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Thermal Behavior of Polyhydrazides and Poly-1,3,4-oxadiazoles

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Synopsis

The thermal properties of a series of polyhydrazides and corresponding poly-1,3,4-oxadiazoles have been investigated using differential thermometric and thermogravimetric techniques. In addition, the conversion rates of the polyhydrazides to the corresponding oxadiazole structures have also been measured. In general, weight loss in polyhydrazides occurs in three distinct stages corresponding, respectively, to loss of adsorbed water, cyclodehydration, and decomposition of the poly-1,3,4-oxadiazole formed *in situ*. The polyoxadiazoles generally exhibit only a single weight loss step (below 700°C.) corresponding to decomposition and volatilization of the substrate itself. These data clearly indicate that the presence of aliphatic carbon–carbon linkages in the polymer backbone reduces the temperature at which decomposition of the polyoxadiazoles is noted. Corresponding differential thermometry patterns give additional data on phase transitions in the polymers and indicate, in general, that the poly-1,3,4-oxadiazoles formed *in situ* decompose before reaching their intrinsic melting points (under the specific conditions of these experiments). Comparison of the poly-1,3,4-oxadiazoles prepared under the (rapid) dynamic conditions of the differential thermometry and thermogravimetry techniques employed (30°C./min.) with isothermal rate data clearly suggests subtle structural differences in the polyoxadiazoles prepared by the two different modes. In general, $\Delta E\ddagger$ for the hydrazide–oxadiazole conversion amounts to about 49–53 Kcal./mole while $\Delta S\ddagger$ amounts to 14–17 e.u. However, both $\Delta E\ddagger$ and $\Delta S\ddagger$ for the polymer containing exclusively 1,3-phenylene linkages between incipient oxadiazole groups appear to be considerably higher ($\Delta E\ddagger$ = 62 Kcal./mole, $\Delta S\ddagger$ = 34 e.u.). This striking difference is explained in terms of the increased order resulting from the higher degree of crystallinity in the polyhydrazide.

INTRODUCTION

The preparation and properties of polyhydrazides and poly-1,3,4-oxadiazoles have been reported recently.[1–6] Since the preparation of high molecular weight poly-1,3,4-oxadiazoles involves the thermal cyclodehydration of polyhydrazides, the thermal behavior of polyhydrazides and poly-1,3,4-oxadiazoles has been extensively studied. The differential thermal analysis, thermogravimetric analysis, and the rates of conversion of poly-

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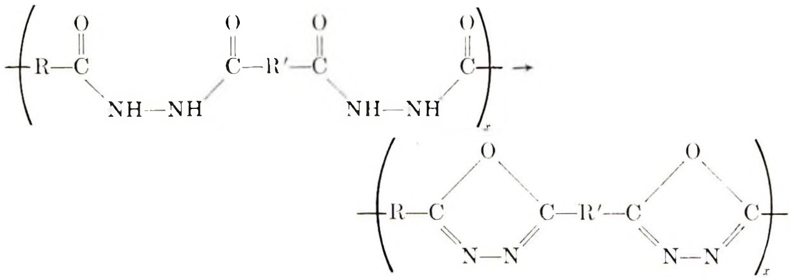
hydrazides to poly-1,3,4-oxadiazoles have been investigated. This paper represents a preliminary report of these findings.

RESULTS AND DISCUSSION

The polyhydrazide and poly-1,3,4-oxadiazole structures investigated are listed in Table I. These polymers have been prepared and characterized by previously reported methods.[1–6]

TABLE I



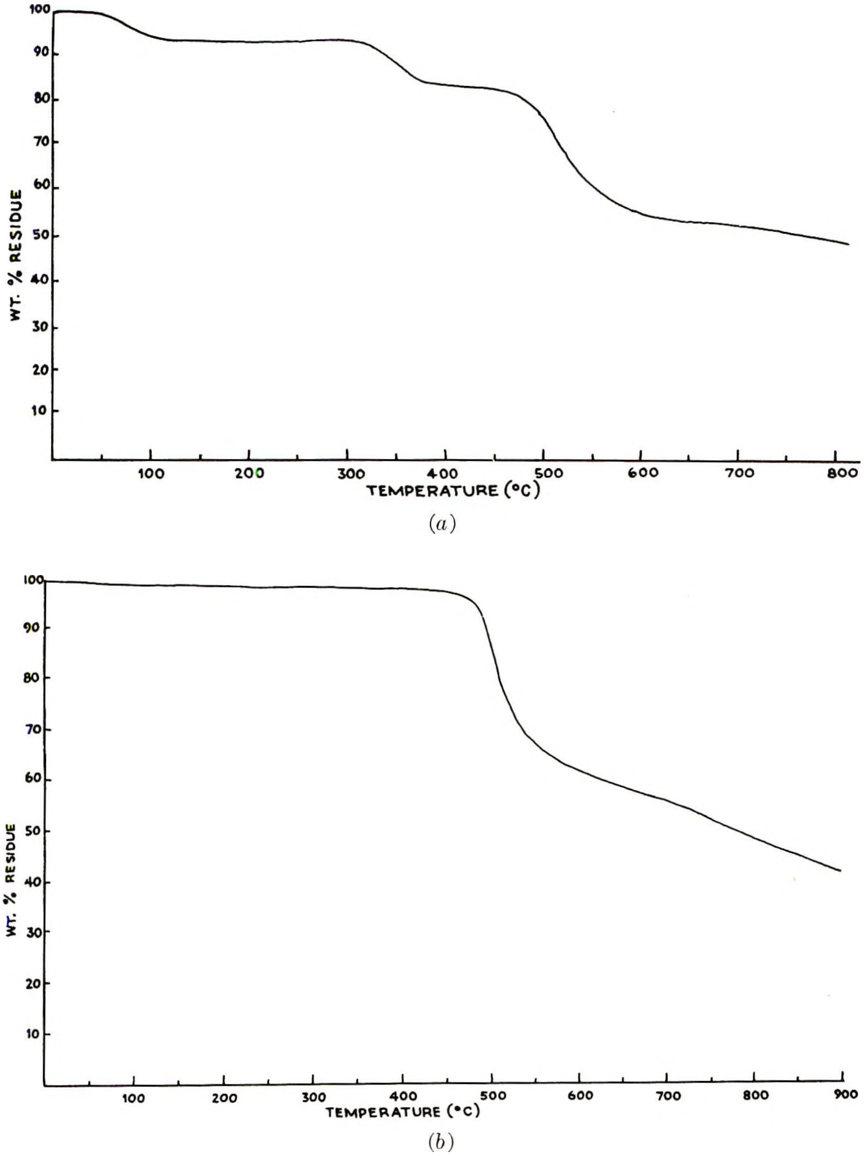
	R	R′
A → A′	1,3-Phenylene	1,4-Phenylene
B → B′	1,3-Phenylene	1,3-Phenylene
C → C′	1,3-Phenylene	
D → D′	1,3-Phenylene	1,4-Tetramethylene
E → E′	1,3-Phenylene	1,8-Octamethylene
F → F′	1,4-Tetramethylene	1,4-Tetramethylene
G → G′	1,8-Octamethylene	1,8-Octamethylene

Thermogravimetric Analysis (TGA)

Thermogravimetry curves were obtained by use of the Du Pont 950 thermogravimetric analyzer.

Figures 1*a* and 1*b* show typical thermogravimetry curves for a representative polyhydrazide–poly-1,3,4-oxadiazole pair. For this study, approximately 10 mg. of sample was heated in a stream of nitrogen (35 ml./min.) at a programmed rate of 30°C./min. Table II summarizes the thermogravimetry data for the polyhydrazides and poly-1,3,4-oxadiazoles listed in Table I. Since the thermogravimetric behavior of poly-1,3,4-oxadiazoles is much less complex than that of the polyhydrazides, these will be considered first.

All of these poly-1,3,4-oxadiazoles exhibit a small weight loss from room temperature up to about 100°C. This loss in weight, ranging from 0.3% to 4% of the original weight, is believed to correspond to loss of adsorbed water. Of particular interest is the thermogravimetric behavior of the poly-1,3,4-oxadiazoles consisting solely of benzene and 1,3,4-oxadiazole rings, polymers A′, B′, and C′.



(a)

(b)

Fig. 1. Thermogravimetric analysis of polymers under nitrogen: (*a*) polyhydrazide B; (*b*) poly-1,3,4-oxadiazole B′.

For polymer A′, after loss of adsorbed water, no weight loss is seen up to a temperature of approximately 450°C., where a rapid loss in weight occurs and continues up to approximately 560°C. Then the residue slowly loses weight up to 700°C. At this temperature, 51.8% of the original weight remains (based on dry polymer).

For the poly-1,3,4-oxadiazole B′, after loss of adsorbed water, the first significant break in the curve occurs approximately 50°C. lower than that

TABLE II

Summary of Thermogravimetric Data for Poly-1,3,4-oxadiazoles and Polyhydrazides

Polymer	$(T_i/T_f)_1$[a]	Δ_1[b]	$(T_i/T_f)_2$[c]	Δ_2[d]	$(w/w_0)_{700}$[e]	(Δ_1) calc.
Poly-1,3,4-oxadiazoles						
A′	447/560	37.5	—	—	51.8	
B′	400/494	19.6	494/560	16.3	54.7	
C′	275/355	26.0	355/541	36.0	26.6	
D′	314/532	44.8	—	—	46.8	
E′	372/579	64.3	—	—	34.8	
F′	275/343	9.4	343/508	60.2	26.2	
G′	290/348	2.0	348/508	86.8	11.4	
Polyhydrazides						
A	275/390	10.6	466/550	32.8	40.6	11.0
B	280/376	10.4	428/611	32.5	55.0	11.0
C	275/367	34.3	367/541	30.5	22.8	14.5
D	275/352	11.8	352/495	35.5	38.9	11.8
E	251/357	9.7	357/513	63.9	21.2	10.0
F	285/362	17.2	362/499	55.8	23.5	12.7
G	266/381	10.7	381/513	79.0	8.6	9.8

[a] $(T_i/T_f)_1$ = (onset temp., °C./terminus temp., °C.) for step 1.

[b] $\Delta_1 = (\Delta w/w_0)100$ for step 1.

[c] $(T_i/T_f)_2$ = (onset temp., °C./terminus temp., °C.) for step 2.

[d] $\Delta_2 = (\Delta w/w_0)100$ for step 2.

[e] $(w/w_0)_{700}$ = % original weight remaining at 700°C.; w = sample weight at temperature T, w_0 = original sample weight (based on dry polymer).

for A′ (i.e., at 400°C.). After losing 19.6% of the original weight, a second step occurs in the curve at 494°C., during which another 16.3% of the weight is lost up to 560°C. At 700°C., 54.7% of the original weight still remains.

For the poly-1,3,4-oxadiazole C′, the first break in the curve occurs at approximately 275°C. (with 26.0% weight loss), and it is followed by a second break in the curve at 355°C. with a rapid loss in weight up to 541°C. At 541°C. the sample has lost approximately 62% of its original weight and weight loss continues at a much slower rate. At 700°C., the polymer has lost about 73% of original weight.

This difference in behavior of these three poly-1,3,4-oxadiazoles, which consist only of benzene and 1,3,4-oxadiazole rings, suggests inherent differences in stability. In the case of A′ and B′, where the polymer chain consists of alternating benzene and 1,3,4-oxadiazole rings, the upper limit of stability appears to be between 400 and 450°C. For C′, the first break occurs at 275°C. with a second break at 355°C. These significant differences would seem to reflect a difference in stability between the alternating benzene–1,3,4-oxadiazole structure and that of the alternating benzene-bis(1,3,4-oxadiazole) structure.

The thermogravimetric behavior of the other poly-1,3,4-oxadiazole structures, i.e., D′, E′, F′, and G′, reflects the presence of the thermally unstable aliphatic carbon–carbon linkages in the polymer chain. In the case of D′ and E′, in which not only does the polymer chain consist of 1,3,4-oxadiazole rings and aliphatic carbon–carbon rings, but also benzene rings, the initial rapid loss in weight occurs between 315 and 375°C. and continues in a single step up to 530–580°C. For F′ and G′, in which the polymer chain consists solely of 1,3,4-oxadiazole rings and aliphatic carbon–carbon linkages, the initial rapid loss in weight occurs between 275 and 300°C. with a second break in the curve at 340–350°C. For all of these poly-1,3,4-oxadiazoles containing aliphatic carbon–carbon linkages, less than 50% of the original weight remains at 700°C.

The thermogravimetric behavior of the polyhydrazides is somewhat more complex than that of the poly-1,3,4-oxadiazoles. Typically, polyhydrazides show a loss in weight up to about 100°C. which corresponds to loss of adsorbed water. This initial weight loss amounts to 4–10% (based on dry polymer) and roughly corresponds to the water adsorption of thin films of these polyhydrazides. Weight loss corresponding to conversion of the polyhydrazides to poly-1,3,4-oxadiazoles starts at temperatures in the vicinity of 275°C. and continues for another 100°C. A final step in the thermogravimetry curve occurs in the vicinity of 360–460°C. and corresponds to decomposition of the poly-1,3,4-oxadiazole structure formed *in situ.*

It can be noted from Table II that the final step in the thermogravimetry curve occurs between 430 and 470°C. for polymers having only benzene rings and (incipient) 1,3,4-oxadiazole rings in the chain. Polymers containing aliphatic linkages apparently initiate degradation at considerably lower temperatures (i.e., 350–380°C.).

