curves obtained by using VO(Acac)₂-AlR(OR)Cl initiator, in the copolymerization of vinyl fluoride with vinyl chloride, vinylidene fluoride, and hexafluoropropene. The same figure also shows the copolymerization curve with C_3F_6 (C_3F_6/T_i), resulting from the use of a different Ziegler-Natta system based on titanium tetraisopropylate and triisobutylaluminum.

Tables V and VI list the reactivity ratios $(r_1 \text{ and } r_2)$, calculated for the various copolymerization systems by the usual methods. (The Fineman and Ross modification³⁶ was used to evaluate all of the copolymerization data obtained in this investigation.)

	Cat	alysts		
Initiator	M_2	r_{ι}	r_2	$r_{1}r_{2}$
$\frac{(i-C_4H_9O)ClAl - (i-C_4H_9)}{VO(acetylacetou)} =$	= 2			
ate) ₂	Vinyl chloride Vinylidene fluoride Hexafluoropropene	$\begin{array}{l} 0.07 \pm 0.002 \\ 4.2 \pm 0.4 \\ 1.1 \pm 0.05 \end{array}$	$9 \pm 1 \\ 0.18 \pm 0.02 \\ 0$	$\begin{array}{c} 0.63 \\ 0.75 \\ 0 \end{array}$
$\frac{\text{Al}(i-\text{C}_{4}\text{H}_{9})_{3}}{\text{Ti}(\text{O}i-\text{C}_{3}\text{H}_{7})_{4}} = 3$	Hexafluoropropene	25 ± 5	0.04 ± 0.02	1.0

TABLE VI Reactivity Ratios in the Copolymerization of Vinyl Fluoride (M1) at 30°C. Ziegler-Natta

No account was taken of possible deviations from conventional copolymerization behavior, which can be often observed for systems involving high polar or sterically hindered monomers. Moreover, although monomers were usually soluble in the reaction medium, the copolymers were highly dispersed but not dissolved by this medium. We are aware that in systems involving precipitation of the copolymer from the reaction medium anomalies in the reactivity ratios, which are related to preferential adsorption of monomers to precipitated polymer, may result. We believe, however, that this will not introduce serious error in the calculated r_1 and r_2 values, which should actually provide a reliable picture of the copolymerization behavior of vinyl fluoride with the initiators used.

It is apparent, from the reported data, that there is an identity between the copolymerization parameters obtained with either boronalkyl- or vanadium-based initiators. The identity clearly proves that the same mechanism of polymerization has to be attributed to both types of initiator. This, in turn, is a good evidence of the free-radical nature of the polymerization of these monomers induced by the Ziegler-Natta system used.

On the other hand, a different behavior of the copolymerization with C_3F_6 was observed in the presence of the titanium-based binary catalyst. This indicates that such a Ziegler-Natta system is able to promote a different polymerization mechanism of these fluoroolefins. In this connection, it is interesting to note that while the vanadium-based catalyst proved ineffective for C_3F_6 polymerization $(r_2 = 0)$, the cited titanium-based catalyst, though unsuitable for the homopolymerization of vinyl fluoride (due to exceedingly low rates of polymerization and degrees of polymerization) has been found to induce stereospecific polymerization of C_3F_6 to isotactic polymer, probably through an ionic coordinated mechanism.²⁴

In conclusion, there is evidence that vinyl fluoride could be copolymerized, by suitable catalysts, even through a mechanism not a free-radical mechanism.

If we take into consideration the copolymerization parameters with some reference comonomers (C₂H₄, VCl, C₂F₄, C₂F₃Cl, VA, AN) whose Q and e values are reported in the literature,³⁷ Q and e values for vinyl fluoride can be calculated in the Alfrey-Price scheme.³⁸

Table VII shows the results for the various comonomer combinations. There is apparent that positive e values cannot be accepted, mostly on the basis of the copolymerization parameters with acrylonitrile and fluorinated ethylenes, and that all results are fairly consistent with $Q = 0.010 \pm 0.005$ and $e = -0.8 \pm 0.2$.

These values are distinctly different from previous values tentatively assigned to vinyl fluoride.³⁷ The reported values, however, were probably inaccurate, since they were determined from a single experiment of a single copolymerization system. On the contrary, the present Q and e values are based on a thorough copolymerization analysis; they allow one to draw some general conclusions regarding the reactivity of this fluoroolefin in free-radical reactions.

	0	Jopolymerizatio	n Parameters for	Vinyl Fluoride (M_1)			
Monomer 2	r	r_2	r_1r_2	e2ª	$Q_{2^{16}}$	eıb	Qıb	
						(+0.61)	(0.005)	
$CH_2 = CH_2$	0.3	1.7	0.51	-0.21	0.010	-1.03	0.0065	
						(+0.97)	(0.0046)	
CH ₃ =CHCl	0.05	п	0.55	+0.20	0.044	-0.57	0.0035	
						(+3.29)	(12.6)	
$CF_2 = CF_2$	0.27	0.05	0.013	+1.22	0.049	-0.85	0.08	
						(+3.60)	(7.7)	
CF2=CFCI	0.18	0.06	0.011	+1.48	0.020	-0.64	0.015	
						(+3.13)	(0.25)	
CH2=CH-CN	ca. 1×10^{-3}	24	ca. 0.024	+1.20	0.60	-0.73	0.0025	
						(+0.66)	(0.001)	
CH ₂ =CHOCOCH ₃	0.16	2.9	0.46	-0.22	0.026	-1.10	0.010	
^a Data taken from Youn	g. ³⁷							

TABLE VII

^b Data in parentheses refer to the alternative solution of the Alfrey and Price equation.³⁶

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Since the Q value is a measure of the resonance effect of the substituent on the double bond, the very small value of Q for vinyl fluoride is a good evidence of the poor ability of a fluorine atom to resonance stabilization of the radical on the adjacent carbon. This situation makes the vinyl fluoride radical a highly unstable and reactive radical, which accounts for the need of very reactive radicals—like alkyl radicals—to initiate polymerization at room temperature. This also accounts for the observed tendency towards chain transfer reactions with solvents.

Moreover, the small value of Q, which is of the same order as ethylene, is well in accord with the tendency of vinyl fluoride to give additions inverse to the head-to-tail type during the chain propagation step. As a matter of fact, only at the lowest temperatures the very small difference in the stabilization energies of the radicals -CFH and -CH₂ would assure a regular head-to-tail growing of the chain. On the contrary, the e value of vinyl fluoride determined in this work is rather surprising. The high negative value of the polarity factor indicates that the monomer has to be regarded as electron-rich at the point of attack; much more, it indicates that the double bond of vinyl fluoride is far more electron-rich than the double bond of ethylene. It is well known that, during ionic-type reactions, the inductive effect of fluorine (electron-withdrawing) may be overbalanced by its electron-releasing ability by mesomeric effect; it is quite unexpected, however, to find such a situation to hold even in free-radical reactions, as pictured by the negative value of e, which, on the contrary, would be expected to be mostly related to inductive, permanent effects.

The typical behavior of vinylic fluorine is also shown in Table VIII, where the e and Q values of simple fluoro monomers are listed. The values are partly taken from the literature, and partly from our own studies. It can be noted that also in the case of vinylidene fluoride, fluorine acts as an electron-releasing substituent (mesomeric). Only in the case of perfluorin-

	e	Q	Notes
CII ₂ =CIIF	-0.8	0.010	a
$CH_2 = CF_2$	-0.5	0.03	b
$(CH_2 = CH_2)$	(-0.21)	(0.010)	с
$CF_2 = CF_2$	+1.22	0.049	с
$CF_2 = CFCl$	+1.48	0.020	c
CF ₃ —CF=CHF(cis)	+2.1	~ 0.002	b,d
CF_3 — CF = CF_2	+1.8	~ 0.002	b.d

	TABLE V	III	
Copolymerization	Parameters	for Some	Fluoroolefins

* Present work.

^b Values derived from unpublished copolymerization studies carried on in these laboratories; the data are also in accord with the copolymerization systems with vinyl fluoride reported in the present work.

^c Data taken from Young.³⁷

^d Where r_1 or r_2 was zero, a small, finite value was assumed for r_1r_2 in order to calculate e.

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ated olefins, does the strong inductive effect of fluorine, which makes the π -electrons of the double bond less available, become evident.

It is necessary to note, however, that there is no concordance between the negative e values which have been assigned here to vinyl fluoride and vinylidene fluoride and the general chemical reactivity of these fluoroolefins in ionic reactions. Common monomers having similar negative e values are in fact generally endowed with a high degree of reactivity toward electrophylic reagents, which is not the case for the fluoroolefins. This would suggest that some caution must be used with the Q-e scheme when dealing with sterically unhindered simple fluoroolefins. Of course, the obtained parameters can be used to predict reactivity with untested monomers, however, the Q, e concept is probably too simplified an approach to discuss the reactivity of vinyl fluoride in free-radical reaction based only on separate resonance and polarity factors.

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Morphological Changes of Twisted Nylon 66 and Poly(ethylene Terephthalate) Monofilaments

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Synopsis

A comparison of the x-ray diffraction from twisted nylon 66 and poly(ethylene terephthalate) monofilaments is made with the scatter predicted by a model assuming an affine deformation of the fiber. The x-ray diffraction of the model is characterized by an approximately constant intensity over the entire range of the azimuthal dispersion. With twisted nylon 66 fibers the (010) reflection is split into a bimodal intensity distribution about the equator, while the (100) reflection maintains a distinct maximum on the equator. It is proposed that this difference is due primarily to the fact that a plastic deformation involving rotation of crystal planes occurs more readily when the shear stress acts in [010] direction than in the case when it acts in the [100] direction. A similar behavior is found with poly(ethylene terephthalate) fiber.

Introduction

The twisting of highly oriented polymeric fibers leads to complex reorganization of fiber structure. Evidence for this lies in the inconsistent and at times unpredictable effect of twist upon the mechanical response of oriented fibers.¹⁻³ One largely unanswered question was whether the response of the crystalline domains on twisting differs appreciably from the microscopically imposed deformation on the fiber. Knowledge of the structural rearrangements taking place during twisting would contribute to the understanding of the mechanical behavior of twisted fibers. In addition, it was expected that an interpretative analysis of the crystallographic changes resulting from twisting would also contribute to clarifying some questions related to fiber structure. Specifically, does a crystalline domain in highly oriented fibers preserve its characteristic behavior found in unoriented systems responding to the applied stress more or less as an independent entity, or should the fiber be regarded as a one-phase system? In this latter case one would expect the existence of strong cooperative effects among various domains and thus the rearrangements of crystallites under stress would follow the applied deformation rather closely.

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This study is an attempt to analyze the responses of crystalline domains resulting from twisting of oriented nylon 66 and poly(ethylene terephthalate) fibers by x-ray diffraction technique.

Experimental and Results

Nylon 66 and poly(ethylene terephthalate), (PET), monofilaments were subjected to varying amounts of twist under constant load. The diameter of the nylon fiber was 17 mil, that of the PET fiber 12 mil, and the load during twisting was 200 g. with both types of fibers. The twisted filaments were mounted on suitably designed frames to prevent untwisting during x-ray exposure. The wide-angle diffraction patterns were recorded on flat photographic film by using nickel-filtered CuK α radiation. The instrumental parameters were as follows: 15 ma., 35 kv., 4.5 hr. exposure, and a sample-to-film distance of 9.0 cm.

The x-ray diffraction diagrams of nylon 66 and PET fibers as a function of twist are shown in Figures 1 and 2, respectively. Most important in these photographs is the observation that at high twist levels the outer equatorial reflections [nylon $(010) + (110)^4$ and PET $(100)^5$] are split into a bimodal intensity distribution. The inner equatorial arcs, however, maintain a unimodal distribution with a maximum of intensity on the equator.

In order to establish a basis for interpretation of the presented x-ray results the intensity distribution of an equatorial arc was calculated for



Fig. 1. X-ray diffraction of twisted nylon monofilament: (A) control; (B) 5 turns/in.; (C) 10 turns/in.; (D) 15 turns/in.



Fig. 2. X-ray diffraction of twisted poly(ethylene terephthalate): (A) control; (B) 10 turns/in.; (C) 18 turns/in.

the case of an affine deformation of the fiber. It was found that in this case the intensity distribution at high twist levels should be rather uniform in angle, falling sharply to zero at the end of the arc. The procedure used in this calculation is outlined in the Appendix.

Discussion

Referring to Figures 1 and 2 one observes that the distribution of diffracted intensity upon twisting does not follow the prediction of the calculations assuming an affine deformation. The main discrepancy in the case of real fibers is that the outer reflections split with new maxima formed near the ends of the arc, while the inner reflection is affected much less and shows a well defined maximum on the equator. In an affine deformation due to twisting both equatorial arcs should show similar intensity profiles with approximately constant intensity in the azimuthal direction (see Appendix).

Furthermore, the observed values of Φ_{max} are lower than expected assuming an affine deformation of the fiber. This latter observation that the crystal deformation is smaller than calculated from the bulk deformation is in agreement with previously reported data.^{6,7} An example of such data obtained on the polyester used in the x-ray studies of this work is presented in Table I.

An unambiguous explanation cannot be put forward at present regarding the mechanism leading to the observed differences in the intensity distri-

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I WISU,	Calculated	Measured	Φ_{\max} (X-ray –
turns/in.	Φ_{\max}	Φ_{\max} (x-ray)	4°30′) ^a
0.0	0°0′	4°30′	0°0′
2.5	5°23′	6°0′	1°30'
5.0	10°41′	6°30′	2°0'
10.0	$20^{\circ}40'$	19°30′	15°0′
15.0	$29^{\circ}23'$	$28^{\circ}40'$	$24^{\circ}10'$
18.0	33°567	35°35′	$31^{\circ}5'$

TABLE I
Comparison of Calculated and Measured Twist Angles in
Poly(ethylene Terephthalate) Fibers

 a Value of Φ_{max} (x-ray) compensated for the dispersion of $4^{\circ}30'$ measured in the untwisted fiber.

butions of the equatorial arcs. However, since knowledge of the structural rearrangements taking place during twisting would contribute both to the understanding of mechanical properties of twisted fibers and to the elucidation of fiber structure, this paper presents below an interpretation based upon the observations reported above and consistent with reported data on deformation of semicrystalline polymers.⁸⁻¹² Although for purposes of illustration, the discussion deals specifically with nylon 66, it should be noted that the same arguments apply also for PET fibers.

In considering possible mechanisms for plastic deformation of crystallites which could lead to the observed x-ray scatter, it must be recognized that a "pure" translational slip cannot produce the disorientation observed on twisting. A more complex plastic deformation involving slip and rotation of planes which are normal to a component of the applied shear strain can, however, lead to disorientation. It will be shown below that the observed changes in crystallite orientation can be attributed to a large extent to the



Fig. 3. Schematical presentation of crystal tilting involving (010)[001] slip: (A) crystal orientation before slip; (B) crystal orientation after slip.

fact that under a shearing stress the entire crystallite or parts of crystallite can tilt similarly as shown schematically in Figure 3. It is important to note that this type of plastic deformation results in a disorientation of (0k0) and (00l) planes while the (h00) plane remains unaffected.

Following the criteria that a unit dislocation has lowest energy when its Burgers vector is parallel to a direction of closest packing in the lattice and that slip may occur most easily on closely packed planes,¹³ one can infer that the most favorable plastic deformation of nylon 66 crystals would involve a simple translational slip (010) [001].^{9,10} Favorable conditions for plastic deformation involving (010) [001] slip exist in crystalline



Fig. 4. Proposed model of crystallite disorientation in twisted fibers: (A) shear stress component in [100] direction; (B) shear stress component in [010] direction; (B_1) and (B_2) crystal before and after tilting.

domains in which there exists a component of shear stress in the [001] or in [010] direction. These conditions exist in twisted fibers. Plastic deformation involving (100) [001] slip is energetically less favorable, since it involves breakage of hydrogen bonds.

In highly oriented fibers, crystallites can be regarded as being oriented uniaxially with the a and b axes assuming more or less randomly all possible orientations with respect to the radius. For purposes of this qualitative discussion it is sufficient to examine the responses of only two orientations of crystallites; those that might contribute most to the disorientation of the a and b axis under the applied straining conditions. In the case of a twisted nylon fiber, (010) [001] slip would be favored in orientations finding (010) planes oriented parallel to the fiber radius. Upon twisting the shear stress builds up, until at a critical value, tilting occurs producing further disorientation (Fig. 3B). Under these conditions the (010) planes diffract at their highest diffraction angle since $\cos \beta = 1$, for this orientation. Here, β is the angle the reflecting plane makes with the radial direction [see eq. (3) in Appendix]. Furthermore, the (100) planes, being in this case nearly perpendicular to the radius, would be affected little by twist. Considering next the other extreme orientation in Figure 3A, one finds the (010) planes perpendicular to the shear stress. Here, since slip of the (100) [001] type is less favorable, tilting would require a higher shearing stress.

At low twist levels one might assume that both crystallites disorient to approximately the same extent and that little difference should be expected between the reflections associated with the (100) and (010) planes. This is in agreement with the experimental data. At sufficiently high twist angle, however, Figure 4 schematically shows parts of the crystallite Byielding through tilting, while the crystallite A still preserves its original shape. Reference to Figure 4 where the arrows indicate the orientation of the crystallographic axis illustrates that such a deformation leads to a disorientation of the b axis. The fact that not all tilt angles are energetically equally favorable might be another factor contributing to the observed differences between predicted and observed distribution of this reflection.

In case A one can imply that the observed intensity distribution of the (100) reflection with a strong maximum on the equator is to a large extent due to the fact that during twisting portions of the fiber not contributing to the coherent scatter (low modulus amorphous regions) were strained more than the crystallites.

In the case that the crystalline domains are long in the direction of fiber axis and relatively narrow in the direction of the applied shear stress, it might be possible that only a part of the crystallites would undergo tilting while the rest would preserve its original orientation. This type of plastic deformation which is usually referred to as kinking is often observed with oriented polymers which are subjected to bending or compression.^{9,11} It is evident that the considerations regarding the disorientation through this type of plastic deformation are analogous to those that apply for tilting of crystallites as a whole.

It should also be noted that in nylon the outer arc which splits is a superposition of two reflections, (010) and (110). However, since the first of these reflections is much stronger, the qualitative argument is not affected.

In summary, it is believed that the observed differences in the azimuthal intensity distributions of equatorial arcs in twisted nylon 66 fibers are primarily due to the fact that a plastic deformation involving rotation of crystal planes occurs more readily when the shear stress acts in the [010] direction than in the case when it acts in the [100] direction. The reason for this is that the (100) [001] slip is less favorable than the (010) [001] one.

APPENDIX

Distribution of Diffracted Intensity in an Equatorial Arc of a Twisted Fiber : Case of Affine Deformation of a Fiber

Consider the monofilament, regarded as perfectly oriented, to be divided into a series of annular regions of equal mass. The annuli are very thin, so that for purposes of this calculation they may be characterized by a radius r. It is also assumed that initially the a and b axes are oriented randomly with respect to the fiber axis. On choosing one particular reflection, only those crystallites with their reflecting plane at the Bragg angle to the x-ray beam contribute to this reflection.

Now consider a twisted fiber, in which the chains in any annulus undergo a helical distortion, with a tilt angle,

$$\Phi_c = \tan^{-1} 2\pi r t \tag{1}$$

where r is the radius of the annulus and t is the twist in turns per unit length. It is desired to calculate the angle of dispersion, χ of the x-ray arc as a function of the angle the reflecting plane makes with the radial direction of the fiber. This angle of dispersion is zero when the reflecting plane is perpendicular to the radius, since the crystallite planes in this orientation do not change their orientation with twist. On the other extreme, when the plane is initially parallel to the radius, the tilt angle of the crystal plane is Φ_c , the angle of tilt of the helically distorted annulus. The relation between χ and Φ , where Φ is the angle between the fiber axis and the crystal plane, is shown below as eq. (2)^{14,15} for the geometry of a flat film. θ is the Bragg angle of reflection.

$$\sin \Phi = \sin \chi \cos \theta \tag{2}$$

It was next desired to calculate Φ as a function of β , the angle the reflecting plane makes with the radial direction. This relation, obtained by application of Napier's rules to spherical triangles, is given by eq. (3).

$$\sin \Phi = \cos \beta \sin \Phi_c \tag{3}$$

With this result, one can calculate the azimuthal intensity distribution of an equatorial arc for a given value of Φ_{max} (the angle of tilt of a linear element on the fiber surface originally parallel to the fiber axis). This procedure is outlined below, and will be presented in detail elsewhere.

If a random distribution of crystallite orientations in the angle β is assumed in an annulus, the number of crystallites with an angle Φ diffracting $N(\Phi)$, is proportional to $-d\beta/d\Phi$ (since $d\beta/d\Phi$ is negative).

$$N(\Phi) = -kd\beta/d\Phi \tag{4}$$

Here k is a proportionality constant which may be arbitrarily chosen since it does not affect the shape of the final distribution. Thus, putting k=1, it follows from eq. (3) that

$$N(\Phi)d\Phi = -d\beta = \cos \Phi \, d\Phi/\sqrt{\cos^2 \Phi - \cos^2 \Phi_c} \tag{5}$$

This is the distribution of crystal planes in Φ for an annulus of tilt angle Φ_c .

The total intensity diffracted from the whole fiber at angle Φ is the area under the curve of $N(\Phi)$ versus Φ_c from $\Phi_c = \Phi$ to $\Phi_c = \Phi_{max}$. This is,

$$N_T(\Phi) = \int_{\Phi}^{\Phi_{\rm innx}} \cos \Phi w \ d\Phi_c / \sqrt{\cos^2 \Phi - \cos^2 \Phi_c} \tag{6}$$

where w is an appropriate weighing factor, which weighs $d\Phi_c$ according to the mass distribution. Since

$$dm/d\Phi_c = (dm/dr)(dr/d\Phi_c)$$
(7)



Fig. 5. Plot of calculated diffraction intensity vs. dispersion angle X for three levels of twist. Angle of helical twist at surface of cylinder (Φ_{\max}) equals: (A) 21°; (B) 36°48'; (C) 51°.

and since $dm/dr = 2\pi r$, and $\tan \Phi_c = 2\pi r t$, the weighing factor, which gives $N_T(\Phi)$ on an arbitrary scale, is, $\sec^2 \Phi_c \tan \Phi_c$. Thus,

$$N_T(\Phi) = \int_{\Phi}^{\Phi_{\text{max}}} \frac{\cos \Phi \sec^2 \Phi_c \tan \Phi_c \, d\Phi_c}{\sqrt{\cos^2 \Phi - \cos^2 \Phi_c}} \tag{8}$$

A comparison of this intensity profile with the experimental result obtained with a densitometer, $N_T(\chi)$, was made possible by integrating eq. (8) and converting the distribution to χ by using eq. (2). This results in eq. (9), where $a = \cos \theta$.

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$$N_{T}(\chi) = \frac{1}{2\sqrt{1 - a^{2} \sin^{2} \chi}} \left[\frac{a\sqrt{\cos^{2} \chi - \cos^{2} \chi_{\max}}}{(1 - a^{2} \sin^{2} \chi_{\max})} + \frac{1}{\sqrt{1 - a^{2} \sin^{2} \chi}} \cdot \log \left(\frac{\sqrt{1 - a^{2} \sin^{2} \chi} + a\sqrt{\cos^{2} \chi - \cos^{2} \chi_{\max}}}{\sqrt{1 - a^{2} \sin^{2} \chi_{\max}}} \right) \right]$$
(9)

Equation (9) is the expression for the intensity distribution in χ for a fiber with a given maximum angle of twist, Φ_{\max} . Figure 5 shows normalized curves of $N_T(\chi)$ versus χ for various values of Φ_{\max} . It can be seen that at higher twist levels the intensity distribution is rather uniform in angle, falling off sharply to zero at Φ_{\max} .

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Aminimides. IV. Homo- and Copolymerization Studies on Trimethylamine Methacrylimide

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Synopsis

Trimethylamine methacrylimide (TAMI) has been homo- and copolymerized with methyl methacrylate, vinyl acetate, vinyl chloride, hydroxypropyl methacrylate, and acrylonitrile by free-radical initiators to soluble, low molecular weight polymers containing pendant aminimide groups along the backbone of the polymer chains. The reactivity ratios in the copolymerization of TAMI (M_1) with acrylonitrile (M_2) were determined: $r_1 = 0.10\pm0.01$, $r_2 = 0.37\pm0.04$. The Alfrey-Price Q and e values for TAMI were also calculated: Q = 0.18, e = -0.60. This preliminary work indicates that TAMI has potential for the preparation of reactive polymers.

INTRODUCTION

Much work has been accomplished in recent years on the preparation of polymers having chemically reactive groups.

Recently, an easy synthetic procedure has been developed in this laboratory¹ for the preparation of trimethylamine methacrylimide (TAMI).



It has been demonstrated by various research groups that pyrolysis of trimethyl aminimides gives isocyanates.¹⁻⁴ For example, pyrolysis of TAMI gives an excellent yield of isopropenyl isocyanate.¹ Thus, it is apparent that monomers such as TAMI should have utility in the preparation of a wide variety of new, interesting, and potentially useful reactive polymers.

The present work was undertaken to study some of the homo- and copolymerization characteristics of this new diffunctional monomer and obtain an estimate of its Alfrey-Price Q and e values.

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EXPERIMENTAL

The NMR spectra were obtained on a Varian A-60 spectrometer with tetramethylsilane as internal standard, and the infrared spectra were obtained with the use of a Perkin-Elmer Infracord spectrophotometer.

Monomers

Trimethylamine Methacrylimide. This monomer was prepared according to a procedure developed in this laboratory.¹ A stirred mixture of 11.0 g. (0.1 mole) of 1,1,1-trimethylhydrazinium chloride, 10.0 g. (0.1 mole) of methyl methacrylate (10 ppm *p*-methoxyphenol) and 5.4 g. (0.1 mole) of sodium methoxide in 75 ml. of *tert*-butanol were heated at 48°C. for 6 hrs. While still warm, the reaction mixture was pressure filtered. Evaporation of the filtrate gave 12.5 g. (91%) of a white solid. Recrystallization from benzene gave m.p. 149–150°C. (reported,⁵ m.p. 146–147°C.). The infrared spectrum (halocarbon mull) exhibited expected bands due to the CH₂=C grouping at 3040 and 1645 cm.⁻¹ and the expected carbonyl absorption at 165 cm.⁻¹. The NMR spectrum (CDCl₃, τ) exhibited a singlet at 6.55 ppm and multiplets at 8.05, 4.85 and 4.25, ppm, in an expected ratio of 9:3:1:1, respectively.

ANAL. Caled. for C;H₄N₂O: C, 59.12%; II, 9.92%; N, 19.70%. Found: C, 59.24%; H, 9.89%; N, 19.54%.

Other Monomers. The monomers methyl methacrylate, vinyl acetate, styrene, and acrylonitrile (commercially obtained) were purified by distillation under nitrogen through a 12-in. Vigreux column immediately before use. The hydroxypropyl methacrylate and vinyl chloride monomers were used as received from Rohm and Haas and the Matheson Companies, respectively.

Solvents and Initiators

All of the solvents used in the polymerizations were purified according to standard procedures. Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. The potassium persulfate was of the highest purity commercially available.

DTA and TGA

Differential thermal and thermogravimetric analyses were obtained on finely divided polymer samples by using a DuPont Model 900 DTA and 950 TGA unit. Alumina was employed as a reference material, and the analyses were performed under nitrogen from 0 to 500°C, with a heating rate of 20°C./min.

Titration

The non-aqueous titration procedure used in this work is a standard procedure developed for amine determination. The amine is titrated in a

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suitable nonaqueous solvent (such as glacial acetic acid) with standardized perchloric acid with gentian violet indicator. The aminimide functional group is leveled or neutralized according to the eq. (1):

$$\begin{array}{cccc} & & & & & & \\ & & & & \\ -CN & -N & -CH_3 & + & HClO_4 & \rightarrow & -C & -NH & -N & -CH_3 & & ClO_4 \\ & & & & & CH_3 & & ClO_4 \\ & & & & & CH_3 & & ClO_4 \end{array}$$
(1)

Therefore, from a knowledge of the weight of polymer titrated and equivalents of perchloric acid used, the TAMI unit fractions in the copolymers could be calculated. By using this procedure, TAMI is calculated to be 97.93%.

Molecular Weight Determination

Number-average molecular weights of some of the polymers were obtained on a Mechrolab 301A vapor-pressure osmometer. Results are shown in Table I.

Polymerizations

Homopolymerization (Trial 1, Table I). The polymerization solution was poured into acctone and the precipitate washed several times with acctone. After drying *in vacuo* at 60°C, the white, powdery polymer was found free of TAMI by TLC. The infrared spectrum (halocarbon mull) exhibited a strong aminimide carbonyl absorption at 1565 cm.⁻¹. The NMR spectrum (D₂O, τ) exhibited peaks at 6.63, 8.14, and a multiplex at 8.81 ppm in a 9:1.9:2.24 ratio (expected 9:2:3). No vinyl protons were detected in the NMR spectrum. Thermal gravimetric analyses (TGA) shows the polymer starts losing trimethylamine at ca. 125°C.

TAMI-Methyl Methacrylate Bulk Polymerization (Trial 2, Table I). The polymerization mixture was poured into a large volume of vigorously stirred, warm acetone. The white, granular precipitate was collected, washed several times with methanol, and dried *in vacuo* at 60°C. The polymer was shown to be free of TAMI by TLC. The polymer, when dissolved in chloroform and spread on glass plates, formed a hard, colorless film that remained clear when baked in an oven at 110°C. for 16 hr. The infrared spectrum (halocarbon mull) exhibited carbonyl absorption bands at 1725 (ester) and 1565 cm.⁻¹ (aminimide). The NMR spectrum (CDCI₃, τ) had singlets at 6.65 and 6.30 ppm, giving further proof of copolymerization. No vinyl protons were indicated in the NMR spectrum. On the basis of nitrogen analysis (found: N, 1.65%) the polymer consists of ca. 15 methyl methacrylate units to 1 TAMI unit (caled.: N, 1.69%).

The DTA curve exhibited a reasonably strong, sharp endotherm at ca. 175°C. The TGA curve exhibited a 0.5 mg. weight loss from ca. 175 to 200°C. [caled. for $N(CH_3)_3$ loss, 0.57 mg.].

TAMI-Vinyl Acetate Bulk Polymerization (Trial 3, Table I). Polymer isolation was achieved by pouring the polymerization mixture into a

			General Poly	TABLE I merizations of 1	'AMI"			
	Trial 1 ^b	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8
Monomers, g. (moles Methvl	(
methacrylate	1	6.8(0.068)	I	I		25(0.25)	ľ	1
Acrylonitrile	1		ļ	[5.3(0.10)		1	
Styrene]	-	1			[9.0(0.087)
Vinyl chloride	1		1	23.3(0.37)	l		167(2.7)	
Vinyl acetate		[6.5(0.076)	I	J	Ĩ	Ι	Į
TAMI	3.7(0.026)	1.0(0.007)	1.4(0.01)	2.0(0.014)	3.6(0.025)	7.3(0.05)	2.31(0.016)	1.0(0.007)
Solvents, ml.								
Distilled water	15	1	1	I	Ī	l	<u>~·</u>	1
Methyl ethyl								
ketone		I	Į	30]]		I
Acetonitrile	J	I	1	l	l	100]	20
Initiators, g.								
AIBN	0.04	0.06	0.04	0.20	0.01	0.06	I	0.01
$ m K_2S_2O_8$	I	[L	1	1	3.0	l
Polymerization ^a								
Time, hr.	2.25	1.5	12	20	5	2	18	ಣ
Temp., °C.	82	70	20	60	20	80	50	60
Conversion, %	50	Į	Ĩ	ļ	10	[I	20
Molecular								
weight	1	3455	3197	I]	5600	1	1
^a All polymers were plates, methanol solv ^b The AIBN dissolv	e checked for p ent, and I ₂ dev red in 1 ml. of A	urity, i.e., absenc veloper. AR acetone and ca	e of TAMI, by t talvst solution ad	hin-layer chrom lded to the aquec	atography (TL) us monomer sol	C). The TLC π lution.	aethod employed	silica gel coated
			C	•				

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large volume of chloroform and washing the collected precipitate several times with hexane. After drying *in vacuo* at 60°C., TLC indicated the polymer to be free of TAMI monomer. The polymer was partially soluble in hot chloroform, from which free films could be cast or glass plates. The infrared spectrum (free film) exhibited carbonyl absorption bands at 1735 (ester) and 1565 cm.⁻¹ (aminimide). The NMR spectrum (CDCI₃, τ) exhibited singlets at 6.65 and 8.00 ppm indicating copolymerization. On the basis of nitrogen analysis (Found: N, 6.83%), the polymer consists of ca. 2.8 vinyl acetate units to 1 TAMI unit (calcd. for 2.8:1: N, 6.73%).

TAMI-Vinyl Chloride Solution Polymerization, (Trial 4, Table I). Polymerization was terminated by cooling the reaction vessel to -75°C., opening the vessel, and allowing the excess vinyl chloride to escape as the vessel and contents came to room temperature. It was apparent that as polymerization proceeded, the polymer came out of solution on the wall of For purification, the polymer was dissolved in a small the reaction vessel. amount of distilled water and the water azeotropically removed with As the water was removed, the polymer precipitated from the benzene. The polymer was collected, washed several times with benzene benzene. to remove traces of TAMI, checked for purity by TLC, and dried in vacuo The infrared spectrum (halocarbon mull) exhibited a carbonyl at 60°C. absorption band at 1565 cm.⁻¹. The NMR spectrum (D_2O, τ) exhibited the expected singlet at 6.65 ppm for the trimethylamine moiety. On the basis of nitrogen analysis (Found: N, 8.15%), the polymer contains ca. 3.3 vinyl chloride units to 1 TAMI unit (calcd.: N, 8.07%).

TAMI-Acrylonitrile Copolymerization (Trial 5, Table I). After venting and opening the polymerization bottle, the polymerization mixture was poured into a large volume of vigorously stirred ether. The white, granular precipitate was collected, washed several times with ether, dried *in vacuo* at 60°C., and shown to be free of TAMI by TLC. The infrared spectrum (Nujol mull) exhibited the expected carbonyl absorption band at 1565 cm.⁻¹ and the NMR spectrum (deuterated dimethyl sulfoxide, τ) exhibited the expected singlet at 6.65 ppm for the trimethylamine moiety.

TAMI-Methyl Methacrylate Solution Copolymerization (Trial 6, Table I). The polymerization mixture was poured into a large volume of vigorously stirred water. The polymer was collected, redissolved in acetone, and again precipitated by a large volume of water. The polymer was collected, washed five times with distilled water, and dried *in vacuo* at 60°C. The polymer was shown to be free of TAMI by TLC. The infrared spectrum (halocarbon mull) exhibited the expected aminimide and ester carbonyl absorption bands at 1565 and 1725 cm.⁻¹, respectively. On the basis of nitrogen analysis (found: N, 1.29%), the monomer ratio in the polymer is ca. 20 methyl methacrylate to 1 TAMI (calcd.: N, 1.30%). The DTA and TGA curves for the polymer exhibited an endotherm at 165°C. and a 0.5% weight loss from 165 to 180°C., respectively.

TAMI-Vinyl Chloride Emulsion Copolymerization (Trial 7, Table I). A 1-liter Parr bomb was flushed with nitrogen, cooled to -75°C., flushed
with vinyl chloride, and had condensed into it 167 g. (2.7 mole) of vinyl chloride. The sealed bomb was then placed in the heater and the contents stirred at 400-500 rpm. Separately, a solution was prepared containing 850 ml. distilled water, 6 g. of concentrated ammonium hydroxide, 0.20 g. of silver nitrate, 3.0 g. (0.011 mole) of potassium persulfate, 40 g. (0.281 mole) of TAMI, and 18.0 g. of anionic surfactant sodium dodecyl benzenesulfonate. When the bomb had reached room temperature, 53 g. of the above emulsion were added under pressure. Polymerization was allowed to proceed for 18 hr. at 50°C. After venting the excess vinyl chloride, the precipitated polymer was collected and washed liberally with water until TLC indicated the absence of TAMI and other impurities and dried

Reactivity Study of TAMI						
Run"	Moles amin- imide	Moles acryloni- triles	Mole ratio	Yield,	Mole-% TAMI	$f = \frac{M_1/M_2}{(\text{mole})}$ ratio polymer)
I	0.05	0.2	1/4	6.2	33.50	0.5037
11	0.075	0.175	3/7	4.0	35.55	0.5517
111	0.10	0.15	2/3	4.1	39.48	0.6524
IV	0.125	0.125	$^{1}/_{1}$	5.0	40.14	0.6704
V	0.15	0.10	$^{3}/_{2}$	5.0	50.70	1.0285
VI	0.175	0.075	4/3	5.0	52.00	1.0832
VII	0.10	0.025	4/1	5.0	56.26	1.2860

(I) A TAT 1 A TT

^a Copolymerizations were run under nitrogen in acetonitrile solvent (75 ml., run VII had 37 ml.) at $70 \pm 0.5^{\circ}$ C, for 2 hr. in 100-ml. serum bottles with AIBN catalyst (0.030 g., run VII had 0.015 g.).

^b Due to isolation and purification problems, weights of samples V-VII were less than 0.5 g, each and conversions are estimated to be no greater than 5%.

• All polymers were checked for purity, i.e., absence of TAMI, by TLC. The TLC method employed silica gel-coated plates, methanol solvent, and I₂ developer.

in vacuo at 60° C. The infrared spectrum (halocarbon mull) of the polymer exhibited a carbonyl absorption band at 1565 cm.⁻¹ (aminimide). On the basis of nitrogen analysis (found: N, 1.61%), the ratio of monomers in the polymer of vinyl chloride: TAMI is ca. 26:1 (calcd.: N, 1.59%).

TAMI-Styrene Solution Copolymerization (Trial 8, Table I). Polymerization was terminated by pouring the solution into vigorously stirred methanol. The white, fluffy polymer was washed several times with methanol and shown to be free of TAMI by TLC. The infrared spectrum (free film) of the polymer exhibited absorption bonds attributable only to polystyrene.

TAMI-Acrylonitrile Copolymerizations (Table II). Polymerizations were terminated by pouring the contents of each bottle into a large volume of ether, collecting, and washing the precipitate several times with ether. Purification of the polymers was achieved by dialysis, i.e., each polymer

was dissolved in 50 ml. distilled water, sealed in Visking seamless regenerated cellulose tubing, and immersed at room temperature into 1 liter of distilled water. Periodically, each polymer solution was checked for TAMI by TLC. After ca. 2 hr., TLC indicated all samples were free of TAMI. Isolation of the purified polymers were accomplished by azeotropic distillation of the water using benzene. After washing several times with benzene, the white, granular polymers were dried overnight at 60°C. *in vacuo* (0.1 mm. Hg.). Nonaqueous titration of the polymers in a 50:50 mixture of glacial acetic/acetic anhydride with 0.1088N perchloric acid (Gentian violet indicator) was used for determination of copolymer compositions (Table II).