The somewhat different thermal behavior of the poly-1,3,4-oxadiazoles prepared *in situ* from those prepared by isothermal conversion deserves some comment. One explanation for the dissimilar behavior would suggest a difference in thermal behavior based on differences in structure which depend on the mode of preparation. Poly-1,3,4-oxadiazoles prepared *in situ* involve rapid conversion periods (<1 min.) and high temperatures (>300°C.); the polyoxadiazoles prepared under isothermal conditions are converted slowly with residence periods as long as 30 hr. at temperatures below 255°C. The final stages of conversion of the hydrazide to the 1,3,4-oxadiazole structure is probably diffusion-controlled (note the decrease in the first-order rate constants above 80% conversion, Figs. 3–6), and it is tempting, therefore, to suggest that some other reaction or reactions such as crosslinking, degradation, or even another cyclization mode may be competing with the main cyclodehydration reaction. If $\Delta E\ddagger$ for some other such reaction or reactions is considerably greater than $\Delta E\ddagger$ for the cyclodehydration reaction, then the relative importance of the secondary reaction would increase as the sample temperature increases under the dynamic conditions involved in the *in situ* preparation of the poly-1,3,4-oxadiazoles. The differential thermometry curves for conjugate polyhydrazide–poly-1,3,4-oxadiazole pairs (see next section) are fairly complex, but together with polymer melt temperature measurements suggest crosslinking for polymers F′ and G′. Furthermore, the thermal profile for B′ is clearly different from the poly-1,3,4-oxadiazole decomposition section of the curve for B. This suggests basic differences in structure, although these differences cannot be specifically defined at this time. A rather strong argument against extensive crosslinking of the isothermally prepared poly-1,3,4-oxadiazoles is solubility of these polymers in concentrated sulfuric acid.

Polymer C appears to be particularly interesting, in view of the fact that the thermogravimetry curves for conjugate polyhydrazide and poly-1,3,4-oxadiazole structures appear to be almost identical. This would appear to result from the instability of the poly-1,3,4-oxadiazole which initiates weight loss at approximately the same temperature as does cyclodehydration from the polyhydrazide. Interestingly, differential thermometry curves for corresponding poly-1,3,4-oxadiazole and polyhydrazide are quite similar except for the strong endotherm at 321°C. in the polyhydrazide which presumably results from the cyclodehydration reaction (see below).

Differential Thermal Analysis (DTA)

DTA thermograms were obtained by using the Du Pont 900 differential thermal analyzer.

Figures 2*a* and 2*b* show typical DTA thermograms for a representative polyhydrazide–polyoxadiazole pair. For the purposes of this study approximately 10 mg. of sample was heated in a nitrogen atmosphere at a programmed heating rate of 30°C./min. These data are summarized in Table III. The numbers in the table correspond to peak temperatures and have been coded with reference to the sign of the thermal reaction (a negative sign refers to an endothermic reaction, a positive sign refers to an exothermic reaction). The entries in this table have also been coded for peak size (w = weak, m = medium, s = strong). Asterisks (*) and daggers (†) mark the thermal reactions which are associated, respectively, with the first and second breaks in the corresponding thermogravimetry curve (after initial loss of adsorbed water).

All samples of these polyhydrazides and poly-1,3,4-oxadiazoles exhibit broad endotherms which peak between 100 and 150°C. These endotherms are believed to be associated with loss of adsorbed water. Corresponding weight loss is seen in the conjugate thermogravimetry curve generally at temperatures somewhat below 100°C. The apparent differences in these thermograms describing the volatilization of adsorbed water is a consequence of the dynamic conditions for measurements in the Du Pont 950 Thermogravimetric Analyzer and the static conditions in the Du Pont 900

Differential Thermal Analyzer. In the Thermogravimetric Analyzer, the nitrogen purge stream passes directly over the sample allowing rapid saturation of the purge gas with effluents and permitting effluent removal at lower temperatures. In the Differential Thermal Analyzer, the conditions

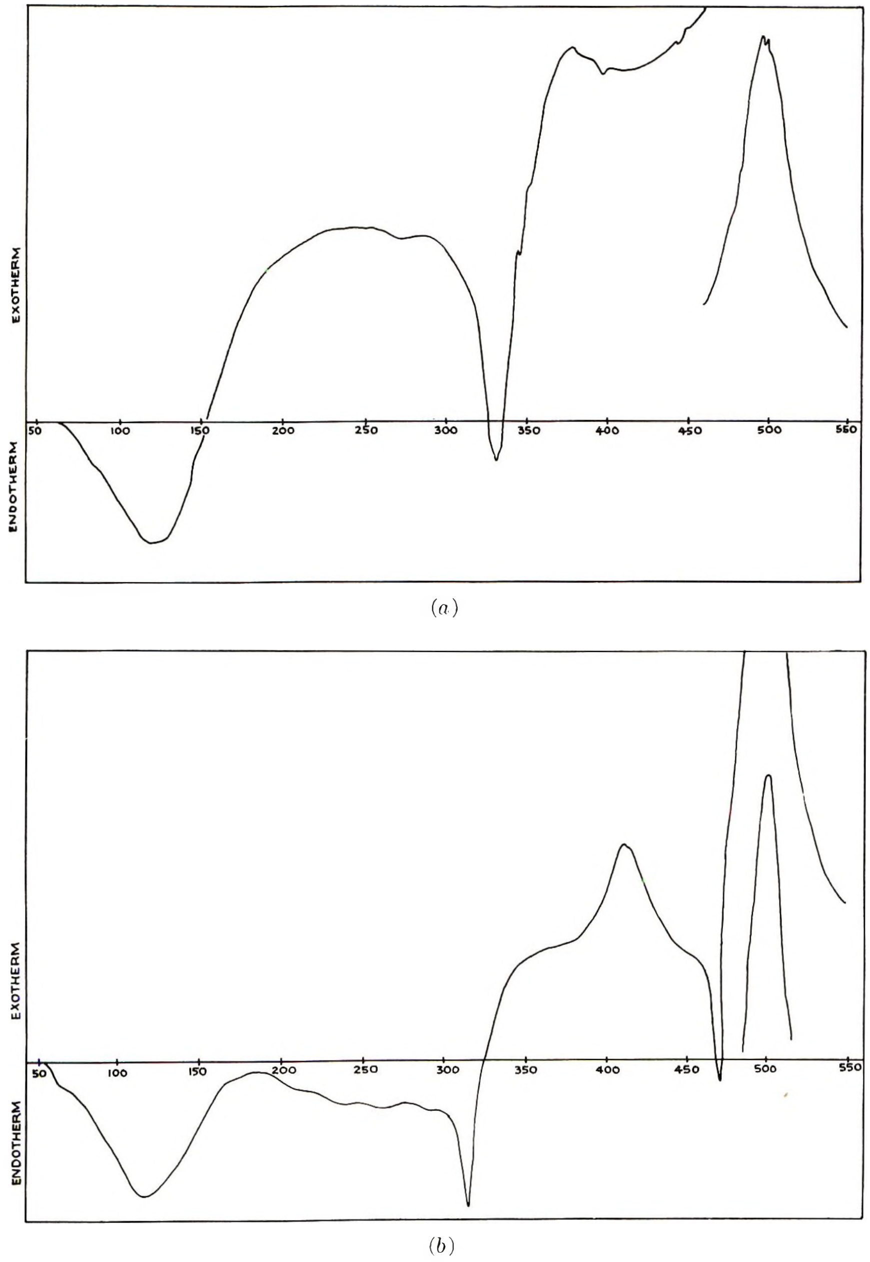


Fig. 2. Differential thermograms of polymers under nitrogen: (*a*) polyhydrazide B; (*b*) poly-1,3,4-oxadiazole B′. Numbers are degrees Centigrade.

TABLE III
Summary of Differential Thermal Data for Poly-1,3,4-oxadiazoles and Polyhydrazides

Polymer	Peaks[a]
Poly-1,3,4-oxadiazoles	
A′	−100(w), +375(m), +505(s)*
B′	−112(m), −307(m), +402(m),* −457(s),* +489(s)†
C′	−112(s), +288(m),* +331(s)†
D′	−123(m), +343(msh)* → +419(s)*
E′	−66(s), −115(w), −258(w), +367(sh)* → +433(s)*
F′	−130(s), −278(s), +333(s),* +410(w)†
G′	−82(m), +152(w), −249(s), +324(s),* +438(s)†
Polyhydrazides	
A	−132(s), −285(sh)* → −307(s),* +390(w), +502(s)†
B	−122(s), −264(ww), −324(s),* −483(s)†
C	−135(s), +285(m),* −321(s), +338(s)†
D	−134(sh) → −151(s), −209(s) ← −236(sh), −288(m),* +367(s),† +398(s)†
E	−122(sh) → −138(s), −182(s), −238(s), −260(s)* → −269(m),* +343(m),† +430(w),† +500(ww)†
F	−122(s), −316(s),* +353(s),† +397(s)†
G	−110(s), −269(sh)* → −278(s),* +333(s), +381(m)†

[a] Key: minus (−) denotes endotherm peak, plus (+) denotes exotherm peak; asterisk (*) denotes peak corresponding to first break in TG curve (excluding adsorbed water), dagger (†) denotes peak corresponding to second break in TG curve (excluding adsorbed water); relative peak size: ww = very weak, w = weak, m = medium, s = strong, sh = shoulder; *x*(sh) → *y* or *y* ← *z*(sh) denotes a shoulder at temperature *x*(or *z*) which precedes (i.e., *x*) or follows (i.e., *z*) the main peak. The main peak itself reaches a maximum temperature at *y*.

for this study were such that removal of adsorbed water was essentially diffusion-controlled and required higher temperatures.

Several of the poly-1,3,4-oxadiazoles show endotherms at temperatures considerably below the endotherm corresponding to loss of adsorbed water (E′ and D′). Several polyhydrazides exhibit sizable endotherms without a corresponding weight loss (B, E, F, and G). While the reversibility of these thermal transitions has not been fully investigated, it is suspected that they may be associated with chain transitions of primary or secondary nature (i.e., melting or glass transitions). Future communications will clarify these observations.

The differential thermometry curves for poly-1,3,4-oxadiazoles show wide variations depending on structure of the polymer. Polymers A′, C′, and D′ exhibit no endotherms in their thermal profiles (excluding loss of adsorbed water). Polymer B′ which has a similar thermogravimetry curve to polymer A′, has a remarkably different differential thermometry curve which exhibits two sharp medium-sized endotherms at 307 and 457°C., respectively, in addition to exotherms at 402 and 489°C. (All the poly-1,3,4-oxadiazoles examined in this study and those arising from *in situ* preparation from the corresponding hydrazide show a strong, sharp exotherm in the 400–500°C. region.) The strong endotherms exhibited by polymers F′ and G′ at 278 and 249°C., respectively, suggest crystalline melting. Since the polymer melt temperature (PMT) for both these polymers occurs at 400°C. (with decomposition), it would be tempting to suggest that the polymers are crosslinked, except for the fact that they are soluble in concentrated sulfuric acid (see discussion in preceding section). The weak endotherm exhibited by polymer E′ at 258°C. is too small to be attributable to the melting of this highly crystalline polymer. However, from differential thermometry and thermogravimetry measurements and in conjunction with polymer melt temperature (PMT) measurements, it appears that only one polymer in this series (E) melts before it decomposes. Apparently, all of these poly-1,3,4-oxadiazoles decompose (i.e., lose weight) during an exothermic reaction.

The differential thermometry curves for polyhydrazides are considerably more complicated than those for poly-1,3,4-oxadiazoles. In addition to a very large (and broad) endotherm which occurs at temperatures between 120 and 150°C. (presumably volatilization of adsorbed water), strong endothermic peaks are exhibited between 250 and 325°C. which are attributable to loss of water during polyoxadiazole formation. Typically, these endotherms are 50–100°C. broad at the baseline. Following the endotherm which corresponds to poly-1,3,4-oxadiazole formation, the thermal profile of the residue should be identical with that for the corresponding poly-1,3,4-oxadiazole prepared under isothermal conditions. For the conjugate pairs A–A′, D–D′, E–E′, F–F′, and G–G′, this appears to be correct. Unfortunately, the definition of these large exotherms in this region is frequently poor and reproducibility of ±10–15°C. is not unusual. Thus, temperature differences less than approximately 20°C. for peak positions are of doubtful significance. For polymer C, it appears that the polymer undergoes an exothermic degradation at 285°C. before losing water during the 321°C. endotherm. A strong exotherm at 338°C. completes the thermal profile in this region. The corresponding poly-1,3,4-oxadiazole exhibits exotherms at 288 and 331°C. The thermogravimetry curves are practically identical for polyhydrazide (C) and poly-1,3,4-oxadiazole (C′) with about 8% greater weight loss occurring during the first step in the thermogravimetry curve for the polyhydrazide (excluding the loss of adsorbed water). Polymer B, however, exhibits a thermal profile in the poly-1,3,4-oxadiazole degradation region which is clearly different from that exhibited by polymer B′ in the corresponding region. While the sharp exothermic peak at 489°C. is in good agreement with the corresponding exothermic peak for B (483°C.), polymer B′ has in addition a medium-sized exothermic peak at 402°C. and a sharp strong exotherm peak at 457°C. B′ also has a medium sharp endotherm at 307°C. which suggests a transition in the polymer chain. The clear difference in differential thermometry curves for polymer B′ and B (in corresponding sections) suggests basic differences in the poly-1,3,4-oxadiazole structures which depend on their mode of preparation (see above).