TAMI-Methyl Methacrylate-Hydroxypropyl Methacrylate Terpolymer. A 150-ml. resin pot, fitted with a stirrer, nitrogen ebullator, condensor and addition funnel, was purged with nitrogen and charged with 50 ml. acetonitrile, 0.5 g. (0.003 mole) of AIBN, 8 g. (0.056 mole) of TAMI, 4.0 g. (0.027 mole) hydroxypropyl methacrylate and 28 g. (0.28 mole) of methyl methacrylate. Under a thin stream of nitrogen, polymerization was carried out at 85°C. for 1 hr. The polymer was purified by evaporation to dryness, dissolving in acetone, and precipitation into water. After washing several times with water, the polymer was dried in vacuo to obtain a 53%yield of solids. The polymer was shown to be free of TAMI by TLC. The infrared spectrum (free film) of the polymer exhibited hydroxyl and carbonyl absorption bands at 3590-3650, 1730 (ester), and 1565 cm.⁻¹ (aminimide). In addition, NMR (CDCI₃, τ) indicated the presence of the trimethyl amine moiety (singlet at 6.65 ppm). Differential thermal analysis (endotherm) and TGA (weight loss) indicated that the polymer losses $N(CH_3)_3$ at ca. 165°C. On the basis of nitrogen analysis (found N, 2.48%), the monomer ratio in the polymer is estimated as 9:1:1 of methyl methacrylate: hydroxypropyl methacrylate: TAMI (calcd.: for 9:1:1: N, 2.36%).

The polymer was dissolved in acctone (50% solids) and used to coat glass plates. After air drying for 2 days the films were ca. 3 mil thick and exhibited an average Sward hardness of 42. Heating the films for 15 min. at 170°C. caused evolution of trimethylamine and an increase in the Sward hardness to 55. The changes in the infrared spectrum of the free film supported loss of aminimide functionality (no carbonyl band at 1656 cm.⁻¹) and formation of urethane bonds.

RESULTS AND DISCUSSION

Monomer Synthesis and Monomer Properties

Trimethylamine methacrylimide (TAMI) was prepared (from readily available starting materials) in excellent yields according to the procedure of egs. (2) and (3):

$$CH_{3}Cl + (CH_{3})_{2}N \longrightarrow NH_{2} \rightarrow NH_{2}N(CH_{3})_{3}Cl$$
(2)

Trimethylamine methacrylimide exhibits excellent solubility in water similar to acrylamide. Some of the solubility properties are summarized in Table III.

Solvent	Solubility ^a
Water	+++
Ethanol	+++
Methanol	+++
Acetonitrile	+++
Tetrahydrofuran	++
Dimethyl sulfoxide	+++
Chloroform	++
Acetone	++
Dioxane	+
Benzene	+
tert-Butyl alcohol	+
Dimethylformamide	+
Ethvl acetate	+
Carbon tetrachloride	
Hexane	_
Diethyl ether	_

TABLE IIISolubility Characteristics of TAMI at 25°C.

"+++ = highly soluble; ++ = good solubility; + = poor solubility; - = in-soluble.

Trimethylamine methacrylimide has good thermal stability and long shelf life. There is no evidence of polymer formation after long periods of storage at room temperature. The monomer can be readily recrystallized from benzene without apparent polymerization or decomposition.

Polymerizations

Some of the results from the initial homo- and copolymerization screening experiments on TAMI are shown in Table I.

Homopolymerization of TAMI was accomplished using AIBN as a catalyst. Both the infrared and NMR spectra of the polymer showed no C—C double bond but the presence of the aminimide moiety. Differential thermal analysis and TGA indicated the polymer started losing trimethylamine at ca. 125°C. Further, TGA indicated the polymer lost 42% of its weight when heated from 125 to 200°C. (theory, 41%).

Initial experiments (Table I) indicates that TAMI can be copolymerized with a wide variety of other vinyl monomers to give water soluble, low molecular weight polymers. The presence of the aminimide moiety

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 $[--CONN(CH_3)_3]$ in the copolymer was well established by nitrogen determination, infrared, NMR and TGA analyses. On the basis of nitrogen determination, these initial copolymerization experiments suggested that TAMI was much more reactive than vinyl chloride and vinyl acetate, less reactive than methyl methacrylate and acrylonitrile, and much less reactive than styrene. Differential thermal analysis and TGA indicates that the copolymers start losing trimethylamine very rapidly at ca. 170°C.

Determination of Monomer Reactivity Ratios

The composition of the monomer feeds and the copolymers obtained, for the TAMI-acrylonitrile system, are summarized in Table II. From these results, the monomer reactivity ratios were obtained by the method of Fineman and Ross:⁶ $r_1 = 0.10 \pm 0.01$; $r_2 = 0.37 \pm 0.04$.

In Figure 1 the mole per cent in the monomer feed (M_1) is plotted against the corresponding mole per cent (m_1) in the copolymer. The line in the figure was calculated from the monomer reactivity ratios and the spots were from experimental data.



NOTE FLOCTION LANT IN MONOMER NAME

Fig. 1. Copolymer composition curve for the copolymerization of TAMI and acrylonitrile.

The Alfrey-Price Q and e values⁷ for TAMI were obtained from the monomer reactivity ratios in the copolymerization with acrylonitrile: Q = 0.18, e = -0.60. The Q and e values of acrylonitrile⁸ used in the calculations were as follows: Q = 0.60, e = 1.20.

A look at the Q and e values of some other acrylamide, methacrylamide, acrylate, and methacrylate monomers will help explain the calculated Q and e values of TAMI (Table IV).

The *e* values of both acrylamide and methacrylamide are positive and >1. In contrast the *e* value for both acrylamides and methacrylamides change to negative values upon introduction of electron repelling groups to the nitrogen atom. For example, the *e* value for methacrylamide (c = 1.24) changes to a fairly large negative *c* value for *N*-methylmetha-

Vinyl monomers	Structure	Q	с
Acrylamide	CH ₂ =CH-CONH ₂ CH ₃	1.18	1.30
Methacrylamide	$CH_2 = CONH_2$ CH_3	1.46	1.24
Methaerylic acid N-tert-Octy]-	$CH_2 = C - CO_2H$ $CH_2 = CHCONHC(CH_3)_2(CH_2)_4CH_3$	$\frac{2.34}{0.20^{\mathrm{b}}}$	$0.65 - 0.10^{\rm b}$
N-Acryloylbenz-	$CH_2 = \!$	0.55°	-0.47°
N.N-Dimethyl-	$\rm CH_2 = CH + CON(CH_3)_2$	1.08°	-0.56°
N-Methylmeth-	CII ₂ =CCII ₃ CONHCII ₃	0.32	-0.60
TAM	$CH_2 = C - CONN(CH_3)_3$	0.183	-0.60
Sodium methacrylate N,N-Di(p-anisyl)- methacrylamide	$CH_{3} CH_{2} = CCH_{3}CO_{2}Na CH_{2} = C - CON(C_{6}H_{3}OCH_{3})_{2}$	1.36 2.80 ^b	-1.18 -1.19 ^b
Vinyl acetate Vinyl chloride Methyl methacrylate	$CH_{3}CO_{2}CH=CH_{2}$ $CH_{4}=CHCI_{1}$ $CH_{4}=CHCI_{1}$ $CH_{2}=C-CO_{2}CH_{3}$	0.026 0.04 0.74	$-0.22 \\ 0.20 \\ 0.40$
Styrene	$C_6H_5CH=CH_2$	1.00	-0,80

 TABLE IV

 Q and e Values of TAMI and Other Vinyl Monomers*

^a Data of Young⁸ unless otherwise noted.

^b Data of Ham.⁹

° Data of Azuke and Nakamura.¹⁰

crylamide (e = -0.60). The large negative *e* value for TAMI can possibly be explained by the electron-repelling tendency of the trimethylamineimide (-N-N) group which cancels electron attraction by the carbonyl group attached to the unsaturated residue. An analogous situation occurs when methacrylic acid is neutralized, i.e., the *e* value changes from a positive to a negative number.

Introduction of alkyl groups on the nitrogen atom of methacrylamide and the C_6H_5 CONH— moiety on the nitrogen atom of acrylamide lowers the Q values of the two monomers. Thus, it is expected that the general reactivity of TAMI would be much lower than the general reactivity of methacrylamide.

The data clearly show that TAMI is more reactive than vinyl chloride and vinyl acetate, less reactive than methyl methacrylate and acrylonitrile, and much less reactive than styrene.

It is reasonable to assume that the transition of a growing chain ending

in TAMI . . . CH_2 - CCH_3 - $CON-N(CH_3)_3$ is not appreciably resonancestabilized. The lack of appreciable stabilization is probably due to the

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spreading of the negative charge of the TAMI over the carbonyl oxygen. This is supported by the low frequency $(1565 \text{ cm}.^{-1})$ of the carbonyl group.

$$\begin{array}{c} CH_3 & O \\ \downarrow & \downarrow \\ CH_2 = C - C - N - N (CH_3)_3 \end{array}$$

Strong alternation occurs in the TAMI-acrylonitrile copolymer, as noted by the crossover on the copolymer composition curve (Fig. 1). This is expected for two monomers, one of which can give rise to a radical of high electron density and one having a double bond of low electron density.

The TAMI monomer was used to prepare a terpolymer consisting of TAMI, methyl methacrylate, and hydroxypropyl methacrylate monomers. The presence of hydroxyl and aminimide moieties in the terpolymer was established by infrared and NMR analyses. Further, nitrogen determination and TGA also demonstrated the presence of the aminimide group. It was shown that the polymer could be deposited as a coating and crosslinked with heat. Changes in the infrared spectra of the heated films supported the assumption that crosslinking occurred by formation of urethane bonds. This brief, introductory work supports the contention that TAMI should have utility in the preparation of reactive polymers.

CONCLUSION

Some homo- and copolymerization properties of trimethylamine methacrylimide have been reported. Preliminary experiments have indicated the potential of this chemical as a new reactive vinyl monomer.

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Polymer Reactions. II. Thermal Decomposition of **Polyethylene Hydroperoxide**

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Synopsis

Polyethylene hydroperoxide (PEH) was prepared by low-temperature autoxidation initiated by AIBN. Over 85% of the total hydroperoxyl groups decompose by a rapid process, the remainder dissociate at about one-tenth of that rate. The results are the same whether PEH is decomposed in solution or in the solid state. Large amounts of scavenger have no effect on these decompositions; there is no radical-induced processes. The results suggest mechanisms of decomposition involving neighboring group assistance.

INTRODUCTION

Attack of polyethylene by an initiator radical results in a polyethylene peroxy radical. This radical could undergo rapid termination to form alcohols and carbonyl compounds. Hydroperoxides are formed when this radical abstracts a hydrogen by either intramolecular or intermolecular processes. The latter gives polyethylene hydroperoxide (PEH) containing no neighboring functional groups.

Intramolecular abstraction of an equivalent neighboring hydrogen atom is most probable for the β hydrogen atom.¹ This reaction would proceed via a six-membered ring transition state. If this reaction does not proceed any further, the product PEH would be predominantly that represented by structure I:



where P may be an hydroxyl or a carbonyl group. On the other hand, if the chain propagation continues, P could be another hydroperoxyl group.

In this work, we studied the thermal decomposition of PEH. The results suggest that PEH has the structure represented by I where P is not a hydroperoxyl group.

J. C. W. CHIEN

EXPERIMENTAL

Preparation of PEH

The hydroperoxide of low-density polyethylene was prepared by a procedure already described.² Chlorobenzene was used as the solvent. The product was precipitated, washed with heptane, and vacuum-dried at room temperature. Better than 98% of the polymer was recovered. Two samples, PEH-1 and PEH-2, contained 0.694 and 0.064 meq./g. of hydroperoxides, respectively.

High-density polyethylene is not completely soluble in chlorobenzene at 100°C. This polymer was oxidized in the highly swollen state in chlorobenzene with vigorous agitation. Otherwise, the procedure used is the same as above. A sample of PEH-3 thus prepared had a hydroperoxide content of 0.65 meq./g.

PEH showed slow changes in active oxygen content even when kept in the dark at 0°C. The hydroperoxide concentration was determined immediately before each experiment.

Thermal Decomposition Experiment

The procedure used to follow the decomposition of PEH in chlorobenzene solution was the same as that given previously.² PEH is insoluble in chlorobenzene at room temperature. It dissolved rapidly with heating and agitation. However, the results were often erratic during the period of dissolution.

Decomposition was also performed in the solid state. The polymer was swollen by a benzene solution of the scavenger overnight. The solvent was subsequently removed by vacuum evaporation for 1 day. Samples were sealed into separate vials under vacuum and immersed in a constant temperature bath. The reaction was followed by the determination of hydroperoxides in these vials.

Determination of Radical Yield

The yield of radicals formed upon the decomposition of PEH was determined by the method given earlier.³ A 1:2 cumene-chlorobenzene solution of PEH containing known amounts of 2,6-di-*tert*-butyl-*p*-cresol (IH) was heated in a stirred cylindrical cell (2 cm. in diameter and 5 cm. in length). The cell was connected via a condenser and a trap containing Linde 5A sieve to an automatic system for measuring oxygen adsorption.⁴ The radical yield was calculated from the observed induction period.³

RESULTS

The decomposition of PEH is initially very rapid. After most of the hydroperoxides have decomposed, the rate decreases to less than one-tenth of the initial rate. Within the temperature range from 100 to 135° C., more than 85% of the hydroperoxides decomposed by the rapid process.

The data were analyzed as two consecutive first-order reactions. This analysis is justified because neither the rate constants nor the relative amounts of the fast versus the slow reactions is dependent upon the initial concentration of PEH. In fact, the results were the same whether the decomposition was carried out in chlorobenzene solution or in the solid state. Table I summarizes these results.

	Polyet hydrop	hylene eroxide			Initial reaction	l n	Slow
Run no.	Sample	Conen., mole/l.	Temp., °C.	[IH] ₀ , mole/l.ª	$k_d imes 10^4$, sec. ⁻¹	%	$k_{d}' \times 10^{5}$, sec. $^{-1}$
21	PEH 1	0.0231	135	0	6.3	91	4.52
22	PEH 1	0.0231	135	0.0038	6.0	91	4.52
23	PEH 1	0.0231	135	0.38	6.3	93	5.0
24	PEH 1	0.035	120	0	1.87	85	1.34
25	PEH 1	0.035	120	0.0038	1.75	92	1.55
26	PEH 1	0.035	120	0.38	1.67	90	1.45
27	PEH 2	0.0043	120	0.0038	1.72	100	
28	PEH 2	0.0043	120	0.38	1.47	100	_
29	PEH 3	0.022	120	0.38	2.00	85	1.90
30	PEH 3	0.022	120	0.0038	1.35	90	_
31	PEH 1	0.023	100	0.0038	0.31	100	_
32	PEH 1	0.023	100	0.38	0.33	100	_

TABLE I Thermal Decomposition of Polyethylene Hydroperoxide^{a,b}

^a Chlorobenzene solvent.

^b Reaction at 85°C. is not possible because PEH is not completely soluble.

° 2,6-Di-tert-butyl-p-cresol.

In some of the experiments a large excess of scavenger was introduced. This corresponds to more than 10 times the amount of hydroperoxides. There was no noticeable effect on the course of decomposition.

Several experiments were made to determine the radical yields from the decomposition of PEH at 100°C. An average yield of 0.2 was obtained.

The intrinsic viscosities of all the samples taken during four of the experiments in Table I were determined. There was no appreciable decrease of intrinsic viscosity during the course of any of these reactions.

DISCUSSION

The decomposition of PEH consists of two clearly resolvable processes. Both reactions are unaffected by scavengers. There is no indication of radical-induced reaction in this system. It will be shown in the subsequent papers^{5,6} that when there are neighboring hydroperoxides on the same chain (such as in polypropylene hydroperoxide), an intramolecular, radicalinduced, decomposition occurs. It is concluded that PEH does not contain neighboring hydroperoxides, i.e., P is not a hydroperoxyl group in I. This is understandable because of the ease with which secondary peroxy radicals can undergo termination. $^{7-9}$

The rate constant of the slow and the fast decompositions are about two and twenty times faster than that of squalene hydroperoxide (SH),² respectively. One plausible explanation is that these correspond to the decompositions of PEH having different polar neighboring groups, such as β -hydroxy and β -keto hydroperoxides. These different PEH's are assumed to decompose at different rates both with greater ease than the isolated hydroperoxides in SH.

From the observed temperature dependencies of decomposition, we estimate energies of activation of 25 and 27 kcal./mole for the fast and the slow processes, respectively. They have the same entropy of activation of -14 e.u. In these reactions of high activation energies, stabilization of the transition states by hydrogen bonding is probably significant,¹⁰ and the difference between the activation energies for decompositions may be largely attributed to the difference between the ΔH of formation of the intramolecular hydrogen bonds. The hydrogen-bonded hydroxyl bands of 1.3-propanediol and of diacetone alcohol in the infrared region are shifted by 76 cm.⁻¹ and 152 cm.⁻¹, respectively.^{11,12} If the hydrogen bond in diacetone alcohol, has a ΔH_{f} of 4–6 kcal./mole, then according to Badger's rule,¹³ the ΔH_{f} for the weaker hydrogen bond in 1,3-propanediol should be about 2-3 kcal./mole. If one assumes a similar difference between the ΔH , of the β -hydroxy and β -keto hydroperoxides, then the observed activation energies of the fast and the slow decomposition of PEH can be qualitatively accounted for. We tentatively propose that PEH contains β -keto and β -hydroxy hydroperoxides and that the former decomposes about ten times faster than the latter.

The decomposition of PEH yields on the average only 0.2 radicals. It is suggestive that cage recombination of the type shown in eq. (1)

$$\begin{array}{ccc} H & H & O \\ -CH_2 - C - CH_2 - \rightarrow (-CH_2 - C - CH_2 - + OH \cdot) \rightarrow -CH_2 - C - CH_2 - + H_2O \\ 0 & O \\ 0 & O \\ H \end{array}$$

could be important. This process should contribute toward the known stability of polyethylene¹⁴ against autoxidation as compared to polypropylene.

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Polymer Reactions. III. Structure of Polypropylene Hydroperoxide

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Synopsis

Oxidation of polypropylene introduces hydroperoxide groups into the polymer. Infrared spectroscopy has determined that more than 90% of these groups are intramolecularly hydrogen bonded. The sequential lengths and sequence distributions of these neighboring hydroperoxides were estimated from the electronic spectra of the polyenes derived from the polypropylene hydroperoxide by two methods: (1) reduction, acetylation, and pyrolysis, and (2) reduction and dehydration. The results indicate that all the hydroperoxide groups are present in sequences of length two and greater. Intramolecular hydrogen abstraction during oxidation could account for the formation of these neighboring hydroperoxides.

INTRODUCTION

Rust¹ has shown that air oxidation of 2,4-dimethyl pentane gives predominantly 2,4-dimethyl-2,4-dihydroperoxypentane. A "back-biting" hydrogen abstraction mechanism by the peroxy radical via a six-membered ring transition state was believed to be important. This mechanism is often postulated²⁻⁴ for the propagation steps in autoxidations of polyolefins; it has been refuted by others.⁵ Definite proof for either contention is needed. In this paper we report a study of the structures of hydroperoxides contained in oxidized polypropylene (PPH). The results afford strong support to the occurrence of back-biting hydrogen abstraction in the autoxidation of polypropylene.

EXPERIMENTAL

Preparation of PPH

Commercial polypropylene was extracted with an excess of chlorobenzene at room temperature; the extract was precipitated and vacuum dried. NMR spectra showed this sample to contain predominantly syndiotactic triads.⁶ A sample of this polymer was redissolved in 300 ml. of chlorobenzene and oxidized according to a procedure previously described.^{7,8} These preparations are summarized in Table I. Less than 5% of the hydroperoxides formed could have decomposed during the 33 min. reaction time.

Run	Polypropylene, g.	AIBN, g.	Hydroperoxide, meq./g.	
20	25	0.5	0.26	
22	10	0.2	0.12	
28	40	0.6	0.42	
32	60	2.4	0.34	
72	42	3.4	0.50	
88	21	1.7	0.33	

TABLE I reparation of Polypropylene Hydroperoxic

The intrinsic viscosity of the starting material measured as a 1% solution in decalin at 135°C. was 0.95; the oxidized products had viscosities between 0.5 and 0.3. This viscosity decrease is not accompanied by a corresponding decrease in molecular weight determined with a Mechrolab osmometer. The number-average molecular weight of the polypropylene (13,500) is nearly the same as those for the PPH samples (12,500 \pm 700). The second virial coefficients of toluene solutions of PPH were found to be smaller by a factor of 2 to 3 than that of the parent polymer. It is concluded that little scission becurred during the autoxidation under these mild conditions.

Reduction of PPH

A 1-g. portion of PPH was swollen in 5 ml. of benzene. After 1 hr., 25 ml. of isopropyl alcohol, 2 ml. of glacial acetic acid, and 10 ml. of a saturated isopropyl alcohol solution of NaI were added to the swollen polymer and the mixture was refluxed for 5 min. The iodine liberated was titrated with standard thiosulfate solution. The reduced polymer, designated as RPH, was filtered, washed with acetone, and vacuum dried at 25°C. The intrinsic viscosity of RPH was slightly higher than that of the corresponding PPH. (For example, the intrinsic viscosities of PPH-20 and RPH-20 are 0.52 and 0.65, respectively.) This increase is probably significant but not sufficiently great to merit consideration of the effects of functional groups and of hydrogen bondings on the second virial coefficients.

Dehydration of Reduced PPH

A tube containing 0.2 g. of RPH was evacuated at room temperature and 1μ Hg for 1 hr. It was immersed in an oil bath for several minutes and subsequently quenched in a Dry Ice-C₂HCl₃ mixture. At the temperature used, there was no appreciable degradation. For example, heating of RPH-20 for 5 min. at 181, 196, and 219°C. gave products with $[\eta]$ of 0.64, 0.67, and 0.68, respectively. The number-average molecular weights of a sample before and after dehydration are 21,400 and 23,000, respectively. Heating at 200°C. for periods up to 30 min. also had no effect on the molecular weight. The dehydration products obtained after 5, 10, 20, and 30 min. gave essentially the same ultraviolet absorption spectra and showed no distinct hydroxyl bands in the infrared region.

Acetylation of RPH

RPH was acetylated by Allen's procedure.⁹ The resulting polymer was washed with methanol and vacuum dried.

Pyrolysis of Acetylated RPH

A procedure similar to that for dehydration was used for pyrolysis; it was carried out at 300° C. for 1–2 hr. to give the same polyenes (Table II).

		$\begin{bmatrix} CH_3 \\ \\ C=CH \end{pmatrix}_{\hat{n}}$], mmole/g.
n	11	nr. pyrolysis	2 hr. pyrolysis
2		0.070	0.0715
3		0.027	0.0216
4		0.012	0.0127
5		0.0035	0.004
6		0.0025	0.0024
7		0.0016	0.0016
≥ 8		0.0007	0.0006
	Total	0.117	0.114

		TABLE	п	
Effect	of	Duration	of	Pvrolvsi

Electronic spectra were obtained with a Cary-14 spectrophotometer with methylene chloride as the solvent. Infrared spectra were obtained with a Beckman IR-7 instrument, with CCl₄ as the solvent. Total unsaturation was measured by reaction with molecular bromine.¹⁰ In this procedure, bromine adds quantitatively to conjugated dienes; the extension of this method to higher polyenes has not been established.

RESULTS

Infrared Studies

Intramolecular hydrogen abstraction via a six-membered ring transition state should yield hydroperoxide groups capable of forming intramolecular hydrogen bonds with a neighboring one. These groups are easily detected in polypropylene hydroperoxide (PPH) by infrared spectroscopy. The results are summarized in Table III.

The infrared spectrum of PPH is characterized by two absorption peaks, one at 3378 cm.⁻¹ ($\nu_{1/2} = 153$ cm.⁻¹) and the other at 3553 cm.⁻¹ ($\nu_{1/2} = 35$ cm.⁻¹). Whereas the latter is certainly the free hydroxyl band, the former is believed to be the intramolecular hydrogen-bonded hydroxyl band. This assignment is based upon the following observations. The frequency of the band lies in the region of bonded hydroxyl stretching

[DDH _39]	Integrated intensity				
(in CCl ₄), wt%	3550 cm. ⁻¹	3378 cm1	Ratio		
10	100	623	0.16		
4	40	294	0.14		
1.6	17	119	0.14		
0.64	6	40	0.15		

TABLE III

vibration; the band width is characteristic of this type of vibration. Neither the frequency nor the half-bandwidth changes with concentration. The relative intensity of this and the 3550 cm. $^{-1}$ bands remains constant These last three features are consistent with intramolecular with dilution. hydrogen-bonded hydroxyl stretchings. The hydroxyl band absorption coefficients were found¹¹ to increase by less than 0.5% upon the formation of intramolecular hydrogen bonds. Similarly, Kuhn¹² reported that the absorption coefficients for the free and the intramolecular hydrogen-bonded

Sample ^a	PPH concn., wt%	Intramolecular hydrogen-bonded hydroperoxide, %
PPH-22	5.1	92
PPH-22	1.0	91, 92
PPH-22	0.51	92
PPH-32	10.0	86
PPH-32	4.0	88
PPH-32	1.6	88
PPH-32	0.64	87
PPH-72	0.96	92
PPH-72	0.19	91
PPH-88	1.0	91
PPH-88	0.21	91

TABLE IV

^a Descriptions of these samples are given in the Experimental section.

hydroxyl bands are the same in ethylene glycol and tetramethylethylene They did not vary with concentration in tetramethylene glycol. glycol.

Assuming equal absorption coefficients for the 3550 and the 3378 cm. $^{-1}$ bands in PPH, the infrared spectra of several samples of PPH showed that about 90% of the hydroperoxy groups are intramolecularly hydrogen bonded (Table IV). The remaining 10% of free hydroxyl will be shown below to belong to the nonbonded hydroperoxy groups in odd sequences. Isolated hydroperoxides do not appear to be formed in appreciable amounts during oxidation.

This study was aimed at determining the sequential length and the sequence distribution of neighboring hydroperoxide. The experimental scheme is given in Figure 1.



Fig. 1. Determination of the distribution of neighboring hydroperoxide blocks.

A sample of PPH, represented as II in Figure 1, was quantitatively reduced to the corresponding polyol (RPH). The polyol was converted to the corresponding polyene (VI) by two methods. In method 1, the polyol was exhaustively acetylated, and the resulting acetate ester (V) was pyrolyzed. The product (VIA) was dissolved in methylene chloride and its ultraviolet spectra determined at several concentrations (Figs. 2–4).

The spectra of these polyenes have maxima at about 2300 and 2650 A. and shoulders at about 2950, 3350, 3650, 4000, and 4400 A. In some specimens, not all the shoulders were resolved. These absorptions corre-

spond to the λ_{\max} reported¹³⁻¹⁵ for CH₃(—CH=CH—)_nCH₃ and for H(—CH=CH—)_nH. From the known values of ϵ_{\max} ,¹⁵ the concentrations of polyenes of various lengths were calculated. Concentrations of polyenes are given in terms of [—CH=CH—]; therefore, [(—CH=CH—)_n] = n[—CH=CH—].



Fig. 2. Electronic spectrum of dehydrated RPH-22; 0.05% in CH₂Cl₂.



Fig. 3. Electronic spectrum of dehydrated RPH-22; 0.57% in CH₂Cl₂.

In method 2, polyols were converted directly to polyenes (VIB) by dehydration at 200°C. The electronic spectra of these products are essentially the same as those obtained by method 1 as evidenced by comparison of the results given in Figure 2 and Table V. Because the pyrolysis of olefin acetate is known¹⁶ to occur without isomerization, the agreement of the



Fig. 4. Electronic spectrum of dehydrated RPH-22; 5.7% in CH₂Cl₂.

results noted above indicates the absence of double-bond migration during dehydration in method 2.

The distribution of conjugation for polycne samples derived from several PPH preparations are summarized in Table VI and Figure 5. Table VI

	U		$\begin{array}{c} \text{(CH}_3 \\ \text{(CH}_3 \\ \text{(C=CH)} \end{array} \end{array}$, mmole,	/g.
n		VIB	VIA	Avg.
2		0.079	0.070	0.0745
3		0.028	0.027	0.0275
4		0.014	0.012	0.013
5		0.0031	0.0035	0.0033
6		0.0014	0.0025	0.002
7		0.0037	0.0016	0.0026
≥ 8		0.0014	0.0007	0.001
	Total	0.13	0.12	0.12

TABLE V

also shows that the total hydroperoxide concentrations as determined by iodimetry and the total olefinic unsaturation calculated from the electronic spectra of the polyenes are in agreement with each other. This is confirmed by bromination of the polyenes to determine the total unsaturation. This



Fig. 5. Distribution of conjugation in polyenes: (○) RPH-22; (●) RPH-28; (●) RPH-32; (●) RPH-72; (●) RPH-88.

result is again comparable to the total hydroperoxide content of the initial sample.

				= CH n,	mmole/g.		
п	RPH-28ª	RPH-28 ^b	RPH-32	RPH-72 ^a	RPH-72 ^b	RPH-72 ^b	RPH-88
2	0.121	0.116	0.304	0.435	0.386	0.400	0.127
3	0.063	0.042	0.182	0.131	0.121	0.112	0.042
4	0.035	0.021	0.076	0.104	0.096	0.080	0.019
5	0.016	0.015	0.036	0.036	0.052	0.040	0.005
6	0.006	0.006	0.019	0.015	0.019	0.011	0.003
7	0.005	0.005	0.016	0.012	0.019	0.009	0.002
8	0.003	0.002	0.009	0.007	0.012	0.007	0.001
Total	0.254	0.2	0.64	0.74	0.70	0.66	0.20
[ROOH]° Total unsat-	0.22	0.22	0.65	0.71	0.71	0.71	0.23
urationd	0.23	0.20	0.60	0.73	0.71	0.68	0.20

TABLE VI Electronic Spectra of Polyenes

^a Polyene via method 1.

^b Polyene via method 2.

° [ROOH] determined by iodimetry.

^d Total unsaturation calculated from bromine number.

DISCUSSION

The presence of intramolecular hydrogen bonds in PPH has been established. These bonds are attributed to neighboring hydroperoxyl groups. We define neighboring groups as those groups which are in close proximity for chemical interactions. However there could also be contribution from any hydroperoxyl groups hydrogen bonded to a neighboring polar group such as hydroxyl or carbonyl group. These complications would obscure the interpretation of both the infrared and electronic spectra. However, this possibility can be justifiably discounted. Hydroxyl and carbonyl groups are largely formed during the termination processes. Two termination processes need to be examined, the scission and the abstraction routes. The former may be written as shown in eqs. (1)-(3).

$$2 \quad -CH_2 - CH_2 - CH$$

$$\begin{array}{cccc} O \cdot & O \\ -CH_2 - C - CH_2 - \rightarrow & -CH_2 - CH_2 - + CH_3 \cdot \\ & & \\ & & \\ CH_3 \end{array}$$
(2)

$$\begin{array}{cccc} O \cdot & O \\ -CH_2 - C - CH_2 - \rightarrow & -CH_2 - C - CH_3 + - CH_2 \cdot \\ & U \\ CH_3 \end{array}$$
(3)

The primary and the secondary peroxy radicals thus formed can terminate rapidly by disproportionation. In the latter, the tertiary peroxy radical generates secondary peroxy radicals by either α or γ hydrogen abstraction [eqs. (4) and (5)], followed by oxygenation and reaction with another peroxy radical.

$$-CH_{2}-C-CH_{2}-C-CH_{2}-C-CH_{2}-C-CH_{2}-CH_{2$$

Under the mild conditions used in the preparation of PPH, chain scission is improbable. This is substantiated by the observation that the starting polypropylene and the PPH have nearly the same number-average molecular weights. In regard to the alternate termination mechanism, Rust¹ showed that γ -hydrogen abstraction does occur during the autoxidation of branched hydrocarbons but that α -hydrogen abstraction was not observed even if it is an activated hydrogen atom. Therefore, reaction (5) and its subsequent reactions is the most likely termination process here. This process yields γ -hydroxy and γ -keto products. These groups would not form intramolecular hydrogen bonds with a hydroperoxyl group γ to them. It is concluded that only neighboring hydroperoxides contribute toward the infrared band in this system.

It is possible to infer from the electronic spectra of the polyenes, the sequential distribution of the neighboring hydroperoxides in the parent PPH, though this deduction is not without uncertainties. For instance, isolated hydroperoxides would not contribute to the absorption spectra in the region accessible to our instrument. However, the agreement noted in Table VI between the concentrations of the total hydroperoxide and the total unsaturation indicates that there is a negligible amount of non-conjugated olefins in the polyenes. Therefore, there are no appreciable amounts of isolated hydroperoxides in the PPH samples.



Fig. 6. Estimated sequential distribution of neighboring hydroperoxides in PPH.

The direction of *cis* elimination during pyrolysis could influence the distribution of double bonds. Thermodynamic effect favors the pyrolysis of 4-acetoxy-1-pentene to give the more stable 1,3-pentadiene by a factor of three.¹⁷ It is assumed here that elimination occurs primarily to give the more stable product. This assumption tends to increase the relative amounts of the short sequences at the expense of the longer ones.

Either the primary or the secondary hydrogen atoms could be eliminated during pyrolysis leading to isomeric conjugated olefins. Statistical weight was given to these alternate reaction paths. In this manner we obtained Figure 6 from Figure 5. Figure 6 is assumed to represent the sequential distribution of neighboring hydroperoxides in the parent PPH.

The infrared results have other ramifications. Unlike the glycols,^{11,12} where the neighboring hydroxyl groups form one intramolecular hydrogen bond; the hydroperoxides of PPH are 90% intramolecularly hydrogenbonded. If we assume that only hydroperoxyl groups are present in the sequence (*vide supra*), then most of the neighboring groups participate in two intramolecular hydrogen bonds. Both oxygen atoms of the hydroperoxyl group are suggested as being involved in hydrogen bonding.^{18,19}

Two possible structures for the intramolecular hydrogen-bonded PPH are: (A) pairs of neighboring hydroperoxides form two intramolecular hydrogen bonds in a bicyclic arrangement, (B) all the hydroperoxides in a block form a linear sequence of intramolecular hydrogen bonds. In the former, one OOH contributes to the free hydroxyl band for odd sequences and none for even sequences. In the latter, there is one nonbonded OOH group in any sequence. Clearly, structure B predicts a higher amount of free hydroxyl absorption in infrared measurements than structure A. From the estimated distribution of neighboring hydroperoxides, structure A and B predicted 8 and 37% of free hydroperoxides, respectively. The result of infrared determinations showed 7–9% of free hydroperoxides. Of the two possible structures, A is favored by the experimental evidence. Using space-filling models, built according to the known²⁰ O-H---O configuration and C-O-O dihedral angle, structure A may be represented as shown:



A similar structure has been proposed by Walling and Heaton²¹ for the intermolecular hydrogen bonds in *tert*-butyl hydroperoxide.

The absence of isolated hydroperoxide and the sequential distribution of neighboring hydroperoxides in PPH ascertain the importance of backbiting hydrogen abstraction as the predominant propagation reaction.

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Polymer Reactions. IV. Thermal Decomposition of Polypropylene Hydroperoxides

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Synopsis

The thermal decomposition of polypropylene hydroperoxide (PPH) consists of two consecutive reactions. The initial, faster reaction has rates up to 60 times that of the slower process. The former is largely suppressed by the addition of an excess of 2,6-di-*tert*-butyl-*p*-cresol. The course of reaction is the same in either solid state or in solution. The results are consistent with an intramolecular radical-induced mechanism for the initial reaction. This faster reaction consumes about 70-95% of the total hydroperoxides. The decomposition of PPH yields a maximum of about 1.8 radicals. Samples prepared from crystalline and amorphous polypropylenes have identical decomposition kinetics.

INTRODUCTION

Dilute solutions of alkyl hydroperoxides in inert solvents apparently undergo unimolecular homolytic cleavages.¹⁻⁴ In concentrated solutions, a second-order process has often been postulated.⁵⁻⁷

$$2\text{ROOH} \rightarrow \text{RO.} + \text{ROO} + \text{H}_2\text{O} \tag{1}$$

This reaction is particularly appealing on energetic grounds, as it is nearly isothermic. Benson,⁸ on the other hand, considers this reaction to be unimportant and has shown that available kinetic data may be accounted for by a unimolecular decomposition followed by radical-induced decompositions. However, a proof of Benson's thesis is difficult in simple hydroperoxides because conditions favorable for bimolecular decomposition also favor radical reactions.

Polypropylene hydroperoxide (PPH) has been shown⁹ to consist of sequences of neighboring hydroperoxides. A study of its decomposition could shed light on the importance of either the radical-induced mechanism or the bimolecular process.

A thermal decomposition study of PPH is needed for other reasons. Dulog et al.¹⁰ reasoned that formation and bifunctional decomposition of neighboring hydroperoxides is likely in isotactic polypropylene but not in atactic polymers. The structures of hydroperoxides of these polymers have been shown to be similar,⁹ and crystallographic configurational differences are unlikely to contribute toward dissimilarities in solution

Hydroperoxide
Polypropylene
Decomposition of
Thermal
TABLE I.

	and then		and a distance of the second s						PP9.011C
Run no.	Sample	Tacticity ^b	[ROOH] ₀ , mole/l.	Temp., °C.	Solvente	[IH] ₀ , ^d mole/l.	$k_d imes 10^4,$ sec. ⁻¹	70	$k_{d}' \times 1$ sec
1	35	C	0.0078	135	+-	0.001	19.8	94	5.0
2	32	Α	0.034	135	+	0.001	15.1	93	8.0
?	69	C	0.27	135	I	0.01	19.8	80	12.8
4	32	V	0.011	120	+	0.001	6.3	81	2.7
5 S	35	C	0.0078	120	+	0.001	6.41	78	1.6
9	32	A	0.034	120	+	0	5.01	78	$4_{+}3$
7	69	C	0.27	120	I	0,01	6.13	70	7.9
×	35	C	0.016	100	+	0	0.87	78	2
6	35	C	0.016	100	+ e	0	1.10	78	1
10	35	C	0.0031	100	+	0	0.69	83	
11	69	C	0.048	100	+	0.01	0.73	27	I
12	35	C	0.016	100	+	0.01	0.99	100	
13	69	C	0.27	100	I	0.01	0.73	06	1
14	32	A	0.034	100	+	0.05	0.99	20	1
15	35	C	0.0078	85	+	0	0.33	11	
16	32	Α	0.034	85	+-	0.01	0.25	68	Ι
17	72	Α	0.025	52	+ +	0	0.57	72	
18	35	C	0.27	85	I	0.01	0.12	67	1

^b C = crystalline, A = amorphous.
 ^c Chlorobenzene unless otherwise stated.
 ^d 2,6-Di-*tert*-butyl-*p*-cresol.

• Decalin. ^f tert-Butanol.

* Reaction was too slow to give accurate value of $k_{d'}$.

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kinetics. Therefore, comparison of the rates of decomposition of these hydroperoxides would shed light on the validity of their hypothesis.¹⁰

The thermal decomposition of PPH has not been reported. Brief descriptions^{11,12} of the photodecomposition of PPH have appeared recently.

EXPERIMENTAL

Procedures used for the preparation of PPH,⁹ the decomposition of PPH,¹³ and the determination of radical yields¹ have been already described.