Rates of Conversion of Polyhydrazides to Poly-1,3,4-oxadiazoles

With powdered polymer or unoriented films, the time required for complete conversion of the polyhydrazides to the corresponding poly-1,3,4-oxadiazoles was found to depend on the structure of the polyhydrazide (see Tables IV–VII). Due to the marked difference in infrared spectra and elemental analyses of the poly-1,3,4-oxadiazoles and the precursor polyhydrazides, the completeness of conversion could be easily determined. For a given temperature the rate of conversion of these polyhydrazides, in order of decreasing rate, was: D > C > A >B.

TABLE IV

Thermal Conversion of Polyhydrazide to Poly-1,3,4-oxadiazole (A → A′)

Reaction conditions			Product		
Temp., °C.	Reaction time, hr.	Form	Oxygen, %	Conversion, %	η_{inh} (H_2SO_4)
265	30	Powder	11.37, 11.45	~97	0.63
	30	Film	11.50, 11.55	~96	0.52
277	12	Powder	11.63, 11.70	~94	0.70
	140	Fiber	11.57, 11.65	~95	0.65
285	8	Powder	11.46, 11.50	~96	0.98

TABLE V

Thermal Conversion of Polyhydrazide to Poly-1,3,4-oxadiazole (B → B′)

Reaction conditions			Product		
Temp., °C.	Reaction time, hr.	Form	Oxygen, %	Conversion, %	η_{inh} (H_2SO_4)
265	42	Powder	11.50, 11.55	~96	0.70
	42	Film	11.35, 11.40	~97	0.66
277	17	Powder	11.70, 11.75	~93	0.55
285	10	Powder	11.60, 11.68	~95	0.58
	140	Fiber	11.75, 11.83	~93	0.95

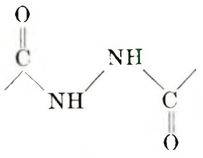
TABLE VI
Thermal Conversion of Polyhydrazide to Poly-1,3,4-oxadiazole (C → C′)

Reaction conditions			Product		
Temp., °C.	Reaction time, hr.	Form	Oxygen %	Conversion, %	η_{inh} (H_2SO_4)
265	20	Powder	15.47, 15.53	~96	0.65
	20	Film	15.83, 15.43	~97	0.60
277	10	Powder	15.68, 15.76	~94	0.53
285	8	Powder	15.75, 15.80	~93	0.57

TABLE VII
Thermal Conversion of Polyhydrazide to Poly-1,3,4-oxadiazole (D → D′)

Reaction conditions			Product		
Temp., °C.	Reaction time, hr.	Form	Oxygen %	Conversion, %	η_{inh} (H_2SO_4)
222	30	Powder	12.36, 12.41	~95	0.66
	30	Film	12.25, 12.33	~96	0.60
242	10	Powder	12.55, 12.60	~93	0.53
255	4	Powder	12.10, 12.20	~98	0.50

The conversion of oriented fibers from A and B required much longer heating times than those necessary for the conversion of A and B as powders, or unoriented films. In fact, the unoriented structures (powders or unoriented films) were converted 14–15 times as fast as the oriented fibers. This difference in rates of conversion of oriented and unoriented structures is believed to be due to the difference in polymer chain configuration in these two structures. In the oriented structure, a greater percentage of the polymer chain is in an extended form (I), whereas the preferred configuration for cyclization is the folded or unextended form (II).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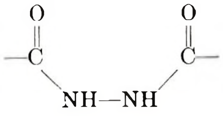
II

Kinetics of the Conversion of Polyhydrazides to Poly-1,3,4-oxadiazoles

In addition to the rates of conversion of A, B, C, D, to A′, B′, C′, D′, the kinetics of the conversion of the polyhydrazides to the poly-1,3,4-oxadiazoles were also studied.

In initial experiments attempts were made to follow the conversion via the changes, on heating, in the infrared spectra, specifically the intensity of absorption at 3.06 μ (NA stretching), of thin polyhydrazide films. On heating, these films were subjected to high shrinkage and became embrittled and opaque. Thus, any quantitative measurement of the decrease in absorption at 3.06 μ was impossible.

Fortunately, the difference in oxygen content of the poly-1,3,4-oxadiazoles and the precursor polyhydrazides was sufficiently large so as to offer an analytical method for following conversion. From oxygen analyses of the heated samples of the polyhydrazides, the per cent of polyhydrazides remaining was readily and accurately determined.

The conversion of these polyhydrazides (Figs. 3–6) to poly-1,3,4-oxadiazoles followed first-order kinetics over 80–90% of reaction. The kinetic data and thermodynamic quantities, determined in the usual manner, are summarized in Table VIII.

TABLE VIII
Kinetic Data and Thermodynamic Quantities for the Conversion of Polyhydrazides to Poly-1,3,4-oxadiazoles

Reaction[a]	Temp., °C.	k, sec.$^{-1}$	$\Delta E\ddagger$, Kcal.	$\Delta S\ddagger$ (255°C.), e.u.
A → A′	255	6.81×10^{-6}	50.4	14.0
	265	2.03×10^{-5}		
	277	5.28×10^{-5}		
	285	8.89×10^{-5}		
B → B′	255	3.06×10^{-6}	62.0	34.2
	265	1.36×10^{-5}		
	277	4.47×10^{-5}		
C → C′	255	8.89×10^{-6}	53.0	16.0
	265	3.40×10^{-5}		
	277	6.81×10^{-5}		
D → D′	222	2.01×10^{-5}	49.0	16.7
	242	7.67×10^{-5}		
	255	2.67×10^{-4}		

[a] For polymer structures, see Table I.

For the reactions of A → A′, C → C′, and D → D′, where there was a wide variation in the substituent groups on the hydrazide linkages, the specific velocity constants (k) were quite different. However, for these same reactions, there were only small differences in the $\Delta E\ddagger$ and $\Delta S\ddagger$ values, and the $\Delta S\ddagger$ values were positive. The explanation of these results may be related to the fact that these reactions were carried out in the solid state and on highly crystalline polymers. It might be argued that the

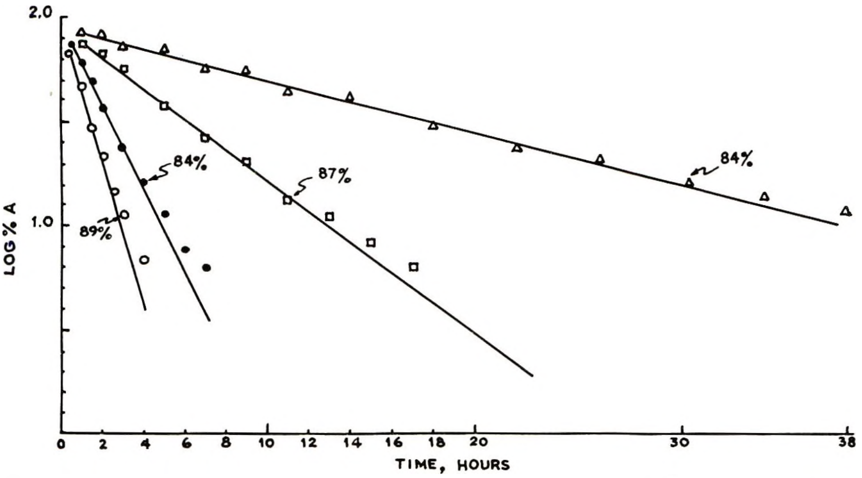

Fig. 3. First-order rate plots of A → A′ at four temperatures: (△) 255°C.; (□) 265°C.; (●) 277°C.; (○) 285°C.

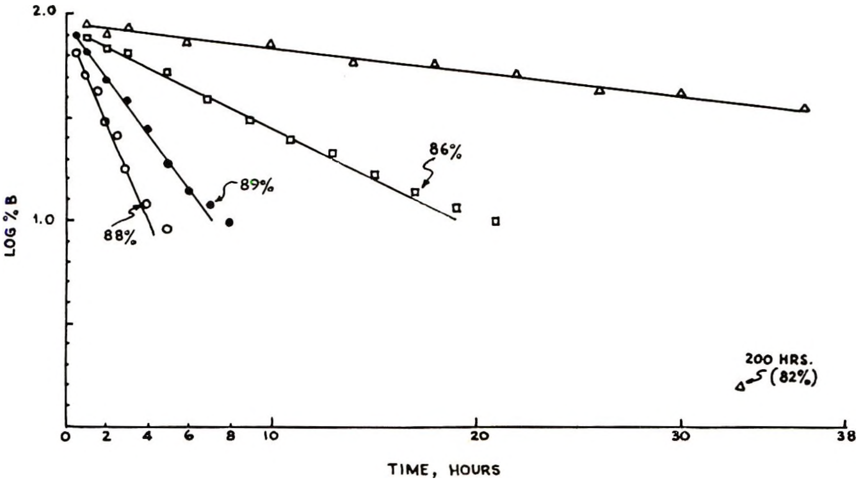

Fig. 4. First-order rate plots of B → B′ at four temperatures: (△) 255°C.; (□) 265°C.; (●) 277°C.; (○) 285°C.

energy required to go from reactants to the transition state is comparable to the lattice energy of the crystallites involved. This is supported by the fact that the poly-1,3,4-oxadiazoles, although crystalline, have different crystalline patterns from the precursor polyhydrazides. Thus, the reactions in question might be represented in this manner:

Reactants (crystalline polymer) → Transition state → Products (different crystalline polymer)

Since the lattice energies of these polyhydrazides should be of the same order of magnitude, the difference in $\Delta E\ddagger$ values should be small. Sim-

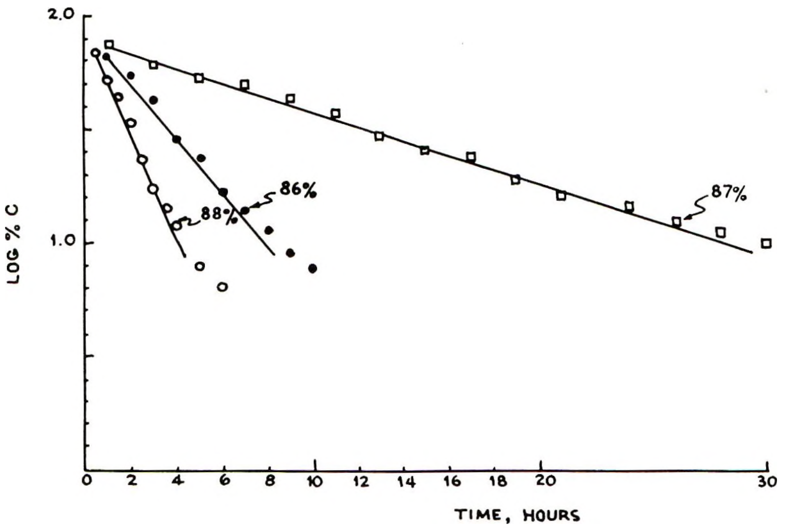

Fig. 5. First-order rate plots of C → C′ at three temperatures: (□) 255°C.; (●) 265°C.; (○) 277°C.

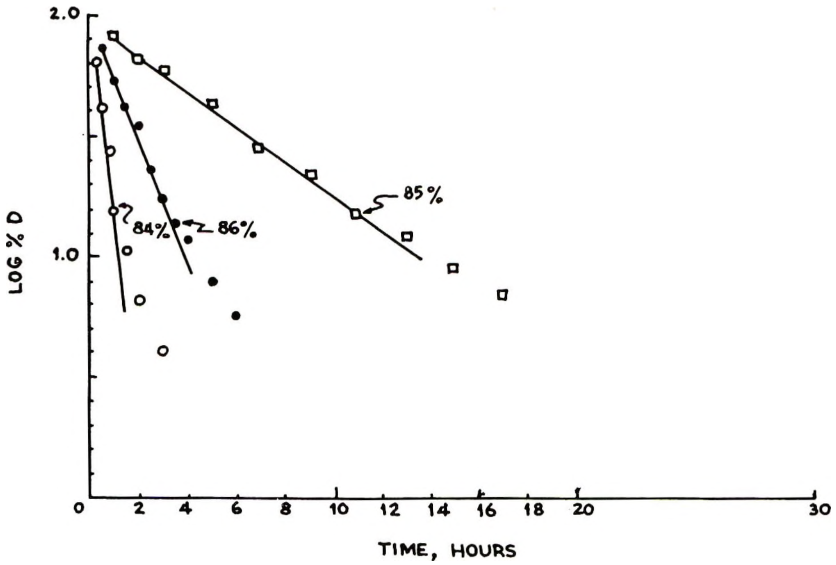

Fig. 6. First-order rate plots of D → D′ at three temperatures: (□) 222°C.; (●) 242°C.; (○) 255°C.

ilarly, the small differences and positive values for the $\Delta S^\ddagger$ might be explained. For, even though in these reactions cyclic intermediates are being formed from noncyclic reactants, the decrease in order in the system on going from the highly crystalline polyhydrazides to the transition state would be such that the $\Delta S^\ddagger$ value would be positive. Since this decrease in order would be comparable for all of the polyhydrazides in question, the $\Delta S\ddagger$ values would not be markedly different.

By the same argument, the larger values of $\Delta E\ddagger$ and $\Delta S\ddagger$ for the B → B′ reaction would be explained on the basis of the increased order in the polyhydrazide B due to the higher crystallinity of the homopolymer.