RESULTS

The decomposition of PPH is very rapid. After most of the hydroperoxides have reacted, the rate of hydroperoxide decomposition slows to about 1 or 2% of its initial rate (Fig. 1). Occasionally, there is a short induction period. This induction period is usually observed in hightemperature experiments and can be reduced by increasing the speed of agitation.

It is apparent that the decomposition of PPH is not a simple first-order process. An analog computer was used to resolve the data into two consecutive or concurrent reactions of various orders. The best fit was



Fig. 1. Decomposition of polypropylene hydroperoxide at 135°C. (Table I, run 1): (B) original data; (A) slow reaction subtracted from original result.

obtained assuming two consecutive first-order reactions. Thus, all the results were analyzed in the manner shown in Figure 1. The filled circles represent the actual data; the open circles were obtained by subtracting the slow reaction from the filled circle curve. From the curves A and B, the rate constants k_d and k_d' , respectively, were calculated. The results of this calculation are summarized in Table I.

At temperatures of 120° C. and above, the fast reaction accounts for 80-94% of all the hydroperoxides decomposed; it is about 70% at 85°C. The rate constants of this reaction at all temperatures are unchanged by 20- to 60-fold variations in hydroperoxide concentrations. These values are about 60 times larger than that of squalane hydroperoxide (SH)¹ in the temperature range of $100-135^{\circ}$ C.



Fig. 2. Variation of $k_{d'}$ with concentration of polypropylene hydroperoxide.

The rate of the slow reaction increases with increasing concentration of PPH. This behavior is characteristic of radical-induced decomposition. It appears that intermolecular induced decomposition of PPH becomes important at concentrations at which the decompositions of alkyl hydroperoxides⁴ and of SH are not complicated by this reaction. When extrapolated to zero hydroperoxide concentration, as was done in Figure 2, the "limiting" rate constants are about twice those for the decomposition of SH.

Neither the rate constant nor the fraction of fast reaction is affected by small or moderate amounts of scavenger. When the latter is added in amounts exceeding that of the hydroperoxides, the fast reaction is greatly suppressed in favor of the slow reaction (Table II). The fast process is reduced to as little as 25% of the total reaction in some experiments (Table II, run nos. 20, 21, and 23). Under these conditions, most of the

	Polypropylene hydroperoxide				Fast reaction		Slow reaction
Run no.	Sample ^a	[ROOH], mole/l.	Temp., °C.	[IH], mole/l. ^b	$k_{d} \times 10^{4},$ sec. ⁻¹	%	$\overline{k_d}' \times 10^{3}$, sec. $^{-1}$
19	72	0.005	135	0.012	18.2	35	4.80
20	72	0.005	135	0.124	_	25	4.52
21	72	0.010	120	0.124		25	1.60
22	35	0.0016	100	0.005	1.0	50	0.245
23	72	0.005	100	0.124	0.70	29	0.242

TABLE II

Effect of Scavenger on the Decomposition of Polypropylene Hydroperoxide

^a Ref. 9.

^b 2,6-Di-tert-butyl-p-cresol.

hydroperoxides decompose at a rate equal to the "limiting" rate described in the previous paragraph.

Scavengers also have a pronounced effect on the slow process. The two pairs of experiments 19, 20 and 22, 23 in Table II show that the rates of the slow reaction become concentration independent when the amount of IH present exceeds that of the hydroperoxide. In general, this amount of scavenger reduced the values of $k_{a'}$ to those limiting values found in Figure 2.

Dulog and Sanner¹⁴ have shown that in the thermal decomposition of 2,4-dimethyl-2,4-dihydroperoxypentane, 3,3,5,5-tetramethyl-1,2-dioxacyclopentane, and hydrogen peroxide are formed. Since we have shown that PPH consists of such 1,3-dihydroperoxides, it is possible that this process might also occur in PPH decomposition. Aqueous extraction of aliquots taken from the thermal, inhibited decomposition of PPH at 130°C. in chlorobenzene, showed that no water soluble peroxidic products were formed. We conclude that hydrogen peroxide is not formed in this decomposition.

The yield of radicals upon thermal decomposition of PPH at 100°C. was determined by the method of inhibited cumene oxidation. It is assumed the 2,6-di-*tert*-butyl-*p*-cresol reacts with two oxygenated radicals under these conditions.¹⁵ The radical yield α is calculated from the observed induction periods and the rates of decomposition of PPH determined in separate experiments under similar conditions. The average value for α is 1.8.

The intrinsic viscosities of samples from several experiments were determined. All values of η from the beginning to the end of a given reaction remained within $\pm 5\%$ of the mean value.

DISCUSSION

The experiments in Table III were performed under conditions such that all the radicals formed upon the dissociation of PPH were scavenged.

Polypropylen	e hydroperoxide			
Sample ^b	Concn., mole/l.	$[\mathrm{IH}]_{0} imes10^{3},\ \mathrm{mole/l}.$	$t_{ m ind} \times 10^4$, sec.	α
35	0.0078	5.16	2.01	1.62
35	0.0078	1.0	0.22	1.54
35	0.0078	1.29	0.19	2.17
35	0.0078	1.6	0.32	1.96
69	0.034	9.6	0.48	1.7
69	0.034	9.5	0.47	1.7

TABLE III									
Radical	Yield	from	the	Decom	oosition	of	Polypropylene	Hydrop	peroxide*

^a At 100°C in cumene-chlorobenzene (1:2).

^b Ref. 9.

The radical yield was found to be about 1.8. It appears that the initial process is that of homolytic decomposition, and reaction (1) is probably only of minor consequence.

The slow process is similar to the corresponding reaction of polyethylene hydroperoxide (PEH). The rate constants for the slow decomposition of PPH are compared in Figure 3 with these of PEH and SH. This process for PEH was postulated¹³ to be the decomposition of a species such as a β -hydroxy hydroperoxide. The same postulate is proposed here as well. The fraction of PPH which decomposes by this route increases with the increase of PPH concentration and of scavenger concentration. These dependencies may be rationalized by eqs. (2)–(4).



Fig. 3. Arrhenius plots of k_d' for the slow decompositions of: (•) polypropylene hydroperoxide: (•) polyethylene hydroperoxide; (•) squalane hydroperoxide.

$$\begin{array}{ccccccccc} OOH & OOH & OOH & \dot{O} \\ -C - CH_{2} - C - & -C - CH_{2} - C - & + & OH \end{array}$$
(2)

$$\begin{array}{cccc} & \text{OOH} & \text{OI} \\ -\overset{[}{\text{C}} -\text{CH}_2 - \overset{]}{\text{C}} - & \text{H} & \text{H} \end{array} \rightarrow \begin{array}{c} & \text{OOH} & \text{OH} \\ \overset{[}{\text{I}} & \overset{]}{\text{C}} - & \text{CH}_2 - \overset{]}{\text{C}} - & \text{CH}_2 - \overset{]}{\text{C}} - & \text{H} \end{array}$$
(3)

$$\begin{array}{cccc} \text{OOH} & \text{O} & \text{OOH} & \text{OH} \\ \hline -\text{C} & -\text{CH}_2 - \text{C} & + & \text{ROOH} & \rightarrow & -\text{C} - \text{CH}_2 - \text{C} & + & \text{ROO} \end{array}$$
(4)

Where IH is the scavenger. In some experiments (Table I, runs nos. 1, 2, 12, 13), less than 10% of the total hydroperoxide decomposed by the slow process. It is concluded that the slowly decomposing species are not initially present in large amounts but rather are produced according to eqs. (2)-(4).

The fast reaction is assumed to be the neighboring group-assisted dissociation, followed by radical-induced decompositions. Because the rate of this reaction is not affected by changes in the hydroperoxide or the scavenger concentration, it is probably an intramolecular radical process. This postulate follows logically from the conclusion that PPH contains blocks of neighboring hydroperoxides.⁹ With this assumed mechanism, the rate of disappearance of PPH is given in the Appendix as

$$-d[\text{TOOH}]/dt \approx (3kk_i^2k_3^2/k_{14}^2)^1/_3(\text{TOOH})^{4/4}$$
(5)

where TOOH is the polypropylene hydroperoxide, and k_i , k_3 , k_{14} , and k are the rate constants for the initiation, propagation, oxygen elimination from peroxy radicals, and termination of two alkoxy radicals, respectively.

Let us assume that the experimentally found k_d is a measure of the quantity in the parentheses in eq. (5). Literature values for k and k_3 are 10 l./mole-sec.⁸ and 12 l./mole-sec.,¹⁶ respectively. The value for k_{14} can be assumed to be comparable to the termination rate constant in autoxiation of hydrocarbons which have secondary hydroperoxides as intermediates,¹⁷ i.e., cyclohexene, tetralin, etc., which is 10⁷ l./mole-sec. The value of k_i at 135°C. is thus calculated to be 6.7×10^{-4} sec.⁻¹. We note that the experimental value of k_d for the decomposition of PEH is 6.1×10^{-4} sec.⁻¹. Based on this analysis, it appears reasonable that the fast decomposition of PPH is primarily a neighboring group-assisted homolysis of a hydroperoxyl group followed by radical-induced reactions. The results of runs nos. 3, 7, 13, and 18 in Table I carried out in the solid state show that both the rate constants of and the fraction of hydroperoxide decomposed by this process are nearly the same as those in solution. It is probable that intramolecular reactions also prevail here.

The results for hydroperoxides derived from either crystalline or amorphous polypropylene are indistinguishable from one another. Furthermore, structural studies on these substances reveal no discernable differences.⁹ Therefore, the conclusion of Dulog et al.¹⁰ based on solution kinetic data is subjected to serious doubts. It is inconceivable that crystallographic configurations of polyolefins are retained in the oxidized polymers in solution. It is our belief that the formation and decomposition of neighboring hydroperoxides are equally probable in crystalline and amorphous polypropylene.

APPENDIX

In the reaction sequence of eqs. (6) for the decomposition of PPH, the tertiary species and the secondary (also primary) species are designated as T and R, respectively.

$$TOOH \xrightarrow{k_1} TO \cdot + OH \cdot$$

$$OH \cdot + TOOH \xrightarrow{k_1} H_2O + TO_2 \cdot$$

$$TO \cdot + TOOH \xrightarrow{k_2} TOH + TO_2 \cdot$$

$$RO \cdot + TOOH \xrightarrow{k_3} ROH + TO_2 \cdot$$

$$OH \cdot + TH \xrightarrow{k_4} H_2O + T \cdot$$

$$TO \cdot + TH \xrightarrow{k_5} TOH + T \cdot$$

$$RO \cdot + TH \xrightarrow{k_6} ROH + T \cdot$$

$$T \cdot + O_2 \xrightarrow{k_7} TO_2 \cdot$$

$$2TO_2 \cdot \xrightarrow{k_8} 2TO \cdot + O_2 \qquad (6)$$

$$TO_2 \cdot + RH \xrightarrow{k_3} RO_2 \cdot$$

$$RO_2 \cdot + TO_2 \cdot \xrightarrow{k_{10}} RO_2 \cdot$$

$$RO_2 \cdot + TO_2 \cdot \xrightarrow{k_{11}} RO \cdot + TO \cdot + O_2$$

$$2RO_2 \cdot \xrightarrow{k_{12}} 2RO \cdot + O_2$$

$$TO_2 \cdot + RO \cdot \xrightarrow{k_{13}} RO + TO + O_2$$

$$TO_2 \cdot + RO \cdot \xrightarrow{k_{14}} RO + TO + O_2$$

$$RO_2 \cdot + TO_2 \cdot \xrightarrow{k_{14}} RO + TO + O_2$$

$$TO_2 \cdot + RO \cdot \xrightarrow{k_{14}} RO + TO + O_2$$

$$TO_2 \cdot + RO \cdot \xrightarrow{k_{14}} TOOH + ketone$$

$$TO \cdot + RO \cdot \xrightarrow{k_{14}} TOH + ketone$$

$$RO \cdot + RO_2 \cdot \xrightarrow{k_{16}} ROOH + ketone$$

$$RO \cdot + RO_2 \cdot \xrightarrow{k_{16}} ROOH + ketone$$

$$ROOH \xrightarrow{k_{16}} RO \cdot + OH \cdot$$

TOOH is assumed⁹ to be always neighboring to another TOOH, whereas ROOH is assumed to be isolated hydroperoxides formed as a decomposition product of TOOH.

$$k_{\mathbf{8}}[\mathrm{TO}_{2}\cdot]^{2} = k_{12}(\mathrm{RO}_{2}\cdot)^{2} + k_{15}(\mathrm{RO}\cdot)(\mathrm{RO}_{2}\cdot)$$
(7)

POLYMER REACTIONS. IV

$$-d(\text{TOOH})/dt = k_1(\text{TOOH}) + k_{12}(\text{RO}_2 \cdot)^2 + k_8(\text{TO}_2 \cdot)^2 + k_{11}(\text{RO}_2 \cdot)(\text{TO}_2 \cdot) + k_{15}(\text{RO} \cdot)(\text{TO}_2 \cdot)$$
(8)

The recognized stability of tertiary oxygenated radicals implies $(RO \cdot) << (TO \cdot)$, and $(RO_2 \cdot) << (TO_2 \cdot)$. Thus, the reaction is likely to involve long chain lengths, and the initiation and termination rates may be assumed to be small in comparison with the propagation rates and $[T \cdot] >> [R \cdot]$. Therefore, eq. (9) becomes

$$k_8(\mathrm{TO}_2 \cdot)^2 = k_{12}(\mathrm{RO}_2 \cdot)^2$$
 (9)

Since alkoxy radicals probably abstract hydrogen much more readily than alkylperoxy radicals, that is $k_{14} >> k_{13}$, eq. (9) can be rewritten as

$$-\frac{d(\text{TOOH})}{dt} = \left[2k_{8} + k_{11}\frac{k_{8}}{\bar{k}_{12}}\right]^{1/2} \\ \times \left\{\frac{(k_{i}(\text{TOOH}) + k_{i}'(\text{ROOH}))(k_{3}(\text{TOOH}) + k_{6}(\text{TH}))}{2k_{13}k_{8} + 2k_{14}k_{12}\left(\frac{k_{8}}{\bar{k}_{12}}\right)^{1/2} + k_{11}k_{13}\left(\frac{k_{8}}{\bar{k}_{12}}\right)^{1/2} + \frac{k_{11}k_{14}k_{8}}{\bar{k}_{12}}\right\}$$
(10)

The rate of the oxygen elimination reaction from the interaction of peroxy radicals is probably independent of the nature of R and $k^8 \approx k_{11} \approx k_{12} = k$; thus eq. (10) becomes:

$$-d(\text{TOOH})/dt = (3k/k_{14})^{1/3} \{ (k_i(\text{TOOH}) + k_i'(\text{ROOH}))(k_3(\text{TOOH}) + k_6(\text{TH})) \}^{1/3}$$
(11)

At the beginning of an experiment (TOOH) >> (ROOH), and hydrogen abstraction from TOOH dominates,

$$-d(\text{TOOH}) = (3kk_1^2k_3^2/k_{14}^2)^{1/3}(\text{TOOH})^{4/3}$$
(12)

This equation has also been obtained by Benson.⁸

When most of the TOOH has decomposed, the isolated ROOH decomposes according to eq. (13):

$$-d(\text{ROOH})/dt = k_t'(\text{ROOH}) + k_{15}(\text{RO}\cdot)(\text{RO}_2\cdot) \approx k_t'(\text{ROOH}) \quad (13)$$

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Polymerization of Vinylcyclopropanes. II

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Synopsis

1,5-Type polymerization of vinylcyclopropane proceeding by the opening of both the double bond and the cyclopropane ring was found. Some other vinylcyclopropane derivatives, 1,1-dichloro-2-vinylcyclopropane, 1,1-dichloro-2-vinylcyclopropane, 1,1-dichloro-2-vinylcyclopropane, 1,1-dichloro-2-winylcyclopropane, 1,1-dichloro-2-winylcyclopropane, and *cis*- and *trans*-1-chloro-2-vinylcyclopropane, were investigated. The observation of infrared spectra, NMR spectra, and other data indicated that the radical polymerization of these compounds gave principally 1,5-type polymer, while in cationic polymerization 1,2-type was predominant. The behavior of the polymerization was discussed in terms of the stability of a cylopropylcarbinyl ion or radical which is formed in the initiation and propagation steps.

INTRODUCTION

The vinylcyclopropanes, such as vinylcyclopropane (I) and 1,1-dichloroand 1,1-dibromo-2-vinylcyclopropane (II and III) gave a ring-opened polymer by radical polymerization.¹⁻³

$$C = C - C - C$$

$$X X \qquad + C - C = C - C - C X_2 + a$$

$$I, X = H$$

$$II, X = CI$$

$$III, X = Br$$

$$(1)$$

This type of polymerization proceeding by the opening of both the double bond and the cyclopropane ring is a new type of polymerization, and we have called this 1,5-polymerization. Recently, Lishansky et al.⁴ also found 1,5-polymerization in 1-carboethoxy-2-vinylcyclopropane.

With cationic initiators, I gave a polymer with predominantly 1,2-structural units resulting from 1,2-polymerization (vinyl polymerization); II and III failed to polymerize. The 1,2-polymerization of I by Ziegler-Natta catalysts has already been reported.⁵⁻⁷

This paper describes the polymerizations of some other vinylcyclopropanes (IV-VII) and discusses structural aspects of the resulting polymers based on experimental results, including data reported previously.



EXPERIMENTAL

The method of purification of initiators and solvents, polymerization, polymer purification, and the spectrographic analysis of the polymers were as previously described.³ Molecular weights were measured by vapor pressure osmometry (Mechrolab Inc.).

Synthesis of Monomers

Isopropenylcyclopropane (IV). Dimethylcyclopropylcarbinol was prepared by Grignard reaction of methylmagnesium iodide with methylcyclopropylketone. Dehydration of this compound gave IV,⁸ b.p. 71° C./ 760 mm. Hg.

1-Methyl-1-vinylcyclopropane (V) and 1-Methyl-1-cyclopropylcyclopropane (VIII). The treatment of isoprene with methylene iodide in the presence of a Zn-Cu couple by the method of Simmons and Smith⁹ gave a mixture of IV, V, and VIII.¹⁰ The three components were separated by gas chromatography (tricresyl phosphate column); V: b.p. 58°C./760 mm. Hg; VIII: b.p. 89°C./760 mm. Hg.

1,1-Dichloro-2-methyl-2-vinylcyclopropane (VI). This was prepared by a method similar to that used by Shono et al.;¹¹ b.p. 62° C./69 mm. Hg.

cis- and trans-1-Chloro-2-vinylcyclopropane (VII). The treatment of butadiene with *n*-butyllithium and methylene chloride by the method of Closs et al.^{12,13} gave a product boiling in the range 100–126°C.¹⁴ This product was separated by gas chromatography (polyethylene glycol column) into four components, A, B, C, and D, in order of increasing retention time. Compounds A and D were found to be *n*-octane and *n*-butyl alcohol, respectively. Compounds B and C were found by infrared spectroscopy to be the expected isomers of VII. The absorption spectra of compounds B and C showed the presence of a carbon-carbon double bond (1645 cm.⁻¹), a vinyl group (910 and 990 cm.⁻¹), and a cyclopropyl skeleton (3080 and 1030 cm.⁻¹). The ratio of yield of compound B to C was 1:2. For compound B, b.p. 96.3°C./760 mm. Hg; n_D^{20} 1.4526. For compound C, b.p. 107.5°C./ 760 mm. Hg; n_D^{20} 1.4615.

ANAL. Calcd. for C_5H_7Cl : C, 58.55%; H, 6.88%. Found for compound B: C, 58.53%; H, 6.91%. Found for compound C: 59.00%; H, 7.17%.