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Résumé

Les propriétés thermiques d'une série de polyhydrazides et des poly-1,3,4-oxadiazoles correspondants ont été étudiées, en utilisant des techniques thermométriques différentielles et thermogravimétriques. En outre, des vitessus de conversion des polyhydrazides en oxadiazoles correspondant ont été mesurées. En général, la perte de poids des polyhydrazides se passent en 3 étapes distinctes correspondant respectivement à la perte d'eau absorbée, à la cyclodéhydratation et à la décomposition in-situ des poly-1,3,4-oxadiazoles formés. Les polyoxadiazoles montrent en général uniquement une perte de poids en dessous de 700°C correspondant à la décomposition et à à la volatilisation du substrat lui-même. Ces données indiquent clairement que la présence de liaisons carbone-carbone aliphatiques dans la chaîne principale du polymère réduit la température à laquelle la décomposition des polyoxadiazoles se manifeste. Les diagrammes thermométriques différentiels correspondants donnent des résultats complémentaires concernant les transitions de phases au sein de ces polymères et indiquent en général, que les poly-1,3,4-diazoles formés in situ décomposent avant d'atteindre leur point de fusion intrinsèque (dans les conditions spécifiques de ces expériences). La comparaison des poly-1,3,4-oxadiazoles préparés dans les conditions dynamiques rapides des techniques différentielles et thermogravimétriques utilisées (30°C./min.) avec les données de vitesses isothermes suggèrent clairement des différences structurelles dans les polyoxadiazoles préparés par les deux méthodes différentes. En général, ΔE^* pour les oxadiazoles de conversion des hydrazides s'élève à 49–53 Kcal/mole alors que ΔS^* s'élève à 14–17 e.u. Toutefois ΔE^* et ΔS^{**} pour le polymère contenant exclusivement des liens 1,3-phénylène entre les groupes oxadiazoles de départ apparait avoir un ΔH beaucoup plus élevé ($\Delta E^* = 62$ Kcal/mole, $\Delta S^* = 34$ e.u.) Cette différence marquée est expliquée sur la base d'un ordre plus élevé résultant d'un degré de cristallinité plus poussé au sein du polyhydrazide.

Zusammenfassung

Die thermischen Eigenschaften einer Reihe von Polyhydraziden und der entsprechenden Poly-1,3,4-oxadiazole wurden mit differentialthermometrischen und thermogravimetrischen Methoden untersucht, Ausserdem wurde die Umwandlungsgeschwindigkeit der Polyhydrazide zu den entsprechenden Oxadiazolstrukturen gemessen. Im allgemeinen tritt ein Gewichtsverlust bei Polyhydraziden in drei Stufen auf, welche dem Verlust von absorbiertem Wasser, der Zyklodehydratisierung und der Zersetzung der in situ gebildeten Poly-1,3,4-oxadiazole entsprechen. Die Polyoxadiazole zeigen im allgemeinen nur eine, der Zersetzung und Verflüchtigung des Substrats selbst entsprechende Gewichtsverluststufe (unterhalb 700°C.) Die Ergebnisse zeigen klar, dass die Anwesenheit aliphatischer Kohlenstoff-Kohlenstoff-Bindungen in der Polymerkette die Zersetzungstemperatur der Polyoxadiazole herabsetzt. Entsprechende differentialthermometrische Diagramme liefern zusätzliche Daten für Phasenumwandlungen in den Polymeren und zeigen im allgemeinen, dass sich die in situ gebildeten Poly-1,3,4-oxadiazole zersetzen, bevor sie ihre Schmelztemperatur erreichen (unter den spezifischen Versuchsbedingungen). Ein Vergleich der unter den (raschen) dynamischen Bedingungen der verwendeten differential thermometrischen und thermogravimetrischen Verfahren (30°C./min) dargestellten Poly-1,3,4-oxadiazole mit isothermen Geschwindigkeitsdaten lassen klar Feinstrukturunterschiede bei den nach den beiden verschiedenen Verfahren dargestellten Polyoxadiazolen erkennen. Im allgemeinen beträgt ΔE^* für die Hydrazid-Oxadiazol-Umwandlung etwa 49–53 Kcal/Mol, während sich ΔS^* auf 14–17 E.U. beläuft. Für Polymere mit ausschliesslich 1,3-Phenylengliedern zwischen Oxadiazolanfangsgruppen scheinen jedoch ΔE^{**} und ΔS^{**} beträchtlich höher ($\Delta E^* = 62$ Kcal/Mol, $\Delta S^* = 34$ E.U.) zu sein. Dieser auffallende Unterschied wird auf Grundlage der durch den höheren Kristallinitätsgrad des Polyhydrazids bedingten erhöhten Ordnung erklärt.

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Cationic Graft Copolymerization of Styrene onto Chlorinated Butyl Rubber

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Synopsis

The graft copolymerization of styrene onto chlorinated butyl rubber (Cl-IIR) with stannic chloride as cationic catalyst was studied in cyclohexane, and the rate of polymerization, per cent grafting and grafting efficiency were obtained. Polymerization was carried out in a sealed tube. The product was precipitated in methanol and dried. The increase in weight of Cl-IIR used was regarded as styrene conversion, and the increase in weight after extraction by boiling acetone as the weight of grafted styrene. Grafting was confirmed by fractional dissolution and infrared spectra. The rate of polymerization of styrene was proportional to concentrations of styrene, Cl-IIR and $SnCl_4$. The per cent grafting increased with styrene and $SnCl_4$ concentration, but was constant with Cl-IIR concentration. It also increased with time and with halogen content in the polymer. The addition of a polar solvent such as nitrobenzene greatly promoted the grafting reaction and the per cent grafting was 200%.

INTRODUCTION

Cationic polymerization can be initiated by carbonium ions formed by reaction of a metal halide with an alkyl halide. If a halogenated polymer instead of an alkyl halide is used in such a reaction, a polymer containing carbonium ions will be obtained, and if suitable monomer which can be polymerized by a cationic mechanism is present in the reaction mixture, the polymerization can start at macromolecular ions and monomer can be grafted onto the polymer. Thus graft copolymer can be obtained.

Plesch[1] treated solutions of poly(vinyl chloride) and of vinyl chloride–vinylidene chloride copolymers containing a monomer, styrene or indene, with aluminum chloride or titanium tetrachloride at 20°C. to 60°C.; the solvents used were chlorobenzene, nitrobenzene, and mixtures of these. And it was found that degradation accompanied grafting but this could be considerably reduced by working at ambient rather than elevated temperature.

Kockelbergh and Smets[2] made other attempts at grafting in which the carbonium ions were produced in the side chains. They treated carbon disulfide solutions of chloromethylated or bromomethylated polystyrenes containing a monomer, isobutene, with aluminum bromide as a catalyst. Graft copolymer was obtained.

Haas et al.[3] obtained grafts of styrene with poly-*p*-methoxystyrene by using another method, in nitrobenzene–carbon tetrachloride mixtures as a solvent at 0–20°C.

Not much research, however, has been conducted in the field of cationic graft polymerization, nor have the influences on rate of polymerization, per cent grafting, etc. been elucidated.

In the present study to prevent degradation, chlorinated butyl rubber (chlorinated isoprene–isobutene copolymer, Cl-IIR) was used as backbone polymer. Copolymerization of styrene and Cl-IIR was carried out with stannic chloride in cyclohexane under various conditions, and mixtures of white rubbery graft copolymer and polystyrene were obtained. The rate of polymerization was obtained from conversion–time curves. Percentage grafting and grafting efficiency were calculated from the increase in weight. The kinetics are also discussed.

Grafting was confirmed by infrared spectra of residues extracted by boiling acetone.

EXPERIMENTAL

Materials

Cl-IIR used was HT 1066 (Esso), molecular weight 3.5–4.0 × 10^5, 1.1–1.3 wt.-% (2 mole-%) chlorine content. Cl-IIR was dissolved in cyclohexane, precipitated in methanol after removal of impurities, filtered, dried *in vacuo*, and used for polymerization.

IIR used was Polysar 301, molecular weight 6 × 10^5. The purification method was the same as described for Cl-IIR.

TABLE I
Reaction Conditions for Obtaining Br-IIR and Bromine Contents of the Product

No.	Wt. IIR, g.	Wt. *N*-bromosuccinimide, g.	Br content, wt.-%
Br-0	56.36	0	0
Br-1	56.36	1.78	1.47
Br-2	56.36	3.56	2.27
Br-3	56.36	5.34	2.73

Brominated butyl rubbers differing in extent of bromination were obtained as follows.[4] A flask containing a cyclohexane solution of IIR and suitable amounts of *N*-bromosuccinimide was heated with stirring on a water bath for 30 min. After purification by precipitation with methanol and drying, the brominated butyl rubber obtained (Br-IIR) was used for graft polymerization. Table I shows reaction conditions for obtaining Br-IIR and bromine content.

Styrene and isoprene monomers were purified by conventional methods just before use.

Cyclohexane and nitrobenzene solvents, and stannic chloride, titanium tetrachloride, and boron trifluoride etherate catalysts were purified by conventional methods.

Polymerization

Purified, dried Cl-IIR was dissolved completely in cyclohexane in a test tube, and styrene was added. The mixture was shaken, cooled, and degassed. The polymerization reaction was started by addition of a cyclohexane solution of stannic chloride. The test tube was cooled and sealed. The polymerization reaction was carried out at 20°C. for a given period of time. The reaction mixture was precipitated with methanol, filtered and dried *in vacuo*.

Styrene conversion was calculated from increase in weight after drying, and grafted styrene from increase in weight of the insoluble portion after extraction with boiling acetone.

Infrared Spectra

Infrared absorption spectra of thin films cast onto rock salt plates from cyclohexane solutions of Cl-IIR, polystyrene (soluble in boiling acetone), and copolymer (insoluble in boiling acetone) were obtained with a Japan Spectroscopic Co., Ltd. spectrometer.

Intrinsic Viscosity

The intrinsic viscosity $[\eta]$ of benzene solutions of polymer were obtained with an Ubbelohde viscometer at 30°C. The intrinsic viscosity of polystyrene $[\eta]_{\mathrm{St}}$ was calculated from the following viscosity equation of mixtures by the conventional method:

$$[\eta] = (a/A)[\eta]_{\mathrm{Cl\text{-}IIR}} + (b/A)[\eta]_{\mathrm{St}} \tag{1}$$

where A is overall yield, a is weight of Cl-IIR, b is styrene conversion and $[\eta]$, $[\eta]_{\mathrm{Cl\text{-}IIR}}$ and $[\eta]_{\mathrm{St}}$ are intrinsic viscosity of polymer mixture, Cl-IIR, and polystyrene (grafted and homopolystyrene), respectively.

The percentage grafting is the ratio of the increase in weight of the acetone-insoluble portion against the weight of Cl-IIR used, namely, the ratio of grafted polystyrene to Cl-IIR used. The grafting efficiency is the ratio of grafted polystyrene to total polystyrene obtained.

RESULTS AND DISCUSSION

The acetone-insoluble portion was considered graft copolymer. When IIR instead of Cl-IIR was used to react with styrene, the weight after extraction with boiling acetone did not increase, that is, no graft polymerization occurred.

Figure 1 shows infrared spectra of the polymers. Figure 1*A* is the infrared spectrum of Cl-IIR, that of Figure 1*B* is polystyrene extracted with boiling acetone, and Figure 1*C* is that of the extracted residue of the product (run C-5). At around 3000 cm.$^{-1}$, the spectrum of Cl-IIR showed a strong band at 2940 cm.$^{-1}$ (associated with —CH_3). Strong bands were seen at 3060, 3026, 2924, and 2850 cm.$^{-1}$ (associated with —CH_2—) in the spectrum of polystyrene (Fig. 1*B*). Both of them appeared, overlapping one another in the spectrum of the residue (Fig. 1*C*).

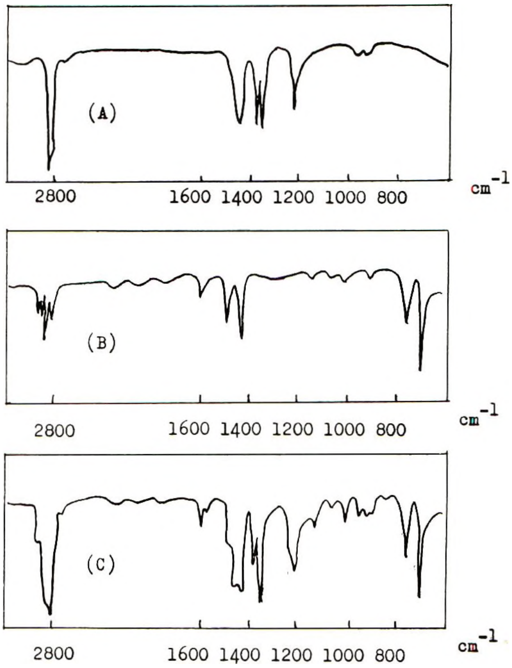

Fig. 1. Infrared spectra of polymers: (*A*) Cl-IIR; (*B*) polystyrene obtained in experiment C-5; (*C*) graft copolymer obtained in experiment C-5.

In the range of 2800–1500 cm.$^{-1}$, Figure 1*A* showed no band, but Figure 1*C* had bands of polystyrene at 1946 and 1603 cm.$^{-1}$. At under 1500 cm.$^{-1}$, in a band was observed at 1475 cm.$^{-1}$ (associated with —CH_2—) in Figure 1*A;* in Figure 1*B* two bands appeared 1495 and 1455 cm.$^{-1}$ (associated with —C = C—). The spectrum of the residue (Fig. 1*C*) had all of them, as well as bands at 1028, 906, 765, and 700 cm.$^{-1}$, associated with polystyrene. Thus, the spectrum of the portion insoluble in boiling acetone showed specific absorptions of both polymers, Cl-IIR and polystyrene, indicating that polystyrene is grafted onto Cl-IIR.

It was similarly confirmed that isoprene grafted onto Cl-IIR. Methyl ethyl ketone was used in extraction.

Kinetics

Effect of Styrene Concentration on Rate of Polymerization. Conversion–time curves such as Figure 2 were obtained for various styrene concentrations at constant Cl-IIR and stannic chloride concentrations.

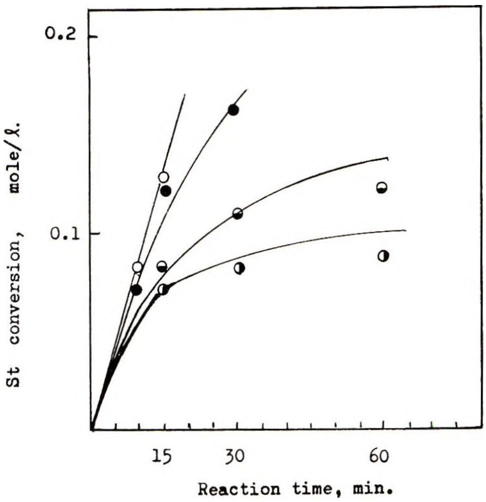

Fig. 2. Influence of styrene concentration on polymerization rate: (○) [St] = 3.500 mole/l.; (●) [St] = 2.625 mole/l.; (◒) [St] = 1.750 mole/l.; (◑) [St] = 0.875 mole/l. $[\mathrm{SnCl}]_4 = 8.57 \times 10^{-2}$ mole/l., [Cl-IIR] = 20 g./l., in cyclohexane, 20°C.

The rate of polymerization increased with increasing styrene concentration. In the case of low monomer concentration, the rate decreased gradually after 30 min. The relations between styrene concentration and polymerization rate in the early stage, R_p, are shown in Table II.

TABLE II
Relation between Styrene Concentration and Polymerization Rate[a]

[St], mole/l.	$R_p \times 10^3$, mole/l. min.
0.875	3.04
1.750	4.56
2.625	6.90
3.500	8.04

[a] Conditions: [Cl-IIR] = 20 g./l., $[\mathrm{SnCl}_4] = 8.57 \times 10^{-2}$ mole/l., in cyclohexane, 20°C.

The logarithm of R_p was plotted versus the logarithm of styrene concentration as shown in Figure 3. The slope is about 0.9. It is considered that R_p is proportional to styrene concentration.

Effect of Stannic Chloride Concentration on Rate of Polymerization. Conversion–time curves were obtained at various stannic chloride concen-

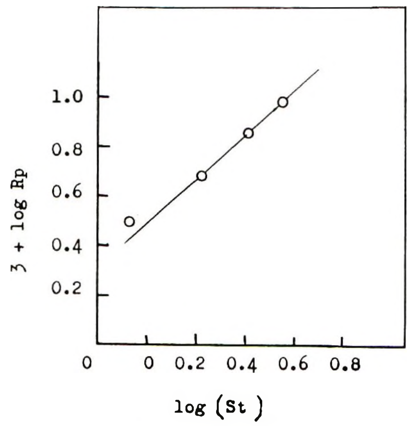

Fig. 3. Relation between styrene concentration and polymerization rate $[SnCl]_4 = 8.57 \times 10^{-2}$ mole/l., [Cl-IIR] = 20 g./l., in cyclohexane, 20°C.

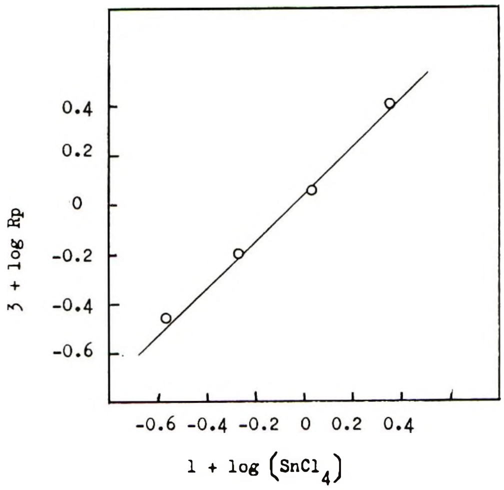

Fig. 4. Relation between stannic chloride concentration and polymerization rate. [St] = 1.75 mole/l., [Cl-IIR] = 20 g./l., in cyclohexane, 20°C.

trations, and R_p was calculated in the early stage of polymerization. These results are shown in Table III and Figure 4.

TABLE III

Relation between Stannic Chloride Concentration and Polymerization Rate[a]

$[SnCl_4] \times 10^2$, mole/l.	$R_p \times 10^3$, mole/l.-min.
2.14	0.42
4.28	0.68
8.57	1.16
17.14	2.44

[a] Conditions: [St] = 1.75 mole/l., [Cl-IIR] = 20 g./l., in cyclohexane, 20°C.

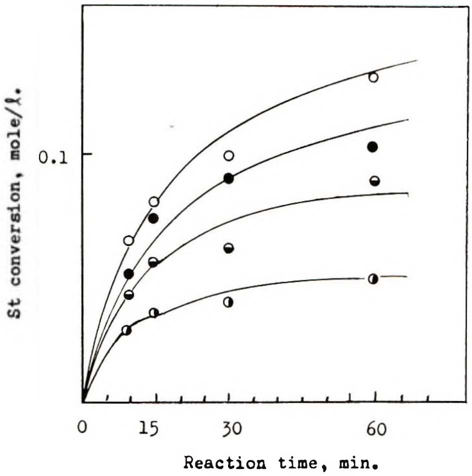

Fig. 5. Influence of Cl-IIR concentration on polymerization rate: (O) [Cl-IIR] = 20 g./l.; (●) [Cl-IIR] = 15 g./l.; (◒) [Cl-IIR] = 10 g./l.; (◑) (Cl-IIR] = 5 g./l. [St] = 1.75 mole/l., $[SnCl]_4 = 8.57 \times 10^{-2}$ mole/l., in cyclohexane, 20°C.

Figure 4 indicates that R_p is proportional to stannic chloride concentration.

Effect of Cl-IIR Concentration on Rate of Polymerization. Conversion–time curves were obtained at various Cl-IIR concentrations. As shown in Figure 5, the styrene conversion increased with increasing Cl-IIR concentration.

Polymerization rates obtained from these curves are shown in Table IV.

TABLE IV

Relation between Cl-IIR Concentration and Polymerization Rate[a]

[Cl-IIR], g./l.	$R_p \times 10^3$, mole/l.
5	0.33
10	0.61
15	0.86
20	1.38

[a] Conditions: [St] = 1.75 mole/l., $[SnCl]_4 = 8.57 \times 10^{-2}$ mole/l., in cyclohexane, 20°C.

Figure 6 shows the relation of Cl-IIR concentration on polymerization rate R_p. It was found that R_p is proportional to Cl-IIR concentration.

From above results, the polymerization rate in the early stage is expressed by eq. (2):

$$R_p = k[\mathrm{St}][\mathrm{SnCl_4}][\mathrm{Cl\text{-}IIR}] \qquad (2)$$

Activation Energy. Graft polymerization of styrene onto Cl-IIR was carried out with stannic chloride at 20, 40, and 60°C. The relation between rate constant k and absolute temperature T is shown in Table V and Figure 7.

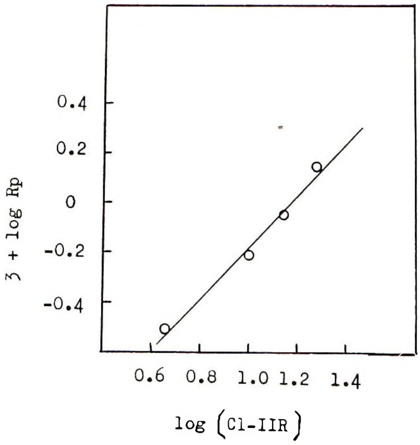

Fig. 6. Relation between Cl-IIR concentration and polymerization rate. [St] = 1.75 mole/l., $[SnCl]_4$ = 8.57 × 10^{-2} mole/l., in cyclohexane, 20°C.

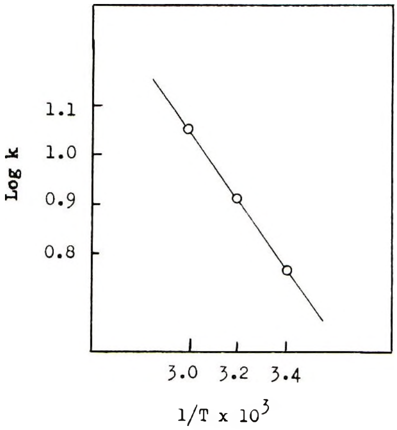

Fig. 7. Relation between rate constant k and absolute temperature T. [St] = 1.75 mole/l. $[SnCl_4]$ = 8.57 × 10^{-2} mole/l., [Cl-IIR] = 20 g./l., in cyclohexane.

Values of the apparent activation energy E and frequency constant A obtained were $E = 3.1$ kcal./mole, $A = 1.53 \times 10^{14}$/min. This value of E was considered to be reasonable for cationic polymerization.

TABLE V

Relation between Rate Constant k and Absolute Temperature T[a]

Temp. t, °C.	$1/T$	$k \times 10^3$	$3 + \log k$
20	3.41×10^{-3}	6.18	0.7910
40	3.20×10^{-3}	8.49	0.9289
60	3.00×10^{-3}	11.64	1.0660

[a] Conditions: [St] = 1.75 mole/l., $[SnCl_4]$ = 8.57 × 10^{-2} mole/l., [Cl-IIR] = 20 g./l., in cyclohexane.

The above results lead to the cationic polymerization mechanism given in eqs. (3)–(8).

$$\text{R-Cl} + \text{SnCl}_4 \xrightarrow{k_i} \text{R}^+ + \text{SnCl}_5^- \tag{3}$$

$$\text{H}_2\text{O} + \text{SnCl}_4 \xrightarrow{k_i'} \text{H}^+ + \text{SnCl}_4(\text{OH})^- \tag{4}$$

$$\text{R}^+ + \text{M} \xrightarrow{k_a} \text{P}_1^+ \tag{5}$$

$$\text{H}^+ + \text{M} \xrightarrow{k_a'} \text{M}^+ \tag{6a}$$

$$\text{M}^+ + \text{M} \xrightarrow{k_a''} \text{P}^+ \tag{6b}$$

$$P_i^+ + \text{M} \xrightarrow{k_p} \text{P}_{i+1}^+ \tag{7}$$

$$P_j^+ \xrightarrow{k_t} P_j \tag{8}$$

where R-Cl is Cl-IRR, M is styrene.
If a steady state is assumed,

$$d[\text{P}^+]/dt = k_a\ [\text{R}^+][\text{M}] + k_a''\ [\text{M}^+][\text{M}] - k_t\ [\text{P}^+] = 0 \tag{9}$$

so that

$$\begin{aligned}[\text{P}^+] &= (k_a/k_t)\ [\text{R}^+][\text{M}] + (k_a''/k_t)\ [\text{M}^+][\text{M}] \\ &= (k_i/k_t)\ [\text{R-Cl}][\text{SnCl}_4] + (k_i'/k_t)\ [\text{H}_2\text{O}][\text{SnCl}_4] \end{aligned} \tag{10}$$

As R_p is equal to k_p [M][P$^+$]

$$\text{R}_p = (k_p k_i/k_t)\ [\text{M}][\text{SnCl}_4][\text{R-Cl}] + (k_p k_i'/k_t)\ [\text{M}][\text{SnCl}_4][\text{H}_2\text{O}]$$

$$R_p = k[\text{M}][\text{SnCl}_4]([\text{R-Cl}] + [\text{H}_2\text{O}])$$

As homopolystyrene was obtained in reaction mixtures as well as graft copolymers, the presence of traces of water in the reaction system was considered, and the above mechanism was obtained. The water in the reaction system might be considered to be involved in Cl-IIR. Thus the scheme proposed is in accord with one obtained from conversion-time curves.

TABLE VI
Intrinsic Viscosities of Polymer Mixture, Graft Copolymer, and Free Polystyrene

reaction time (min).	$[\eta]$[a]	$[\eta]_{\text{graft}}$[a]	$[\eta]_{\text{St}}$[a]
30	0.634	0.642	0.125
60	0.617	0.691	0.310

[a] In benzene, 30°C.