Figure 1 shows the NMR spectra of the isomers. The signals of proton at carbon atom 1, which is less shielded by the chlorine atom bonded to the same carbon, appear at ca. 3 ppm in both isomers. However, the signals due to the proton at carbon atom 1 in the major product (compound C)



Fig. 1. NMR spectra of the isomers of 1-chloro-2-vinylcyclopropane; 100 Mc./sec., ppm downfield from TMS.

appear at a field lower by 0.3–0.4 ppm than those of the minor product (compound B), and coupling constants of the former are distinctly larger than those of the latter. On the basis of the synthesis of other various chlorocyclopropanes,^{12,13} the investigation for coupling constants in cyclopropane system,^{15–17} and assignment of isomers of 1-bromo-2-vinylcyclopropane by tri-*n*-butyltin hydride,¹⁸ the above NMR data strongly suggest that compound B has the *trans* orientation and compound C has the *cis* orientation.

Ultraviolet Spectra

Ultraviolet absorption spectra in *n*-hexane solvent showed for compound I: $\lambda_{\max} = 199 \text{ m}\mu$, $\epsilon_{\max} = 7300$; for compound II: $\lambda_{\max} = 203 \text{ m}\mu$, $\epsilon_{\max} = 4800$; for compound IV: $\lambda_{\max} = 201 \text{ m}\mu$; $\epsilon_{\max} = 9000$. This result shows that these compounds have almost the same degree of conjugation.

RESULTS

Polymerization of Isopropenylcyclopropane (IV)

Details of representative experiments are summarized in Table I. In addition to these, polymerizations with RhCl₃·3H₂O, RuCl₃·H₂O, and IrCl₃ by a method similar to that used for butadiene^{19,20} were unsuccessful. The infrared spectra of the monomer and the polymers obtained from α, α' azobisisobutyronitrile (AIBN) and SnCl₄ are shown in Figure 2. Although the absorption bands assigned to the cyclopropyl group (3080, 1045, and 1020 cm.⁻¹) are absent in the curve *B*, these are found in curve *C*. The existence of the cyclopropyl group was also confirmed by the near infrared spectra.²¹ These spectra indicate that the polymer obtained with AIBN has mainly 1,5-type structural units and the polymer from SnCl₄ has 1,2-
	Initiator		Polymeriza	ution		Polymer	
Initiator	conen., mole-%	Solvent	Temp., °C.	Time, days	Yield, $\%$	M.W.	Character
8P0	0.35	1	80	5	3		Viscous solid
(PO)	3.1	1	80	5	25	1800	**
IBN	0+6	I	80	6	œ		
-Radiation	106 r/hr.	1	Room temp.	7	33		**
nCl4	3.3	I	-50	ů	72	1600	White powder
nCl4	3.3	Toluene	-50	5	58	1700	**
haAl-TiOl4	6.0 - 1.5	n-Hexane	65	2	7		**

TABLE I tion of Isonronenvlevele

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Fig. 2. Infrared spectra of (A) isopropenylcyclopropane and its polymers obtained (B) with AIBN and (C) with SnCl₄.

type. The infrared spectra of other polymers prepared with radical initiators, benzoyl peroxide (BPO), and γ -radiation, showed that the polymers also have 1,5-type structural units, and these spectra are similar to those of 1,4-polyisoprene. The infrared spectra of the polymer from Et₃Al-TiCl₄ showed absorption bands characteristic of the cyclopropyl group. All product polymers were soluble in ordinary solvents such as carbon tetra-chloride, benzene, and ethyl ether.

Polymerization of 1-Methyl-1-vinylcyclopropane (V)

Experimental results are shown in Table II. The infrared spectrum of the polymer obtained with $SnCl_4$ indicates that cationic polymerization gave 1,2-type polymer (Fig. 3).

	Polym	erization	TABLE of 1-Methy) II yl-1-Vinyl	cyclopropan	ie
	Initiator		Polymer	ization		Polymer
Initiator	concn., mole-%	Solvent	Temp., °C.	Time, days	Yield,	Character
AIBN	0.5		80 50	2	Trace	White powder

		Polymerizat	ion of 1,1-Di	TABLE III chloro-2-methy	l-2-vinylcyc	lopropane			
	Tnitistor			Polymerizat	tion			Polymer	
Initiator	concn., mole-%	Solv	ent	Temp., °C.	Time, days	Yield, %	M	.W.	Character
BPO	0.5			80	1	17	10	00(White powder
AIBN	0.5	Ι	I	80	1	9			
γ -Radiation	10 ⁶ r/hr.		j j j	Soom temp.	õ	20	1(000	11
SnCl ₄	3.0	-		-20	2	l			
		Tuitiatan		Polyr	nerization			Polymer	
		TOURDIT		Tamp	Tin	A	hlaid		
	Initiator	mole-%	Solvent	°C.	day	i's c	70	M.W.	Oharacter
cis Isomer	BPO	0.5	I	80	3		9		Viscous solid
	AIBN	0.5	I	80	3		9		11
	γ -Radiation	10 ⁵ r/hr.	1	Room temp	. 4		4	1000	11
	(BPO	0.5							
	γ -Radiation	1.0 ⁵ r/hr.	l	Room tem	o. 2		9	1000	•
trans Isomer	BPO	0.5	I	80	61		5		**
	γ -Radiation	10 ⁵ r/hr.	I	Room temp	2	F	race		11

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Fig. 3. Infrared spectra of (A) 1-methyl-1-vinylcyclopropane and (B) the polymer obtained with SnCl₄.

Polymerization of 1,1-Dichloro-2-methyl-2-vinylcyclopropane (VI)

Experimental results are shown in Table III. Polymerization with $SnCl_4$ gave no polymer, and the polymerization of II and III, which are 1,1dihalo derivatives, was also unsuccessful with $SnCl_4$ and other ionic initiators.³ The chlorine content (39.65%) of the polymer initiated by BPO was found to be comparable with that of the monomer (calculated, 40.46%). Therefore, almost no dehydrochlorination or dechlorination took place during the polymerization process. The infrared spectra showed the structure of all of the polymers to be 1,5-type. All obtained polymers were soluble in ordinary solvents.

Polymerization of *cis*- and *trans*-1-Chloro-2-vinylcyclopropane (VII)

Details of experiments are summarized in Table IV. All polymers have structural units resulting from 1,5-type polymerization on the basis of infrared spectra. Thus a representative spectrum of *cis*-VII and of its polymer prepared from γ -ray-induced polymerization is shown in Figure 4. All product polymers were soluble in ordinary solvents.

Polymerization of 1-Methyl-1-cyclopropylcyclopropane (VIII)

The usual conditions (1.0 mole/% SnCl₄ as catalyst, -50° C., 5 days) gave no polymer of VIII.



Fig. 4. Infrared spectra of cis-1-chloro-2-vinylcyclopropane and (B) the polymer obtained with γ -radiation.

Analysis of NMR Spectra

Infrared spectra were used in the determination of the structures of the polymers. However, as suggested in the previous report,³ some polymers are a mixture of 1,2-type, 1,5-type, and some other saturated types of addition products. The proportions of 1,2- and 1,5-structural units in the polymers were estimated by means of NMR spectroscopy. Figure 5 shows, for



Fig. 5. NMR spectra of (A) vinylcyclopropane and its polymers obtained (B) with AIBN and (C) with SnCl₄; 100 Mc./sec., ppm downfield from TMS.

example, the NMR spectra of I and its polymers obtained with AIBN (curve B) and $SnCl_4$ (curve C). In Figure 5B the ratio to the total area of the area of the signal a appearing at 5.3 ppm is only 0.2, though the area ratio of signal *a* to *b* is 1:2. This result shows that 1,5-structural units are involved to the extent of 80%, and the other is an unidentified structure. In Figure 5C, the area ratio of the signal a (5.4 ppm) assigned to the protons at the double bond and the signal b (0.4 ppm) of the cyclopropyl protons indicates that 1,5- and 1,2-structural units are 9% and 71%, respectively. The amount of unidentified structure is 20%. Table V shows the percentage composition found in each polymer by NMR spectroscopy.

C	omposition of Poly	mers		
		Stru	ctural units	, %
Monomer	Initiator	1,5 - Type	1,2-Type	Unknown
Vinylcyclopropane (I)	BPO	70	_	30
	AIBN	80	_	20
	${ m SnCl}_4$	9	71	20
1,1-Dichloro-2-vinylcyclo-				
propane (II)	BPO	~ 100		_
Isopropenylcyclopropane (IV)	BPO	91		9
	${ m SnCl}_4$		~ 100	
	$Et_3Al-TiCl_4$		~ 100	
1,1-Dichloro-2-methyl- vinylcyclopropane (VI)	BPO	~100		_

TABLE V

DISCUSSION

1,1-Dichloro-2-ethylcyclopropane³ and VIII, which have no double bonds, gave no polymer under the same conditions as those used with monomers II, IV, or V. These results indicate that the cyclopropane skelton can not be opened by direct addition of radical or cation. Therefore, in the process of polymerization of vinylcyclopropanes, one might postulate that a substituted cyclopropylcarbinyl radical or ion may be formed during the initiation and propagation steps. All experimental results are summarized in Table VI. These results clearly show that vinylcyclopropanes are polymerized predominantly through 1,5-type by radical initiators and through 1,2-type by cationic initiators.

Cyclopropylcarbinyl radicals formed by radical-producing initiators might be rapidly opened to give the 1,5-type polymers as shown in eq. (2).



1, 5-type polymer

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		Main Suuccure	e of i orymer	
		Туре	of polymerization	
Monomer	Radical	Cationic	Anionic	Ziegler-Natta
<u>C=C</u>	1,5	1,2	No polymerization	1,2
$C = C \xrightarrow{Cl} Cl$	1,5	No polymerization	No polymerization	No polymerization
$C = C \xrightarrow{Br} Br$	1,5			
C=C-C	1,5	1,2		1,2
$C = C \xrightarrow{C} C$		1,2		
	1,5	No polymerization		
C=C-Y	1,5			

	TABLE V	Ί
Main	Structure of	Polymer

Facile ring opening of cyclopropylcarbinyl radical has been shown in the photochemical chlorination of methylcyclopropane^{22,23} or dicyclopropylmethane.²⁴ 1,1-Dichloro derivatives (II and VI) gave selectively 1,5-type polymer (Table V). This could be interpreted in terms of the resonance stability of chlorine atoms as shown in eq. (3).



Therefore, it seems that the unknown saturated structural unit which is present in the radical-polymerized polymers of I and IV, may be cyclobutane structures rather than branched or cyclized structures, as observed frequently in the polymerization of dienes. Moreover, it seemed that ring cleavage takes place between C_1 and C_2 rather than between C_2 and C_3 .

On the other hand, cationic polymerization through cyclopropylcarbinyl cation gave predominantly 1,2-structural units. This cationic intermediate has received a considerable amount of attention in its apparent easy forma-

tion and its ability to undergo rearrangements.²⁵ As shown in Table V, polymerization of I by SnCl₄ initiator gave a polymer containing 1,2-type (71%), 1,5-type (9%), and unidentified structural units (20%). This result might involve the equilibrium shown in eq. (4).



Cation IX could rearrange to cation X. It is reported²² that the order of stability of the carbonium ions is as follows:



Therefore, the unknown structure may be cyclobutane. However, the proportion of structural units in the polymer argues against the intervention of nonclassical ions such as bicyclobutonium (XI) or homoallyl cation (XII).



Results showing that the cationic polymerization of IV proceeded exclusively through 1,2-addition indicate that the tertiary carbonium ion (X1II) is further stabilized by the methyl group.

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Thermal Decomposition Products of Polyethylene*

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Synopsis

Decomposition products of polymers have been determined by many investigators, but the results are often conflicting because of difficulties in analyzing a large number of products. A comprehensive analysis of the volatile thermal decomposition products of high-density polyethylene has been made with the latest techniques in gas chromatography. The formation of products is explained on the basis of free-radical mechanism. The predominant process in the formation of volatiles appears to be intramolecular transfer of radicals, in which isomerization by a coiling mechanism plays an important role in determining the relative quantities of each product.

Knowledge of decomposition products could be used for elucidating the mechanism of thermal decomposition of polymers. Decomposition products of polymers have been determined by many investigators, but their experimental results often conflict concerning the nature and quantities of different components produced. This discrepancy is due mainly to difficulties in analyzing the products. Other reasons are differences in polymer samples and in experimental methods of decomposition.

Madorsky¹ determined thermal decomposition products of polyethylene by mass spectrometry. Owing to difficulties in the analysis of a large number of components present in small quantities, isomers of olefins were not separated. These data, therefore, are not very satisfactory as a basis for proposing a mechanism. Moiseev et al.^{2,3} used gas chromatography for the separation of decomposition products; the chromatograms presented indicate that the separation of components was not as good as one could obtain with the newest techniques in gas chromatography. Rapid progress has been made in the field of gas chromatography in the past decade, with vast improvements in techniques both of separating and of identifying the components of a mixture. Moiseev² explained the formation of volatile thermal decomposition products of almost linear polymers by assuming intramolecular transfer of radicals or isomerization. He predicted the quantities of different volatile products that should be formed and com-

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pared them with experimental data. The influence of isomerization by a coiling mechanism on the formation of different amounts of various products was not considered.

The purpose of this investigation was to obtain more complete and reliable information on the volatile thermal decomposition products of polyethylene than have been obtained in the past. Gas chromatography was used for determining decomposition products with hydrocarbons of up to C_9 .

EXPERIMENTAL

Material

A commercially available sample of high-density polyethylene was used in this study; its properties are given in Table I.

TABLE I	
Properties of High-Density Polyethylene	Sample
Appearance: white, translucent, solid	
Density: 0.962 g./cm. ³ .	
Softening point: 127°C.	
Crystalline melting point: 135°C.	
Heat-distortion temperature at 66 psi:	88°C.

In preliminary experiments a ceramic boat was used. Because of its high heat capacity there was appreciable delay in elevating the sample and boat to a desired temperature. An aluminum foil boat was therefore used in place of a ceramic boat. The similarity in the experimental results and residue after pyrolysis suggested that aluminum has no catalytic influence on this decomposition reaction.

Thermal Decomposition

The apparatus used for the thermal decomposition of polyethylene is illustrated in Figure 1. An aluminum foil boat containing 1 g. of sample was placed in a quartz tube, which was connected to a vacuum pump by a ground-glass joint. After the quartz tube was evacuated to 1×10^{-4} mm. Hg, the vacuum line to the pump was closed, and the boat was pushed into the hot zone by means of an external magnet. The furnace was set at one of the following selected temperatures: 375, 385, 395, 405, 415, and 425°C. The sample was decomposed for 20 min.

Most of the volatile decomposition products were collected in a liquidnitrogen trap; some condensed on the cooler parts of the quartz tube and on the tube leading to the trap. The fraction volatile at room temperature was transferred from the trap into a flask of known volume by removing liquid nitrogen. The condensates in the tubes and the trap were washed with a predetermined amount of benzene, which was known from preliminary experiments to be a minor component of the decomposition products. The benzene extract and the fraction volatile at room temperature were



Fig. 1. Apparatus for the thermal decomposition of polyethylene.

analyzed separately, and the combined amounts of the various products were recorded.

Analysis

Four different chromatographic conditions were used for the determination of decomposition products. An open tubular column coated with squalane was used at 0°C. for the analysis of gases from methane to hexane (condition 1). The same column was used at 40°C. followed by a nonlinear temperature rise to 140°C. for the analysis of the benzene extract (condition 2). A packed column of deactivated silica gel was used at a temperature rise of 10 for the analysis of both gases and benzene extract (condition 3). A packed column having silver nitrate-diethylene glycol as liquid phase was used for the determination of *n*-butane and isobutylene (2-methyl propene) (condition 4). Further details of the chromatographic conditions are presented in Table II.

Many of the peaks were identified by comparing retention indices with those of pure materials, *n*-alkanes being used as internal standards. A subtraction technique was used for separating unsaturated from saturated hydrocarbons; this facilitated identification of some of the peaks. A tube 4 in. (10.2 cm.) long and 1/4 in. (0.6 cm.) o.d., packed with equal weights of concentrated sulfuric acid and silica gel of 60 to 80 mesh, was used for this purpose. When the squalane column was used (conditions 1 and 2), another method available for the identification of products was the linear relation between boiling point and retention index. For quantitative analysis areas under each peak were measured, and approximate substance correction factors⁴ were used.

Results

The thermal decomposition products of polyethylene found in the fraction volatile at room temperature were as presented in Figure 2. They were calculated in "mole per cent of the original polymer" by considering it to be the monomer, ethylene.

			Column		Pressure.	
Condition	Type	Length	Diameter	Stationary phase	psi	°C.
1	open	150 ft.	0.01 in.	Squalane	20	0
5	tubular open	(45.7 m.) 150 ft.	(0.03 cm. i.d.) 0.01 in.	Squalene	20	(a) 40°C.
	tubular	(47.5 m.)	(0.03 cm. i.d.)			(b) nonlinear rise from 40 to
~	nacked	6 ft.	1/° in.	60-80 mesh silica red	20	140 Linear rise of 10
ſ		(1.8 m.)	(0.3 cm. o.d.)	deactivated with 4%		from 60 to 200
4	packed	2 m.	1/4 in.	30% silver nitrate-	11	25
			(0.6 cm. o.d.)	diethylene glycol on 60-80 mesh diatoma- ceous earth (Perkin		
				-Elmer Column H)		

TABLE II

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Thirty peaks were found for hydrocarbons of C_1 to C_6 when the gaseous components were analyzed with a squalane column (condition 1); these data are presented in Table III. The lower molecular weight hydrocarbons that were not separated into individual components by condition 1 were analyzed by condition 3 with deactivated silica gel. The separation of components from methane to *n*-butane was very good, except for propane and acetylene, which had approximately the same retentions. Results with

	Retent.	Satd. or	Decomposition		Intensity
Peak	index∗	unsatd.	products	b.p., °C.	of peak ^b
I		S + U	methane, ethane,	-161, -89,	S
2		S + U	ethene	-103	
			Propane, propene	-42.2, -47.7	s
3		\mathbf{S}	2-Methylpropane	-11.7	W
4		U	1-butene, 2-methyl- propene	-6.5, -6.6	s
5	400	8	butane	-0.5	s
6	406	U	2-butene, trans	1.0	M, should.
7	415	U	2-butene, cis	3.7	М
8	449	U	3-methyl-1-butene	20.1	W
9	463	U	1,4-pentadiene	26.0	W
10	474	s	2-methylbutane	28.0	W
11	481	U	1-pentene	30.1	S
12	488	U	2-methyl-1-butene	31.0	М
13	496	\mathbf{U}			W
14	500	8	pentane	36.1	\mathbf{s}
15	502	U	2-pentene, trans	35.8	W, should.
16	505	U	2-pentene, cis	37.0	М
17	514	\mathbf{U}	1,3-pentadiene, trans	42.0	М
			(2-methyl-2- butene)°	(38.6)°	
18	523	U	1,3-pentadiene, cis	44.1	W
19	543	U			W
20	547	U	4-methyl-1-pentene	53.9	W
21	558	S			W
22	562	U	(4-methyl-2-pen- tene, cis) ^c	(56.3)°	W
23	569	S	2-methylpentane	60.3	М
24	579	U	2-methyl-1-pentene		Μ
25	581	\mathbf{U}	1-hexene	63.5	\mathbf{S}
26	592				W
27					W
28	597				W, should
29					М
30	600	s	hexane	68.8	\mathbf{S}

TABLE III Analysis of Decomposition Products of Polyethylene by an Open Tubular Column Coated with Squalane

^a Here b = 0.580.

^b S, strong; M, medium; W, weak.

^o Not positively identified.