TABLE VII
Influence of Styrene, Stannic Chloride, and Cl-IIR Concentration on Intrinsic Viscosities of Polymer Mixture[a]

[Cl-IIR], g./l.	[St], mole/.	$[SnCl_4] \times 10^2$, mole/l.	Overall yield, g./l.	Styrene conversion, mole/l.	$[\eta]$	$[\eta]_{St}$[b]	$\bar{P}_n$[c]
5	1.75	8.57	8.8	0.036	0.609	0.450	580
10	1.75	8.57	16.0	0.058	0.623	0.445	570
15	1.75	8.57	22.7	0.074	0.632	0.442	560
20	1.75	8.57	28.3	0.080	0.643	0.433	550
20	0.875	8.57	27.8	0.075	0.648	0.437	555
20	1.750	8.57	28.3	0.080	0.643	0.433	550
20	2.625	8.57	32.6	0.121	0.637	0.488	650
20	3.50	8.57	33.1	0.126	0.632	0.480	635
20	1.75	2.14	25.1	0.050	0.714	0.654	980
20	1.75	4.28	27.0	0.067	0.700	0.617	900
20	1.75	8.57	28.3	0.080	0.643	0.433	550
20	1.75	17.14	30.0	0.097	0.628	0.426	535

[a] Reaction in cyclohexane, 20°C., 15 min.

[b] Value calculated by intrinsic viscosity equation of mixed polymers.

[c] Calculated by $\bar{P}_n = 1770 [\eta]_{St}^{1.40.5}$

Viscosity of Polymers. Intrinsic viscosities of the polymer mixture, graft copolymer, and free polystyrene are listed in Table VI and those of the polymer mixture obtained 15 min. after initiation of polymerization are shown in Table VII.

The intrinsic viscosity $[\eta]$ of the polymer mixture (graft copolymer and polystyrene) increased with increasing Cl-IIR concentration and decreased with increasing styrene concentration and stannic chloride concentration. The intrinsic viscosity of polystyrene $[\eta]_{St}$ was obtained by using the viscosity equation of the mixed polymer for the sake of convenience. $[\eta]_{St}$ decreased with increasing Cl-IIR concentration and stannic chloride concentration and increased with increasing styrene concentration.

These tendencies could be explained by considering that the polystyrene ratio in the product decreased with increasing Cl-IIR concentration, and that thus the per cent grafting became lower with decreasing styrene concentration, and that the intrinsic viscosity of Cl-IIR was 0.730.

These results were also in accord with the rate equation obtained above.

Per Cent Grafting and Grafting Efficiency

Influence of Time. The per cent grafting and grafting efficiency for various reaction times are shown in Table VIII and Figure 8.

The per cent grafting increased with reaction time, but was only 45% after 2 hr. On the other hand, grafting efficiency increased slowly.

Grafting efficiency G_e at the early stage of the polymerization is expressed as follows from rate equation:

$$G_e = k[\text{Cl-IIR}]/(k[\text{Cl-IIR}] + k'[H_2O])$$

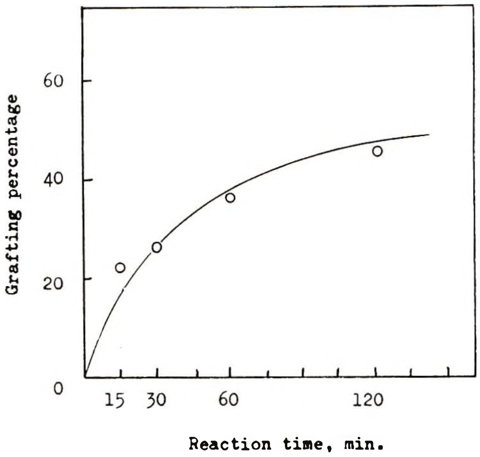

Fig. 8. Influence of time on per cent grafting. [St] = 1.75 mole/l., [$SnCl_4$] = 8.57 × 10^{-2} mole/l., [Cl-IIR] = 20 g./l., in cyclohexane, 20°C.

TABLE VIII
Influence of Time on Per Cent Grafting and Grafting Efficiency[a]

Reaction time, min.	Overall yield, g./l.	Graft copolymer, g./l.	Homopoly-styrene, mole/l.	Branch of styrene mole/l.	Grafting, %	Grafting efficiency, %
15	32.6	24.3	0.080	0.041	21.5	34.1
30	32.7	25.1	0.073	0.049	25.5	40.0
60	35.8	27.1	0.084	0.068	35.5	45.0
120	37.6	28.9	0.084	0.086	44.5	50.6

[a] Conditions: [St] = 1.75 mole/l., [$SnCl_4$] = 8.57 × 10^{-2} mole/l., [Cl-IIR] = 20 g./l., in cyclohexane, 20°C.

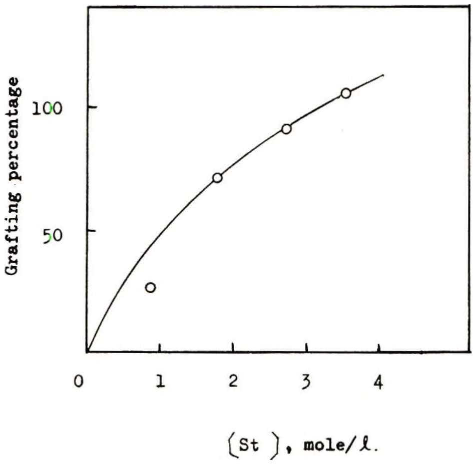

Fig. 9. Influence of styrene concentration of per cent grafting. [$SnCl_4$] = 8.57 × 10^{-2} mole/l., [Cl-IIR] = 20 g./l., in cyclohexane, 20°C., 6 hr.

TABLE IX
Influence of Styrene Concentration on Per Cent Grafting and Grafting Efficiency[a]

Expt. no.	Cyclo-hexane, l.	[St], mole/l.	Overall yield, g./l.	Branch of styrene, mole/l.	Homo-poly-styrene, mole/l.	Grafting, %	Grafting effi-ciency, %
S-1	0.9	0.875	39.2	0.052	0.132	27.0	28.1
S-2	0.8	1.750	172.9	0.135	1.334	70.5	9.2
S-3	0.7	2.625	262.6	0.174	2.160	90.5	7.5
S-4	0.6	3.500	371.2	0.202	3.174	105.0	6.0

[a] Conditions: $[SnCl_4] = 8.57 \times 10^{-2}$ mole/l., [Cl-IIR] = 20 g./l., 20°C., 6 hr.

This equation was in satisfactory agreement with the data over the first 2 hr.

Influence of Styrene Concentration. The polymerization was carried out to determine the influence of styrene concentration on per cent grafting and grafting efficiency at various styrene concentrations. Results are shown in Table IX and Figure 9.

Per cent grafting increased with styrene concentration. But the rate of increasing in per cent grafting decreased, and it was only 100% in the system containing 8.75 mole/l. styrene without cyclohexane. Thus, the increase of styrene could raise the per cent grafting, but a high per cent grafting could not be attained, as grafting efficiency decreased with the increasing styrene concentration due to the formation of a large amount of homopolystyrene.

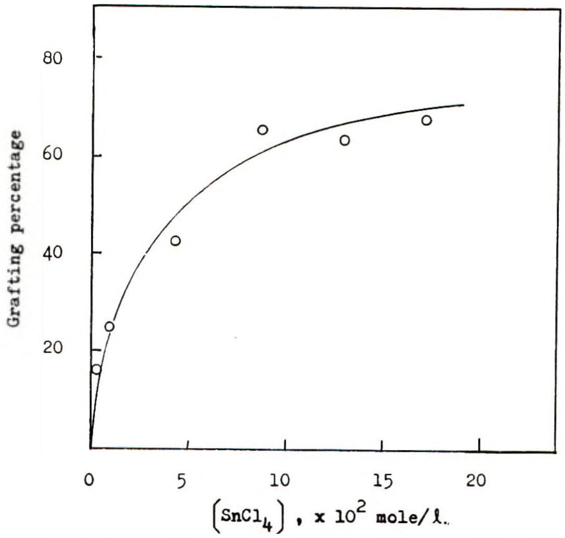

Fig. 10. Influence of stannic chloride concentration on per cent grating. [St] = 1.75 mole/l., [Cl-IIR] = 20 g./l., in cyclohexane, 20°C., 6 hr.

TABLE X
Influence of Stannic Chloride Concentration on
Per Cent Grafting and Grafting Efficiency[a]

Expt. no.	[SnCl] $\times 10^2$, mole/l.	Overall yield, g./l.	Graft copolymer g./l.	Branch of styrene, mole/l.	Homopolystyrene, mole/l.	Grafting, %	Grafting efficiency, %
C-1	0.0857	21.9	20.0	0	0.018	0	0
C-2	0.428	27.2	23.3	0.032	0.038	16.5	45.8
C-3	0.857	29.4	25.0	0.048	0.042	25.0	53.2
C-4	4.28	74.1	28.5	0.082	0.438	42.5	15.7
C-5	8.57	96.9	33.0	0.124	0.614	65.0	16.9
C-6	12.85	96.2	32.6	0.121	0.611	63.0	16.5
C-7	17.14	111.3	33.4	0.129	0.749	67.0	14.7

[a] Conditions: [St] = 1.75 mole/l., [Cl-IIR] = 20 g./l., in cyclohexane, 20°C., 6 hr.

Influence of Stannic Chloride. The polymerization was carried out at various stannic chloride concentrations. Results are shown in Table X and Figure 10.

Styrene did not graft onto Cl-IIR at 0.0857×10^{-2} mole/l. of stannic chloride, in spite of some formation of homopolystyrene. The per cent grafting increased with increasing stannic chloride concentration, but at above 8.57×10^{-2} mole/A. was constant at about 65%. It was not possible to obtain a high percentage of grafting by increasing the catalyst concentration.

Influence of Cl-IIR Concentration. Polymerization was carried out at various concentrations of Cl-IIR, the concentrations of styrene and stannic chloride being kept constant (Table XI and Fig. 11).

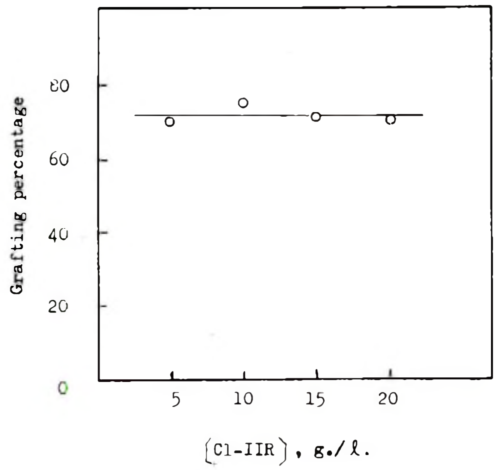

Fig. 11. Influence of Cl-IIR concentration on per cent grafting. [St] = 1.75 mole/l., $[SnCl_4] = 8.57 \times 10^{-2}$ mole/l., in cyclohexane, 20°C., 6 hr.

TABLE XI

Influence of Cl-IIR Concentration on Per Cent Grafting and Grafting Efficiency[a]

Expt. no.	[Cl-IIR], g./l.	Overall yield, g./l.	Graft copolymer, g./l.	Branch of styrene, mole/l.	Homo-poly-styrene, mole/l.	Grafting, %	Grafting effi-ciency, %
R-1	5	127.5	8.5	0.034	1.140	70.0	2.9
R-2	10	126.9	17.5	0.072	1.052	75.0	6.4
R-3	15	110.6	25.7	0.103	0.816	71.3	11.2
R-4	20	97.6	34.0	0.134	0.612	70.0	17.9

[a] Conditions: [St] = 1.75 mole/l. $[\mathrm{SnCl_4}] = 8.57 \times 10^{-2}$ mole/l., in cyclohexane, 20°C., 6 hr.

These results indicate that the per cent grafting was constant at about 70%, regardless of Cl-IIR concentration. This is quite understandable in view of considering the definition of grafting percentage. Since Cl-IIR and grafted polystyrene increased at the same ratio, grafting percentage remained at about the same value. Grafting efficiency, of course, increased with Cl-IIR concentration.

Influence of Polymerization Temperature. Polymerizations were carried out at 20, 40, and 60°C. to investigate the influence of the temperature on per cent grafting and grafting efficiency. Results are shown in Table XII.

Overall yield increased with the temperature, but per cent grafting tended to decrease slightly. The reason for this is considered to be that the rise of the temperature promoted the formation of homopolystyrene but restrained the propagation of grafting polystyrene. Therefore, grafting efficiency decreased with increasing temperature.

Influence of Halogen (Bromine) Content. The polymerization was carried out with brominated butyl rubber of various bromine contents to investigate the influence of halogen content on per cent grafting and grafting efficiency. Results are shown in Table XIII and Figure 12.

Per cent grafting increased with bromine content in Br-IIR. This is only natural because active sites in the polymer increased. Grafting efficiency also increased.

TABLE XII

Influence of Polymerization Temperature on Per Cent Grafting and Grafting Efficiency[a]

Temp. t, °C.	Overall yield, g./l.	Graft copolymer, g./l.	Branch of styrene, mole/l.	Homo-poly-styrene, mole/l.	Grafting, %	Grafting efficiency, %
20	97.6	32.9	0.124	0.622	64.5	16.6
40	126.6	30.7	0.103	0.922	53.5	10.0
60	168.5	29.0	0.087	1.341	45.0	6.1

[a] Conditions: [St] = 1.75 mole/l. $[\mathrm{SnCl}]_4 = 8.57 \times 10^{-2}$ mole/l., [Cl-IIR] = 20 g./l., in cyclohexane, 6 hr.