Fig. 2. Decomposition products of polyethylene.

a subtraction technique indicated that the amount of acetylene produced was negligible.

The hydrocarbons found in the benzene extract were mainly normal alkanes and normal 1-alkenes.

DISCUSSION

The present experimental results on the thermal decomposition products of polyethylene were examined on the basis of a free-radical mechanism. A possible reaction scheme, in which R is a macromolecule and R' is a small n-alkane group, is shown below.

Initiation:

$$R \longrightarrow 2R \cdot$$
 (1)

Propagation:

$$\mathbf{R} \cdot \rightarrow \mathbf{R} \cdot + \mathbf{C} \mathbf{H}_2 = \mathbf{C} \mathbf{H}_2 \tag{2}$$

Intramolecular transfer followed by a decomposition reaction:

$$\mathbf{R} \cdot \rightarrow \mathbf{R} - \mathbf{C}\mathbf{H} - \mathbf{C}\mathbf{H}_2 - \mathbf{R'} \xrightarrow{} \mathbf{R} \cdot + \mathbf{C}\mathbf{H}_2 = \mathbf{C}\mathbf{H} - \mathbf{C}\mathbf{H}_2 - \mathbf{R'}$$
(3)

$$R-CH_2-R + R \rightarrow R-CH-R + RH$$
(5)

$$R - \dot{C}H - R \rightarrow R - CH = CH_2 + R.$$
(6)

Termination:

$$R' \cdot + R' \cdot \rightarrow R' - CH = CH_2 + R'H \tag{7}$$

$$\mathbf{R'} + \mathbf{R'} \to \mathbf{R'} - \mathbf{R'} \tag{8}$$

Initiation consists of preferential scission of weak bonds caused by irregularities in the polymer chain and of random scission of ordinary C-C bonds, resulting in the production of free radicals; see reaction (1). The weak bonds may be due to the presence of oxygen, which forms links that are weaker than C-C bonds, or to the presence of double bonds in the chain, which results in weaker bonds in the β position to the double bonds, or to branching, which results in weaker C--C bonds adjacent to tertiary The propagation reaction, the reverse process of polymerization, carbons. produces the monomer ethylene; see reaction (2). This reaction must compete with intra- and intermolecular radical-transfer reactions. Because of intramolecular radical transfer some of the primary radicals are expected to isomerize and form secondary radicals, which are more stable. The secondary radicals should decompose to form *n*-alkenes and *n*-alkane radicals; see reactions (3) and (4). The latter should either extract hydrogen from the polymer chain, as by intermolecular transfer in reaction (5), or decompose further. The formation of short-chain n-alkenes in reaction (3) is expected to compete with the formation of short-chain n-alkane radicals in reaction (4). Some of the short-chain alkane radicals may be consumed by disproportionation, in reaction (7), or by combination, in reaction (8). Since these involve two radicals, the quantity of volatiles produced by the reactions is expected to be small.

Ethylene, which is expected from reaction (2), was one of the major decomposition products. The quantity of ethylene found in the products increased slightly with increase in pyrolysis temperature: 10 mole-% of volatiles at 395°C. and 11 mole-% at 425°C. These results were in good agreement with the 9.1 mole-% obtained by Moiseev² and the 9.6 mole-% obtained by Bailey and Liotta⁵ at 415°C. but were different from the <1 mole-% reported by Grassie⁶ and the 4.3 mole-% obtained by Madorsky and his co-workers.⁷

The discrepancies in experimental results are probably due to differences in apparatus, experimental procedure, and methods of analysis of the decomposition products. In the present investigation a relatively large amount of polymer (1 g.) was decomposed at a vacuum of 10^{-4} mm. Hg; Madorsky et al.⁷ decomposed smaller amounts (25 to 50 mg.) of polyethylene at a vacuum of 10^{-6} mm. In this study the diffusion of decomposition products from inside a large sample is retarded, and the products are subject to more secondary reactions. Decomposition at 10^{-4} mm. will also tend to increase secondary reactions, resulting in greater fragmentation.



Fig. 3. Alkanes and alkenes produced at 425°C.

These differences may be responsible for the greater yield of monomer in the present study.

According to reactions (3) and (4), normal paraffin radicals having n carbon atoms and normal 1-olefins having n + 3 carbon atoms should be produced from the same radical. The experimental results of the present investigation were in good agreement with products expected from these reactions. The relation between the formation of normal alkane having n carbons and that of normal 1-alkene having n + 3 carbons may be seen in Figure 3.

The relative amounts of different hydrocarbons produced might be discussed further on the basis of the comparative case with which transfer of radicals to the different carbon atoms takes place. Consideration of local coiling indicates that isomerization of a primary carbon radical to the fifth carbon radical should be very favorable for geometrical reasons. This explanation is in agreement with the experimental results. The amount of propane was the largest among alkanes, and that of 1-hexene was the second largest among alkenes. These two products should be formed after radical transfer to the fifth carbon.

Propylene was the most abundant volatile decomposition product. It can be produced by two different routes. One is intramolecular radical transfer to the second carbon and subsequent decomposition reaction; the amount of propylene formed by radical transfer to the second carbon, however, is expected to be small for geometrical reasons. The other route involves scission of the C—C bond in the β position to a terminal double bond, which is formed in large amounts during decomposition. The C—C bond in this position is known to be a weak link of a linear hydrocarbon chain.^{8,9} The large amount of propylene is therefore from the terminal double bonds.

The formation of two other products, isobutylene and 2-butene, may be explained in similar ways. Isobutylene can be produced from an unsaturated group of the type

which is known to be present in polyethylene.¹⁰ Scission of C—C bonds in the position β to a double bond should result in the formation of this hydrocarbon. Isobutylene can also be produced at branches of polyethylene chain as a result of preferential abstraction of a hydrogen atom attached to a tertiary carbon:

$$\begin{array}{c} R & R \\ CH_2 & CH_2 \\ R-CH_2 - C-CH_2 - R \rightarrow CH_2 = C-CH_2 - R \end{array}$$

Scission of C—C bonds in the position β to a double bond should again result in the formation of isobutylene.

2-Butene can be produced from an unsaturated group of the type R-CH=CH-R, present in the original polymer.¹⁰ Scission of C-C bonds in the position β to a double bond should result in the formation of 2-butene.

The logarithm of the mole percent of product increased with temperature for most of the products, and the slopes of the lines were approximately equal (Fig. 2). The sole exception was isobutylene, which was produced in a comparatively larger amount at the lowest decomposition temperature of 375° C. The unsaturated group and branching, which were responsible for the formation of isobutylene, should decrease in the course of thermal decomposition, resulting in proportional decrease of this hydrocarbon in the products. The unsaturated group originally present in the polymer and responsible for the formation of 2-butene should also decrease as decomposition proceeds. To explain the increase of 2-butene with increase in temperature, the possible formation of the unsaturated group R-CH= CH-R during decomposition was considered. One plausible route involves a bimolecular reaction of the type suggested by Slovoklotova et al.,¹¹ shown below:

 $R-CH-CH_2-R + R \rightarrow R-CH=CH-R + RH$

CONCLUSIONS

The volatile thermal decomposition products of high-density polyethylene have been determined with the use of gas chromatography, and the presence of the main products was explained by a free-radical mechanism. The predominant process for the formation of volatiles appears to be intramolecular transfer of radicals, in which local coiling plays an important role in determining the relative quantities of each product.

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Cationic Polymerization of Formaldehyde in Liquid Carbon Dioxide. Part I*

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Synopsis

A cationic polymerization of formaldehyde which gave a high molecular weight polymer was studied in liquid carbon dioxide at 20-50 °C. In the polymerization without any catalyst both the rate of polymerization and the molecular weight of the resulting polymer increased rapidly with a decrease in the loading density of the monomer solution to the reaction vessel, and also increased with an increase in the initial monomer concentration. From these results it was concluded that the initiating species could be ascribed to an impurity contained in the monomer solution. Both the rate of polymerization and the degree of polymerization of the polymer also increased with rising temperature. The carboxylic acid added acted as a catalyst in the polymerization because of increase in the polymer yield, the molecular weight of polymer formed, and the number of moles of polymer chain with increasing dissociation constant of acid used. It was concluded that the polymerization in liquid carbon dioxide proceeded by a cationic mechanism. Methyl formate had no influence on the polymerization, but methanol and water acted as a chain-transfer agent.

INTRODUCTION

It has been well known that monomeric formaldehyde easily forms polymer with a cationic¹⁻² or anionic³⁻⁶ catalyst. Formaldehyde monomer suitable for the polymerization must, in general, be drastically purified, because some impurities, such as water, methanol, and others contained in the monomer act as chain-transfer agents with the consequence that the molecular weight of the resulting polymer is reduced.

As described in the previous paper,⁷ carbon dioxide considerably depresses the spontaneous polymerization of liquid formaldehyde. As an extension of this research, a new polymerization process in liquid carbon dioxide was developed, and it was found that the polymerization proceeded without any catalyst at room temperature and gave a high molecular weight polyformaldehyde, though insufficiently purified formaldehyde was used as a starting monomer. The polymerization process of polymeric monomer in liquid carbon dioxide has never published, except that Biddulph et al.⁸ briefly reported the cationic polymerization of isobutene at -50° C.

*This paper was first presented at the 15th Annual Meeting of the Society of Polymer Science, Japan, held in Nagoya in May, 1966.

The present paper is concerned with detailed research on the polymerization process of formaldehyde in liquid carbon dioxide. An effect of reaction conditions and an influence of various additives on the polymerization were studied.

EXPERIMENTAL

The α -polyoxymethylene and carbon dioxide used were the same as described in the previous paper.⁷ Formaldehyde monomer was prepared by using the apparatus shown in Figure. 1. The dried α -polyoxymethylene (100 g.) was decomposed by being heated at 150–180°C. under a stream of carbon dioxide. Without any purification the gaseous product condensed in a reservoir at -78°C. The condensed formaldehyde was observed to be a transparent and homogeneous liquid. The concentration of formaldehyde in liquid carbon dioxide was found to be in the range of 59–61 wt.-%. The monomer solution contained the following impurities, which were determined by means of a gas chromatograph (Yanagimoto, Type GCG-3D): methanol, 0.79–0.75 wt.-%; water, 1.20–1.18 wt.-%; methyl formate 0.021–0.027 wt.-%.

Commercially obtained additives, such as acetic acid, formic acid, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, trifluoroacetic acid, methanol, and methyl formate, were purified by distillation before use.

As shown in Figure 2, a stainless-steel autoclave having a capacity of 30 ml. was used as a reaction vessel. A chromel-alumel thermocouple with a millivoltmeter was used for the continuous-temperature measurements. The vessel was, in advance, evacuated at room temperature and cooled by liquid nitrogen. Before feeding of the monomer these additives were supplied by syringe into the reaction vessel through a rubber stopper, which



Fig. 1. Apparatus for preparation of formaldehyde monomer.

was fitted on the needle valve (B) of the vessel. Then a measured amount of the monomer solution was fed into the reaction vessel from the monomer reservoir through a tube connected to the side tube (A).

During the polymerization, the reaction vessel was shaken and the reaction temperature was controlled within $\pm 2^{\circ}$ C. Vapor pressure of the solution was measured over a range from 0-35°C. by a Burdon-type gage. In the experiment on the polymerization the pressure gage was demounted together with a tee piece from the reaction vessel; see Figure 2. After the polymerization a white, powdery polymer was obtained only by



Fig. 2. Pressure vessel (capacity, 30 ml.).

purging out the carbon dioxide and the unreacted monomer. The polymer was washed with ethyl ether cooled at -78° C, and was dried *in vacuo* at room temperature and weighed.

The inherent viscosity η_{inh} was determined by an Ostwald viscometer, starting with a solution containing 0.5 g. of the polymer in 100 ml. of *p*-chlorophenol dissolving 2% α -pinene at 60°C. The number-average degree of polymerization of the polymer obtained was estimated by the following equation, which was experimentally determined by the authors:

$$\eta_{\rm inh} {\rm PP} = 2.14 \times 10^{-2} P_n^{0.61}$$

The infrared spectrum of the polymer produced was measured with an infrared spectrometer (Hitachi, EPI-2).

RESULTS AND DISCUSSION

Effects of Reaction Conditions on Polymerization

The vapor pressure of the solution prepared was plotted against the temperature; see Figure 3. The total vapor pressure at 35°C. was 33.7 kg./cm.² and was considerably lower than the critical pressure of carbon dioxide, 75.4 kg./cm.². This fact indicates that carbon dioxide and formaldehyde make a solution even at a temperature above 31°C.

Loading Density of Monomer Solution. Figure 4 shows the effect of the loading density of the monomer solution on the polymerization. Here the loading density was represented as a ratio of the amount of solution fed to the volume of the reaction vessel used. Both the conversion and the degree of polymerization of the polymer increased rapidly with decreasing loading density.

The conversions were plotted against the degree of polymerization, as shown in Figure 5. A linear relation was found to exist between them. On an assumption that the initiation is considerably rapid and that the rates of chain transfer and termination are negligible in the polymerization, the degree of polymerization is represented by the following relation;

$$\bar{P}_n = \frac{\text{moles of monomer polymerized}}{\text{moles of initiating species}}$$
$$= \frac{\text{moles of monomer fed}}{\text{moles of initiating species}} \times \frac{\text{moles of monomer polymerized}}{\text{moles of monomer fed}}$$
$$= \frac{\text{conversion } (\%)}{\text{content of initiating species}}$$

Therefore, the linear relation in Figure 5 means that the content of initiating species is almost constant and that the initiating species is an impurity contained in the monomer solution.

It is also noticeable that polyoxymethylene, having a high degree of polymerization, was easily produced even at a higher temperature, such as 40°C, without any catalyst in the polymerization, which was carried out in liquid carbon dioxide. The infrared spectrum of the resulting polymer was similar to that of the usual polyoxymethylene.³ This result indicates that carbon dioxide does act, not as a comonomer, but as a solvent, because of no absorption band of the carbonyl group from 1550 to 1780 cm.⁻¹ in the infrared spectrum.

Monomer Concentration. For some information on the initiating species in the polymerization the effect of the monomer concentration on the polymerization was examined at 40° C. The study was carried out in experiments in which a constant amount of monomer was fed and the charged amount of carbon dioxide was varied.

As shown in Figure 6, both the polymer yield and the degree of polymerization of the resulting polymer increased rapidly with monomer concentration.



Fig. 3. Vapor pressure of the solution of formaldehyde in carbon dioxide vs. temperature. Volume of reaction vessel, 30 ml.; concentration of monomer, 60 wt.-%; loading density of solution, 10 g. per 30 ml.



Fig. 4. Influence of loading density of monomer solution on polymer yield and degree of polymerization. Monomer concentration, 60 wt.-%; temperature, 40°C. ; time, 10 min.; reaction vessel, 30 ml.



Fig. 5. Degree of polymerization of polymer vs. conversion (plotted from data described in Fig. 4).

Figure 7 shows that the degree of polymerization increased proportionately with the polymer yield. This result indicates that the number of moles of polymer chain is almost independent of the monomer concentration. It is, therefore, supposed that the initiating species originates from an impurity contained in the monomer, and the increase in polymer yield with increasing monomer concentration is caused by an increase in the rate of propagation with the monomer concentration.

On the other hand, rapid decreases of the polymer yield and the degree of polymerization with increasing loading density, as shown in Figure 4, is ascribable to the decrease of monomer concentration in the liquid phase, which is caused by a change in the vapor-liquid distribution of carbon dioxide with loading density.

Temu	Polyme	er yield		N_ b
°C.	g.	wt%	${ar P}_n$	mole $(X10^5)$
20	0.186	3.1	300	2.1
30	0.348	5.8	380	3.1
40	0.901	15.0	440	6.8
50	1.524	25.4	720	7.1

 TABLE I

 Effect of Reaction Temperature on Polymerization*

• Monomer solution, 10 g.; monomer concentration, 60 wt.-%; reaction time, 10 min. reaction vessel, 30 ml.

^b N_p , number of moles of polymer chain of the resulting polymer.



Fig. 6. Effect of monomer concentration on polymerization. Monomer, 3.5 g.; temperature, 40°C.; time, 10 min.; reaction vessel, 30 ml.



Fig. 7. Degree of polymerization of polymer vs. monomer polymerized (plotted from data described in Fig. 6).

Reaction Temperature. The effect of the reaction temperature was examined in the temperature range of $20-50^{\circ}$ C.

As shown in Table I, both the polymer yield and the degree of polymerization of the resulting polymer increased with rising temperature. A slight increase in the number of moles of polymer chain with rising temperature was also observed. Therefore, it seems that the increase of polymer yield with rising temperature was caused by the increase in the initiating species and the promotion of the rate of propagation.

Influence of Addition of Various Additives on Polymerization

Acids. As described above, it is considered that the polymerization of formaldehyde in liquid carbon dioxide was initiated with an impurity contained in the monomer. In addition, it has been found by the present authors' that the rate of polymerization in toluene solution increased by the excess addition of organic, acidic substance. For this reason the effect of carboxylic acid on the polymerization in liquid carbon dioxide was studied.

The experimental results are summarized in Table II. Here, pK_a represents the logarithmic value of the dissociation constant of acid measured in water at 25°C. All the polymer yield, the degree of polymerization, and the number of moles of polymer chain increased with decreasing pK_a .

		Polym	er yield		N., b
Acid	$\mathrm{p}K_a$	g.	wt%	\bar{P}_n	mole (X10 ⁵)
Trifluoroacetic	0.23	3.86	64.3	1500	8.6
Trichloroacetic	0.66	3.57	59.6	1500	7.9
Dichloroacetic	1.25	2.14	35.6	1100	6.5
Monochloroacetic	2.87	1.75	29.2	1050	5.6
Formic	3.75	1,30	21.6	900	4.8
Acetic	4.75	1.14	19.0	850	4.5

TABLE II

• Monomer solution, 10 g.; monomer concentration, 60 wt.-%; temperature, 30°C.; time, 10 min.; reaction vessel, 30 ml.

^b N_p , as described in Table I.

A logarithmic ratio of the polymer yield, $\log Y_0/Y$, which was calculated as the ratio of polymer yield in the polymerization by trifluoroacetic acid (Y_0) to that by another acid (Y), and a similar logarithmic ratio of the number of moles of polymer chain, $\log N_{p_0}/N_p$, were plotted against the relative acidity of the catalyst, ΔpK_a , which was calculated as the difference between the pK_a values of trifluoroacetic acid and the other acid. As shown in Figure 8, a distinct linearity existed in both relations. The slopes for the polymer yield and the number of moles of polymer chain were found to be 0.135 and 0.07, respectively, and the ratio of these was calculated as about 2. The results indicate that the acid acts as initiator and the amount of initiating species increases with decreasing the pK_a . The proton caused by



Fig. 8. Influence of relative acidity of catalyst on number of moles of polymer chain (N_p) and polymer yield (Y). Catalyst/monomer molar ratio, 1×10^{-3} ; monomer solution, 10 g.; monomer concentration, 60 wt.-%; temperature, 30°C.; time, 10 min.; reaction vessel, 30 ml.

the dissociation of acid used in the reaction system is, therefore, considered to act as an initiator of the polymerization. On the other hand, the fact that the ratio of both lines in Figure 8 is larger than unity indicates that these acids also promote the propagation. That is, the rate of propagation varies with the electronic nature of carboxylate anion produced by the dissociation of acid. These results suggest that the polymerization of formaldehyde in liquid carbon dioxide is initiated by the acidic catalyst and proceeds according to a cationic mechanism.

Methyl Formate, Methanol, and Water. The effects of the additions of methyl formate, methanol, and water on the polymerization are given in Table III. No influence of the addition of methyl formate was observed. By the addition of methanol or water the degree of polymerization decreased, whereas no influence was observed on the polymer yield. From these results it is considered that water and methanol act as chain-transfer agents in the polymerization.