TABLE XIII

Influence of Halogen (Bromine) Content on Per Cent Grafting and Grafting Efficiency[a]

Expt. no.	Bromine content, wt.-%	Overall yield, g./l.	Graft copolymer, g./l.	Branch of styrene, mole/l.	Homo-poly-styrene, mole/l.	Grafting, %	Grafting effi-ciency, %
Br-0	0	172.2	20.0	0	1.460	0	0
Br-1	1.47	149.6	23.1	0.030	1.216	15.5	2.4
Br-2	2.27	135.9	27.1	0.068	1.046	35.5	6.9
Br-3	2.73	106.5	28.5	0.082	0.750	42.5	9.9

[a] Conditions: [St] = 1.75 mole/l., [SnCl]$_4$ = 8.57 × 10^{-2} mole/l., [Br-IIR] = 20 g./l., in cyclohexane, 20°C., for 6 hr.

TABLE XIV

Influence of Addition of Nitrobenzene on Per Cent Grafting and Grafting Efficiency[a]

Expt. no.	Nitro-benzene ratio[b]	Overall yield, g./l.	Graft copolymer, g./l.	Branch of styrene, mole/l.	Homo-poly-styrene, mole/l.	Grafting, %	Grafting efficiency, %
N-1	0	101.0	32.5	0.120	0.659	62.5	15.4
N-2	0.0625	114.6	36.5	0.149	0.751	82.5	17.4
N-3	0.1250	153.5	40.4	0.196	1.087	102.0	15.3
N-4	0.1875	182.2	58.9	0.374	1.185	194.5	24.0
N-5	0.2500	202.8	59.8	0.383	1.375	199.0	21.7

[a] Conditions: [St] 1.75 mole/l., [SnCl]$_4$ = 8.57 × 10^{-2} mole/l., [Cl-IIR] = 20 g./l., at 20°C., 6 hr.

[b] Nitrobenzene/cyclohexane + nitrobenzene (volume).

Influence of Solvent. The effect of polar solvent was studied as the polymerization was cationic. Nitrobenzene was added to cyclohexane in the various ratios, as shown in Table XIV and Figure 13. The mixed solvent was used for the polymerization reaction.

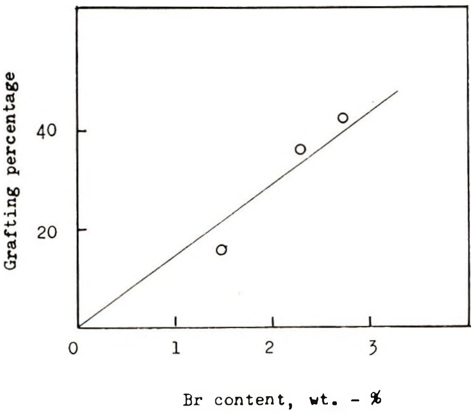

Fig. 12. Influence of halogen (Br) content on per cent grafting. [St] = 1.75 mole/l., [SnCl$_4$] = 8.57 × 10^{-2} mole/l., [Br-IIR] = 20 g./l., in cyclohexane, 20°C., 6 hr.

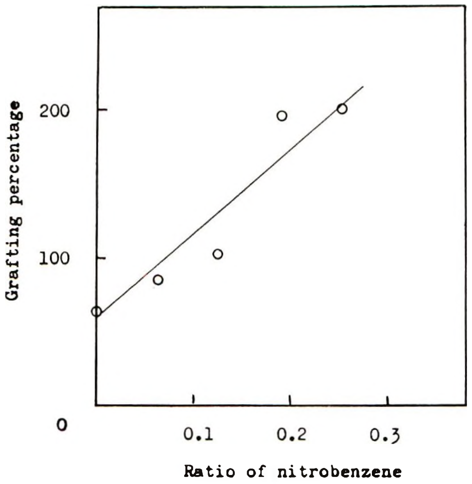

Fig. 13. Influence of a polar solvent (nitrobenzene) on per cent grafting. [St] = 1.75 mole/l., [$SnCl_4$] = 8.57 × 10^{-2} mole/l., [Cl-IIR] = 20 g./l., 20°C., 6 hr.

Grafting percentage increased with the addition of nitrobenzene and attained the highest value of any in the study (200%).

Grafting efficiency reached a considerably high value. The addition of a polar solvent such as nitrobenzene thus increased grafting percentage, but its use was limited as nitrobenzene was a nonsolvent for Cl-IIR.

TABLE XV
Influence of Kinds of Catalyst on Per Cent Grafting Percentage and Graft Efficiency[a]

Catalyst	Overall yield, g./l.	Graft copolymer, g./l.	Branch of polystyrene, mole/l.	Homopolystyrene, mole/l.	Grafting, %	Grafting efficiency, %
$SnCl_4$	107.1	32.5	0.120	0.717	62.5	14.3
$TiCl_4$	81.9	21.5	0.014	0.581	7.5	2.4
BF_3OEt_2	107.6	25.7	0.054	0.785	28.5	6.5

[a] Conditions: [St] = 1.75 mole/l., [Cat.] = 8.57 × 10^{-2} mole/l., [Cl-IIR] = 20 g./l., in cyclohexane, 20°C., 6 hr.

Influence of Type of Catalyst. The polymerization was carried out with stannic chloride, titanium tetrachloride, or boron trifluoride etherate as catalyst (Table XV). Stannic chloride was most active for grafting.

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Résumé

La copolymérisation grefée du styrène à du caoutchouc butylique chloré en présence de chlorure stannique comme catalyseur cationique a été étudié dans le cyclohexane, et la vitesse de polymérisation, le pourcentage de greffage et l'efficacité de greffage ont été déterminés. La polymérisation a été effectuée dans un tube scellé. Le produit était précipité dans le méthanol dessèché. L'augmentation en poids du caoutchouc butylique chloré utilisé était considérée comme un degré de conversion du styrène et l'accroissement en poids après extraction au moyen d'acétone bouillant comme étant le poids du styrène greffé. Les greffages étaient confirmés par dissolution fractionn ée et par spectrométrie infra-rouge. La vitesse de polymérisation styrène était proportionnelle à la concentration en styrène, en caoutchouc butylique chloré et en $SnCl_4$. Le pourcentage de greffage croissait avec la concentration en styrène et en $SnCl_4$, mais était constant pour les différentes concentrations en caoutchouc butylique chloré. Ce pourcentage croissait également avec le temps et avec une augmentation de teneur en halogène au sein du polymère. L'addition de solvants polaires, tel que le nitrobenzène, facilite grandement la réaction de greffage et le pourcentage de greffage peut atteindre 200%.

Zusammenfassung

Die Pfropfcopolymerisation von Styrol mit chloriertem Butylkautschuk mit Zinnchlorid als kationischem Katalysator wurde in Zyklohexan untersucht, und die Polymerisationsgeschwindigkeit, der aufgepfropfte Bruchteil und die Pfropfausbeute wurden bestimmt. Die Polymerisation wurde im zugeschmolzenen Rohr ausgeführt. Das Produkt wurde in Methanol ausgefällt und getrocknet. Die Gewichtszunahme des chlorierten Butylkautschuks wurde als Styrolumsatz angeommen und die Gewichtszunahme nach Extraktion mit siedendem Aceton als Gewicht des aufgepfropften Styrols. Die Aufpropfung wurde durch fraktionierte Auflösung und Infrarotspektroskopie bestätigt. Die Polymerisationsgeschwindigkeit des Styrols war der Konzentration von Styrol, chloriertem Butylkautschuk und $SnCl_4$ proportional. Der aufgepfroptfe Bruchteil nahm mit der Styrol- und $SnCl_4$-Konzentration zu, war jedoch von der konzentration des chlorierten Butylkautschuks unabhängig. Er nahm auch mit der Reaktionsdauer und mit steigendem Halogengehalt des Polymeren zu. Der Zusatz eines polaren Lösungsmittels wie Nitrobenzol begüngstigte die Pfropfungsreaktion stark, und der aufgepfropfte Bruchteil stieg bis zu 200%.

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Zinc Oxide-Sensitized Photopolymerization

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Synopsis

Zinc oxide under ultraviolet excitation causes the polymerization of vinyl monomers if water and oxygen are present. Analysis shows that hydroxyl radicals initiate the chain. Hydrogen peroxide is produced with light-excited zinc oxide and is further decomposed by the reducing action of excited zinc oxide.

Introduction

Aqueous suspensions of zinc oxide, when irradiated with near-ultraviolet radiation, produce hydrogen peroxide.[1] This reaction requires molecular oxygen and is apparently due to autoxidation of the reduced state of zinc oxide produced by the light excitation. One might expect that zinc oxide is a photoinitiator of vinyl polymerization and, indeed, this has been found to be the case.[3] There are divergent opinions as to the nature of the initiating radicals.[4,5] The present paper represents an attempt to clarify this situation and to describe polymerization experiments wherein the amount of water present and the prior treatment of the zinc oxide were controlled. Polymerization induced by excitation of zinc oxide by ionizing radiation is also described.

Experimental Procedures and Results

In all the experiments the zinc oxide powder employed was Type SP-500, spectroscopically pure, obtained from the New Jersey Zinc Co. The ultraviolet light source was a GE AH-4 100-w. mercury lamp with a Wood's glass filter. At the distance employed (20 cm.) the intensity of light (mainly 365 mμ) falling on the sample was 1.44×10^{-6} einsteins/cm.^{2}/hr. The polymerization took place in an Erlenmeyer flask in a constant-temperature bath. The exciting beam of light comes up to the bottom of the flask via a mirror. In some experiments the monomer was flushed with nitrogen 30 min. prior to irradiation and sealed off. In other cases where the zinc oxide received a prior heat treatment *in vacuo*, the monomer was distilled into the flask and the flask was sealed off.

For the ionizing radiation studies, the source was a tungsten target Machlett tube operated at 50 kv., 10 ma., to give an intensity at the surface of the sample of 8000 rads/hr.

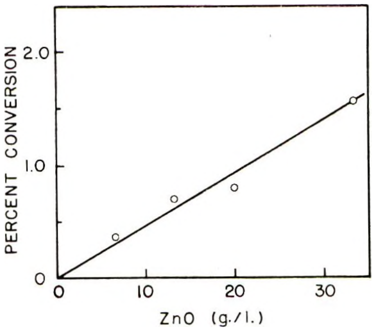

Fig. 1. Conversion vs. amount of zinc oxide added. Monomer is saturated with water. Ultraviolet irradiation for 6 hr. under nitrogen gas.

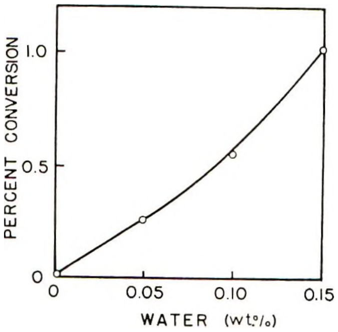

Fig. 2. Effect of water on monomer conversion. ZnO = 20 g./l., ultraviolet irradiation for 12 hr. *in vacuo*.

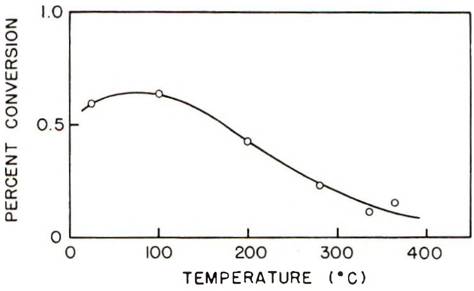

Fig. 3. Effect of prior heat treatment of zinc oxide on polymerization rate. ZnO = 20 g./l.; 0.15% water; ultraviolet irradiation for 12 hr. *in vacuo*.

Purified (i.e., washed and distilled) methyl methacrylate does not polymerize appreciably in 10 hr. on irradiation with the 365 mμ light source employed. In the presence of zinc oxide, however, polymerization proceeds. The amount of monomer converted is linear with time with practically no induction period when the system had been flushed with nitrogen. The rate of polymerization depends on the concentration of zinc oxide suspension on the water content and on the prior heat treatment of the zinc oxide. The rate of photopolymerization is linear with zinc oxide concentration (Fig. 1). It is also approximately linear with increasing water content (Fig. 2). Prior heating of the zinc oxide at 100°C. improves slightly its photocatalytic power, but above this temperature the effect decreases. (Fig. 3).

The photopolymerization was carried out in a temperature bath at temperatures between 10 and 45°C. The rate of polymerization increased with increasing temperature with an activation energy of 2.9 kcal./mole.

The poly(methyl methacrylate) produced was examined at 90°C. by nuclear magnetic resonance (Varian 60 Mc./sec.), and the results, expressed in terms of Bovey's interpretation[6] of the α-methyl proton splitting, are given in Table I.

TABLE I
NMR Analysis of Photopolymerized Methyl Methacrylate[a]

Reaction temperature, °C.	Product		
	Isotactic, %	Heterotactic, %	Syndiotactic, %
10	4.88	32.5	62.6
35	4.46	33.2	62.4

[a] ZnO: 20 g./l.; 0.15% H_2O; 48 hr. ultraviolet irradiation.

A sample of the photopolymer was analyzed for hydroxyl endgroups by the technique of first converting to carboxyl groups (with phthalic anhydride and pyridine) and then observing spectroscopically the interaction with a dye.[7] For the polymer produced after 6 hr. ultraviolet irradiation of a 2% aqueous solution of methyl methacrylate in the presence of a 0.4% suspension of zinc oxide we obtain 2.35 OH endgroups per polymer chain, the molecular weight of the polymer having been determined by viscometry. The molecular weight is obtained from the relation[8] for the intrinsic viscosity of poly(methyl methacrylate) in benzene at 25°C.:

$$[\eta] = 0.74 \times 10^{-4} M^{0.76}$$

Copolymers of methyl methacrylate and styrene were made by zinc oxide-sensitized photopolymerization. The styrene content of the polymer was determined by measuring the optical density at 260 mμ of a chloroform solution of the copolymer.[9] The monomer mixtures contained 2.2 wt.-% ZnO and 0.15% water. After ultraviolet irradiation, the polymer was isolated and analyzed spectroscopically. It was found that the ratio of methyl methacrylate to styrene in the copolymer was a linear function of the styrene content in the original monomer mixture. A similar result was obtained for the x-ray-induced polymerization under the same conditions of zinc oxide and water content.