It is interesting that a high molecular weight polyformaldehyde, similar to that commercially manufactured by an anionic polymerization, was obtained at a temperature above 20°C. in cationic polymerization, in carbon dioxide, by using the crude monomer. This may be attributable to the following roles of carbon dioxide: the depression of initiation by an impurity

	Polyme	er yield		N b
Additives	g.	wt%	\bar{P}_n	mole $(\times 10^6)$
Methyl formate	0.324	5.4	360	3.0
Methanol	0.372	6.2	250	5.0
Water	0.420	7.0	220	6.4
None	0.348	5.8	380	3.1

TABLE III

Influence of Addition of Methyl Formate, Methanol, and Wa

* Additive-to-monomer molar ratio, 1×10^{-3} ; monomer solution, 10 g.; monomer concentration, 60 wt.-%; temp., 30°C.; time, 10 min.; reaction vessel, 30 ml.

 $^{b}N_{p}$, as described in Table I.

such as water or methanol involved in the crude monomer, and the retardation of the chain transfer by water or methanol.

A detailed kinetic study of this polymerization will be reported in a subsequent paper.

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Cationic Polymerization of Formaldehyde in Liquid Carbon Dioxide. Part II: A Kinetic Study of the Polymerization*

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Synopsis

The kinetic behavior on the polymerization of formaldehyde with and without acidic catalyst, in liquid carbon dioxide, in the temperature range of 30 to 50° C. was investigated. In the polymerization without catalyst both the polymer yield and the degree of polymerization increased with reaction time and also with rising temperature. With acidic catalyst, such as acetic acid and dichloroacetic acid, both the polymer yield and the degree of polymerization increased more than that in the polymerization without catalyst. The overall rate of polymerization with acidic catalyst was expressed by the first-order rate equation with respect to monomer concentration. From the results it was concluded that the polymerizations belonged to a type of successive polymerization with rapid initiation and no termination. The rate constant and the activation energy of each elementary process of polymerization were estimated on the basis of the results.

INTRODUCTION

In Part I of this series¹ the authors reported that the polymerization of formaldehyde in liquid carbon dioxide took place without any catalyst at room temperature and gave a polymer having a high degree of polymerization. They also indicated that an acid, such as carboxylic acid, had a catalytic activity on the polymerization. From the results it was concluded that the polymerization proceeded according to a cationic mechanism.

In the present paper a kinetic study of the cationic polymerization in liquid carbon dioxide with and without acidic catalyst was studied.

EXPERIMENTAL

The experimental procedure of polymerization and the preparations of formaldehyde monomer and catalysts, such as acetic and dichloroacetic acids, were carried out as described in the previous paper.¹

*First presented at the 15th Annual Meeting of the Society of Polymer Science, Japan, held in Nagoya, May 1966.

RESULTS AND DISCUSSION

Effect of Reaction Time and Temperature on Polymerization without Catalyst

Table I shows the effects of reaction time and temperature on the polymerization of formaldehyde in liquid carbon dioxide without the addition of any catalyst.

Run no.	Reaction time, min.	Polymer formed		
		g.	wt%	\bar{P}_n
At 30°C.				
1	2	0.112	1.86	200
2	5	0.252	4.20	320
3	10	0.311	5.18	440
4	10	0.346	5.77	380
5	20	0.661	11.0	600
6	30	0.749	12.5	680
7	60	1.202	20.0	750
At 40°C.				
8	5	0.413	6.9	340
9	10	0.898	15.0	570
10	20	1.267	21.1	750
11	30	1.452	24.2	730
12	60	3.077	51.3	890
At 50°C.				
13	5	0.692	11.5	540
14	10	1.525	25.4	700
15	20	2.621	43.7	820
16	30	3 212	53 5	850

 TABLE I

 Experimental Results of Polymerization of Formaldehyde without Catalyst*

 $^{\rm a}$ Monomer solution, 10 g.; monomer concentration, 60 wt.-%; reaction vessel, 30 ml.

As shown in Figure 1, which was plotted with the data described in Table I, the polymer yield increased with reaction time and with rising temperature.

In addition, the overall rate of polymerization was represented as a first-order equation with respect to the monomer concentration, as will be described below. It has been reported that the polymerization in liquid carbon dioxide was initiated by an acidic substance contained in the monomer solution.¹ If the rate of initiation is smaller than that of propagation, and the termination is neglected, the overall rate of polymerization should be accelerated in the earlier stage of polymerization. Therefore, it was concluded that the rate of initiation is considerably faster than the rate of propagation.

On the other hand, the degree of polymerization increased with the polymer formed, as shown in Figure 2, which also was plotted from the data given in Table I. These curves, however, tend to bend convexly. This fact indicates that the number of moles of polymer chain, which was defined as a ratio of the moles of monomer polymerized to the degree of polymerization, increases gradually as the polymerization proceeds. That is, the reaction of chain transfer took place, but that rate was recognized



Fig. 1. Polymer yield vs. reaction time in polymerization without catalyst (monomer solution, 10 g.; monomer concentration, 60 wt.-%; reaction vessel, 30 ml.) at temperature (°C.): (O) 30; (\bullet) 40; (\bullet) 50.



Fig. 2. Degree of polymerization vs. polymer yield in polymerization without catalyst at temperature (°C.): (\bigcirc) 30; (\bigcirc) 40; (\bigcirc) 50.

to be slower than the rate of propagation, according to the shape of these curves. Further, the decrease of the initial slopes of these curves with rising temperature indicates that the number of moles of polymer chain increases with rising temperature. This means that the amount of initiating species increased with temperature.

On the basis of the fact that the rate of initiation was faster than that of propagation and the rate of chain transfer slower, this polymerization was classified as a type of successive polymerization with rapid initiation according to the classification of polymerization proposed by Kagiya et al.²

Polymerization with Acidic Catalyst

It has been concluded that an initiator in the polymerization of formaldehyde in liquid carbon dioxide is an acidic substance contained in the system.¹ For this reason the effect of carboxylic acid on the polymerization was investigated.

Table II shows the results of polymerization with acetic acid and dichloroacetic acid at 30°C. Both the polymer yield and the degree of polymerization of the polymer increased by the addition of acetic acid, and even more so by the addition of dichloroacetic acid.

Daa	Reaction time, min.	Polymer formed		
no.		g.	wt ^c / ₀	\bar{P}_n
Acetic acid				
17	5	0.853	14.2	450
18	10	1.026	17.1	970
19	10	1.140	19.0	850
20	20	2.082	34.7	1600
21	30	3.265	54.4	1750
22	60	4.241	70.7	2200
Dichloroacetic :	acid			
23	5	1.261	21.0	750
24	10	2.027	33.8	1170
25	10	2.136	35.6	1100
26	20	3,539	59.0	1640
27	30	4.052	67.5	1800

 TABLE II

 Experimental Results of Polymerization of Formaldehyde with Acidic Catalyst^a

* Monomer solution, 10 g.; monomer concentration, 60 wt.-%; catalyst/monomer mole ratio, 1×10^{-3} ; temperature, 30°C.; reaction vessel, 30 ml.

Figures 3 and 4 show the plots of polymer yield versus reaction time and of degree of polymerization versus polymer yield. A behavior similar to that of the polymerization induced with no catalyst is observed in these figures. Therefore, the polymerization induced by carboxylic acid catalyst also belongs to the type of successive polymerization with rapid initiation.

In addition, it was found in Figure 4 that the number of moles of polymer chain resulting from the polymerization induced by acetic acid was greater than that in the polymerization without catalyst at the same temperature. The number of moles of polymer chain with dichloroacetic acid, which is the stronger acid, was greater than that with acetic acid. This result in-



Fig. 3. Reaction time vs. polymer yield in polymerization with acidic catalyst (monomer solution, 10 g.; monomer concentration, 60 wt.-%; temperature, 30°C.; reaction vessel, 30 ml.) with: (O) acetic acid; (\bullet) dichloroacetic acid.

dicates that the amount of initiating species increased on the addition of acidic catalyst and further increased with the use of stronger acid. Moreover, the formation of a polymer with a higher degree of polymerization due to the use of acidic catalyst indicates that the added acid not only acts as initiator but also promotes the propagation.

Rate Equation of the Polymerization

Overall Rate. As reported in Part I of this series,¹ both the polymer yield and the degree of polymerization of the resulting polymer in the polymerization of formaldehyde increased with increasing monomer concentration, and these effects were ascribed to the increase of the rate of propagation with monomer concentration. To determine the dependency of monomer concentration on the rate of polymerization, the overall rate of polymerization in the steady state was, therefore, examined.

Figure 5 shows the first-order plot of the polymerization without and with acidic catalyst, taken from the data in Tables I and II. Here $[M]_0$ and [M] represent the initial monomer concentration and the monomer concentration after time t, respectively. A distinct linear relation was observed between the value of log $[M]_0/[M]$ and reaction time. The overall rates of polymerization both with and without acidic catalyst are, therefore, expressed by the first-order equation with respect to the monomer



Fig. 4. Degree of polymerization vs. polymer yield in polymerization with acidic catalyst with: (O) acetic acid; (\bullet) dichloroacetic acid.

concentration. The result indicates that the termination is essentially negligible under the experimental conditions because of rapid initiation, as described above.

Accordingly, the overall rate of polymerization, R, is given by the following equation.

$$R = -d[\mathbf{M}]/kt = k[\mathbf{M}]$$
(1)

where k is the overall rate constant of the polymerization. Integrating eq. (1) gives

$$\ln ([M]_0/[M]) = kt$$
(2)

The overall rate constants of the polymerizations with and without acidic catalyst were estimated from the slopes of the straight line in Figure 5, as shown in Table III. The overall activation energy for the polymeriza-

Catalyst	Temp., °C.	k, min. ⁻¹ (×10 ³)	
None	30	4.33	
None	40	11.5	
None	50	26.5	
Acetic acid	30	22.2	
Dichloroacetic acid	30	41.7	

TABLE III



Fig. 5. First-order relation of polymerization. Without catalyst at temperature (°C.): (O) 30; (\bullet) 40; (\bullet) 50. With catalyst at 30°C.: (\triangle) acetic acid, (\blacktriangle) dichloro-acetic acid.

tion without acidic catalyst was calculated to be 18.0 kcal./mole from the Arrhenius plot of the rate constants. Enikolopyan³ reported about 9 kcal./mole of activation energy for the anionic polymerization of formaldehyde, which was initiated by tetrabutylammonium laurate at a temperature below -20° C., and 10.3 kcal./mole was obtained for gamma-ray polymerization in our previous work.⁴ The activation energy of cationic polymerization estimated in the present work was greater than in those papers.

Elementary Processes. On the basis of the experimental results described above it is assumed that the elementary reactions of the polymerization consist of the following processes.

Initiation:

$$C + M \xrightarrow{A_1} P^*, \qquad R_i = k_i [C] [M]$$
(3)

where P^* , R_i , k_i , and [C] represent the initiating species, the rate of initiation, the rate constant of initiation, and the concentration of catalyst, respectively. The concentration of the initiating species, $[P^*]_0$, however, is constant and equal to that of the propagating species, because of rapid initiation and no termination in the polymerization. Therefore, integration of R_i may be represented as

$$\int R_i \, dt = [\mathbf{P}^*]_0 \tag{4}$$
Propagation:

$$\mathbf{P}^* + \mathbf{M} \xrightarrow{k_p} P_n^*, \qquad R_p = k_p [\mathbf{P}^*]_0 [\mathbf{M}]$$
(5)

where R_p and k_p represent the rate of propagation and the rate constant of propagation, respectively.

Accordingly, by integrating eq. (5) with respect to the monomer concentration the rate equation of the polymerization may be expressed as follows:

$$\ln ([M]_0/[M]) = k_p [P^*]_0 t$$
(6)

Thus, the relation coincides with eq. (2), which represents the overall rate of polymerization.

On the other hand, integration of R_p is expressed as

$$\int R_p \, dt = \left[\mathbf{M}_p \right] \tag{7}$$

where $[M_p]$ is the moles of monomer polymerized.

Chain transfer:

$$\mathbf{P}_{n}^{*} + \mathbf{Y} \xrightarrow{k_{\mathrm{tr}}} \mathbf{P}_{n} + \mathbf{Y}^{*}, \qquad R_{\mathrm{tr}} = k_{\mathrm{tr}}[\mathbf{P}^{*}][\mathbf{Y}]$$
(8)

where R_{tr} , k_{tr} , and [Y] represent the rate of chain transfer, the rate constant of chain transfer, and the concentration of chain-transfer agent, respectively.

Assuming that [Y] in eq. (8) is constant during the course of polymerization, the following equation exists:

$$\int R_{tr} dt = k_{tr} [\mathbf{P}^*] [\mathbf{Y}] t \tag{9}$$

From eq. (6):

$$[P^*] = \ln ([M]_0/[M])/k_p t$$
(10)

Hence, eq. (9) converts to the following equation:

$$\int R_{\rm tr} dt = (k_{\rm tr} |\mathbf{Y}| / k_p) \ln ([\mathbf{M}]_0 / [\mathbf{M}])$$
(11)

Estimation of Rate Constants of Elementary Processes

From the characteristic feature of the present polymerization it was concluded that the polymerization belonged to the type of successive polymerization with rapid initiation and no termination. It also may be concluded that the stationary-state hypothesis, by which the rate of initiation is equal to that of termination, is not realized in the polymerization. In the present kinetic study the experimental results were, therefore, treated according to a graphical method for the nonstationary-state polymerization, proposed by Kagiya et al.⁵ Thus, the rate constant of each elementary process was graphically estimated as follows.

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The number-average degree of polymerization, \bar{P}_n , may be expressed by the following equation for the present polymerization:

$$\bar{P}_n = \int R_p \, dt / \int R_i \, dt + \int R_{tr} \, dt \tag{12}$$

It follows from this equation that

$$1/\bar{P}_u = \int R_i dt / \int R_p dt + \int R_{tr} dt / \int R_p dt$$
(13)

By substituting eqs. (4), (7), and (11) into eq. (13), the following equation is derived:

$$[\mathbf{M}_{p}]/[\bar{P}_{n} \ln ([\mathbf{M}]_{0}/[\mathbf{M}])] = [\mathbf{P}^{*}]/\ln ([\mathbf{M}]_{0}/[\mathbf{M}]) + k_{tr}[\mathbf{Y}]/k_{p}$$
(14)

Calculated Values in Polymerization without Catalyst								
Time, min.	ln ([M] ₀ / [M])	$[M_p],$ moles/l.	${\bar P}_n$	$[M_p]/\bar{P}_n,$ moles/l. $(imes 10^3)$	$\frac{1}{\ln \left([M]_0 \right) [2]}$	$ \begin{array}{c} [{\rm M}_{p}]/\{\bar{P}_{n}\ln \\ ([{\rm M}_{0}]/[{\rm M}])\}, \\ {\rm moles/l.} \\ \overline{{\rm M}]}) \ (\times 10^{2}) \end{array} $		
At 30°C.								
5	0.0217	0.44	260	1.76	46.0	8.11		
10	0.0433	0.86	400	2.15	23.1	4.99		
20	0.0875	1.66	550	3.02	11.5	3.48		
40	0.173	3.16	700	4.52	5.77	2.60		
60	0.259	4.56	800	5.71	3.86	2.20		
At 40°C.								
5	0.0576	1.10	350	3.14	17.3	5.43		
10	0.115	2.08	500	4.16	8.69	3.61		
20	0.230	4.10	670	6.12	4.34	2.66		
4 0	0.461	7.44	830	9.00	2.17	1.95		
60	0.692	10.0	890	11.2	1.45	1.63		
At 50°C.								
2	0.0531	1.06	300	3.54	18.9	6.69		
5	0.131	2.46	520	4.73	7.65	3.61		
10	0.260	4.56	680	6.70	3.84	2.58		
20	0.518	8.10	800	10.1	1.94	1.97		
30	0.783	10.9	860	12.6	1.28	1.61		

TABLE IV

 TABLE V

 Calculated Values in the Polymerization With Acidic Catalyst

Time, min.	$\ln ([M]_0/[M])$	$[M_{\nu}],$ moles/l.	${ar P}_n$	$\begin{array}{c} [\mathrm{M}_{p}]/\bar{P}_{n},\\ \mathrm{moles}/\mathrm{l}.\\ (\times 10^{3}) \end{array}$	$\frac{1}{\ln\left([M]_0/[M]\right)}$	
Acetic acid						
5	0.110	2.08	550	3.78	8.93	33.8
10	0.224	4.00	950	4.21	4.46	18.8
20	0.447	7.16	1450	4.94	2.24	11.1
30	0.671	9.80	1750	5.60	1.49	8.35
40	0.894	11.8	1950	6.05	1.12	6.77
60	1.340	14.8	2200	6.71	0.745	5.00
Dichloroacet	ic Acid					
5	0.207	3.74	700	5.00	4.83	24.2
10	0.414	6.48	1150	5.65	2.42	13.7
15	0.622	9.26	1300	6.62	1.61	10.7
$\hat{20}$	0.829	11.3	1600	7.07	1.21	8.55
30	1.240	14.2	1800	7.90	0.806	6.37



Fig. 6. Estimation of the concentration of initiating species and rate constant of chain transfer in polymerization without catalyst at temperature (°C.): (O) 30; (\bullet) 40; (\bullet) 50.

The values of the left-hand member and of $1/[\ln ([M]_0/[M])]$ were calculated by using the values on the curves shown in Figures 1 to 4. The calculated values in the polymerization both without and with acidic catalyst are listed in Tables IV and V, respectively.

As shown in Figures 6 and 7, which represent polymerization without and with acidic catalyst, a distinct linear relation between the two sets of values was obtained. This fact indicates that the above-mentioned assumption concerning the elementary processes is satisfied.

|--|

Evaluated Values of Concentration of Initiating Species and Rate Constant of Elementary Process

Catalyst	Temp., °C.	[P*] ₀ , moles/l. (×10 ³)	k_p , (l./moles/ min.)	$k_{\rm tr}[Y],$ min. ⁻¹ (×10 ³)	$k_{ m tr}[m Y]/k_p,$ l./mole $(imes 10^3)$
None	30	1.3	3.3	5.7	18
None	40	2.3	5.8	7.5	15
None	50	3.1	8.0	9.4	13
Acetic acid Dichloroacetic	30	3.4	6.5	2.1	3.2
acid	30	4.4	9.5	2.9	3.0

The moles of initiating species, $[P^*]_0$, and the ratio of the rate constant of chain transfer to that of propagation in each case were evaluated from the slopes of each straight line and the intercepts on the ordinate in Figs. 6 and 7, respectively, the evaluated values are listed in Table VI. Here the rate constants of propagation and of chain transfer were calculated by using k, $[P^*]_0$, and $k_{tr}[Y]/k_p$.

In the polymerization without acidic catalyst the rate constant of each elementary process increased with rising temperature, but the ratio of $k_{tr}[Y]$ to k_p decreased. The result indicates that an increase in the rate



Fig. 7. Estimation of concentration of initiating species and rate constant of chain transfer in polymerization with acidic catalyst; (O) acetic acid; (\bullet) dichloroacetic acid.

of propagation with temperature is greater than that in the rate of chain transfer. The activation energies for the initiation, propagation, and chain transfer were estimated from Arrhenius plots to be 8.0, 9.2, and 4.7 kcal./ mole, respectively.

On the other hand, in the polymerization with acidic catalyst the moles of initiating species and the rate constant of propagation increased more than in the polymerization without acidic catalyst at the same temperature; the rate constant of chain transfer, however, decreased. This result indicates that the acid added as catalyst not only acts as initiator but promotes the propagation and depresses the chain transfer. A detailed mechanism of the elementary reactions in the polymerization will be reported in another paper.

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