In all respects, polymerization by ionizing radiation is similar to ultraviolet irradiation. Thus, increased water content and zinc oxide concentration enhanced the rate of polymerization. Incidentally, zinc oxide enormously enhanced the polymerization effect of ionizing radiation on aqueous systems of calcium acrylate and of acrylamide. Thus a paste of zinc oxide with one of calcium acrylate applied to a glass surface produced a water-insoluble image adhering to the glass when as little as 50 rads fell on the system. Part of this sensitive reaction may be due to enhanced imagery arising from adhesion of the zinc oxide particles by the small amount of polymer produced.

The production of hydrogen peroxide as a function of time of ultraviolet irradiation of aqueous zinc oxide suspensions is not simply monotonically increasing (Fig. 4). The cumulative hydrogen peroxide produced increases nearly linearly during the early part of the irradiation but after about 2 hr. the concentration decreases. The hydrogen peroxide concentration was determined by iodometric titration of aliquot samples which were withdrawn from the system at regular intervals during the ultraviolet irradiation. In the presence of methyl methacrylate the concentration of total hydrogen peroxide is slightly higher than when the monomer is absent. Only hydroperoxides are produced, since addition of catalase to the aliquot yields no result with iodometric titration. The time course of the conversion of the monomer for the same system is illustrated in Figure 4. Over the course of this polymerization the viscosity-average molecular weight of the poly(methyl methacrylate) is almost constant ($\bar{M}_v = 1.3 \times 10^6$).

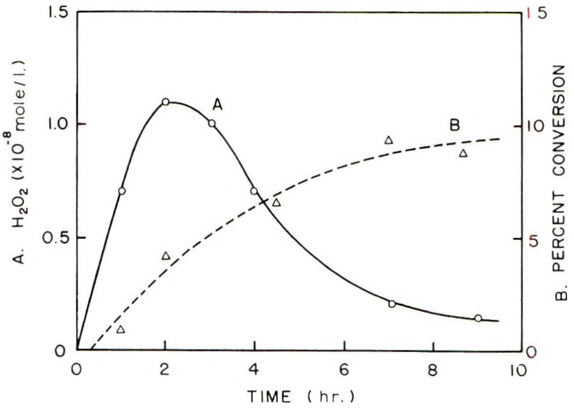

Fig. 4. Hydrogen peroxide concentration (*A*) and per cent conversion of zinc oxide-sensitized photopolymerization of methyl methacrylate in aqueous solution (*B*). ZnO = 4 g./l.; monomer = 2 vol.-%.

Contrary to an earlier report,[4] styrene is photopolymerized by zinc oxide. Here we saturated the styrene with water, for in the absence of water the reaction will not proceed. Incidentally, propylene oxide, both in the presence and in the absence of water, will not undergo photopolymerization with zinc oxide.

Discussion

The endgroup titration of poly(methyl methacrylate) shows that the hydroxyl group is responsible for the initiation of polymerization. The copolymerization results are typical for a radical-initiated polymerization.

The hydroxyl radicals probably arise from the decomposition of hydrogen peroxide. As seen in Figure 4, not only is hydrogen peroxide produced as the irradiation continues, but also the hydrogen peroxide is decomposed. The 365 mμ light can decompose hydrogen peroxide,[10] despite the very small extinction coefficient of the peroxide at that wavelength. More likely, the peroxide is decomposed by the reducing action of irradiated zinc oxide,[2] although the monomer could have a stabilizing effect.[3] Bernas[5] excludes hydroxyl radicals as the initiator of zinc oxide-sensitized photopolymerization because she found that the number of chains initiated exceeds the amount of hydrogen peroxide detected.[5] We, on the other hand, find that, for example, from Figure 4 and the observed molecular weight of the polymer, the number of hydrogen peroxide molecules can be as much as five times the number of initiating chains.

The state of adsorbed oxygen on zinc oxide is influenced by prior thermal treatment.[11] Our Figure 3 is similar to the thermal dependence of the oxygen adsorption data for zinc oxide[12] and corresponds to the low-temperature form of adsorbed oxygen, namely O_2^- or O^-.

The degree of tacticity of the zinc oxide-sensitized photopolymerization of methyl methacrylate is not appreciably different from the results obtained by the γ-ray irradiation polymerization (no zinc oxide) of this monomer at 0°C.[6] Hence we cannot ascribe any special stereospecific surface effect of zinc oxide on the polymerization.

The similarity of polymerization results between x-ray-excited and ultraviolet-excited zinc oxide is not surprising. We have found that both types of radiation on zinc oxide produce the same results as regards luminescence and photoconductivity.[12]

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Taken in part from the dissertation of M. Yamamoto submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirement for the degree of Doctor of Philosophy.

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Résumé

L'oxyde de zinc sous excitation ultraviolette provoque la polymérisation de monomères vinyliques di de l'eau et de l'oxygène sont présents. L'analyse montre que les radicaux hydroxyles sont des initiateurs de chaînes. Le peroxyde d'hydrogène est produit à l'aide de l'oxyde de zinc excité à la lumière et est ultérieurement décomposé par l'action réductrive de l'oxyde de zinc.

Zusammenfassung

Bei Ultraviolettanregung verursacht Zinkoxyd in Anwesenheit von Wasser und Sauerstoff die Polymerisation von Vinylmonomeren. Eine Analyse zeigt, dass Hydroxyradikale die Kette starten. Zinkoxyd liefert bei Lichtanregung Wasserstoffperoxyd, und dieses wird durch die reduzierende Wirkung des angeregten Zinkoxyd zersetzt.

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Thermally Resistant Polymers Containing the *s*-Triazine Ring

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Synopsis

Aromatic dinitriles cyclize to form aromatic polymers containing the *s*-triazine ring. In this paper, these polymers are compared thermally with each other and with aromatic melamine polymers prepared via the aromatic diamine and cyanuric chloride. One perfluoroaromatic melamine polymer was prepared and compared with the other two types of polymers. The polymers (triazines and melamine) in which biphenyl was the backbone were increasingly stable up to 1000°C. in nitrogen. The triazine polymers as a group were the most stable. The perfluoroaromatic polymer was the most stable melamine up to 500°C. in air but was very unstable above 700°C.

INTRODUCTION

Polymers capable of thermal stabilities at temperatures of 500°C. and above are a constant requirement for high-speed aircraft and missiles. The synthesis of such polymers requires the use of a stable organic molecule (monomer), characterized by high-resonance energy, thermally "unreactive" properties, and a flexible structure and the use of a thermally stable link to connect the monomers.

High-resonance energy in the molecule can likely be obtained from the aromatics group of polymers wherein the most thermally unreactive aromatics can be found through the use of the thermal reactivities prepared by Lewis.[1] The need for flexibility within the polymer molecule is readily apparent from usual brick-dustlike properties obtained for thermally stable polymers.[2] Information from the above studies indicates that a polymer having high thermal stability would be some analog of 1,4-disubstituted benzene (the resonance energy of benzene is 36 kcal./mole[3]). To find the best connecting atom or molecular "link" one would attempt to optimize the following properties: high-resonance energy, enhanced resonance along a large portion of the polymer chain, and the capability of being formed through some chemical reaction using reasonable reaction conditions.

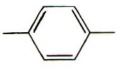
Thermal stability in the link can be achieved through the use of aromatics or heterocyclics. Because the resonance along the polymer chain should greatly enhance the thermal stability of the polymer, the aromatic or heterocyclic should be capable of conjugating with the 1,4-disubstituted benzene used for the monomer. Furthermore, because a chemical reaction of not too drastic conditions is needed to prepare the polymer from the monomer, the area of search is drastically reduced. Examples of the link fitting the above criteria could be imide, imidiazole, or *s*-triazine. The *s*-triazine nucleus was chosen for the link because it contained the optimum of the above stated qualities, i.e., it could be formed via the trimerization of the nitrile; it can achieve high resonance [resonance energy of the cyanuric (triazine) nucleus is 82.5 kcal./mole[4]]; and it is capable of resonance along the polymer chain.

An attempt was also made to prepare a polymer with even greater stability than the aromatic polymers. Madison[5] deduced that the lowest energy decomposition path of aromatics was via the elimination of hydrogen and the formation of intermolecular condensation products. In view of these data,[5,6] it was thought that enhanced stability could be achieved by removing all hydrogen atoms from the aromatic polymer molecule and by replacing them with fluorine. In addition, there is some evidence[7] that the highy fluorinated aromatic compounds will also be at least as stable to atomic irradiation as the aromatics. Because the *s*-triazine nucleus has only three sites for hydrogen or substitution, it was selected for this study.

The purpose of this study was to synthesize and measure the higher temperature properties of a series of aromatic and perfluoroaromatic polymers in which the *s*-triazine nucleus was used, alone or in the form of a melamine, as the connecting link.

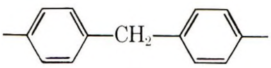
RESULTS AND DISCUSSION

The repeat units chosen for this study were: 4,4′-disubstituted benzene (I), 4,4′-disubstituted biphenyl (II), 4,4′-disubstituted biphenylmethyl (III), and 4,4′-disubstituted biphenyl ether (IV).

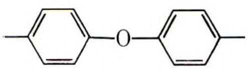


I

II



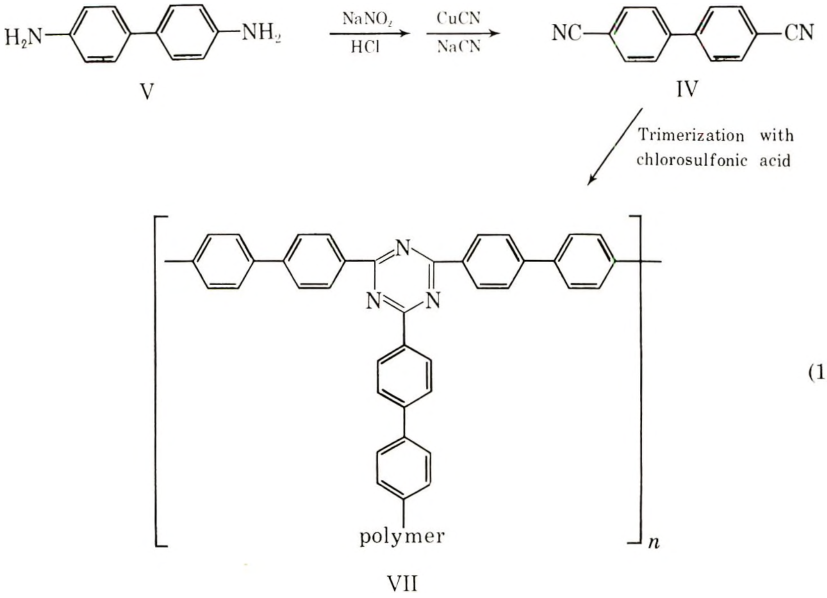
III



IV

Aromatic *s*-triazine Polymers

The reaction scheme using the 4,4′-biphenyl as representative of the series of aromatic *s*-triazine polymers is



(1)

The 4,4′-dicyanoaromatic monomers (VI) were prepared from the corresponding diamine (V) via the Sandmeyer method (diazotization and reaction with a mixture of cuprous cyanide and sodium cyanide).

Aromatic *s*-triazine polymers (VII) were then obtained through the trimerization of aromatic nitriles (by using chlorosulfonic acid as catalyst and heat).[9] In all cases the polymerizations (trimerizations) were assumed to be completed when the peak corresponding to the cyano group disappeared from the infrared spectrum.

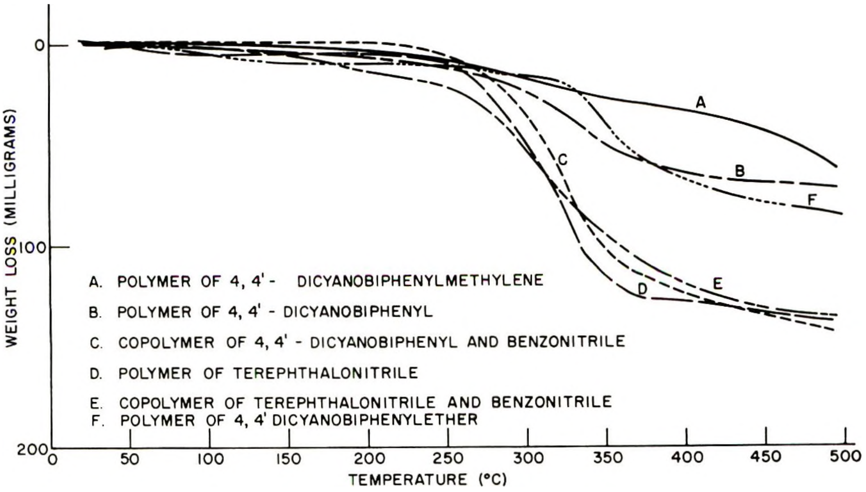
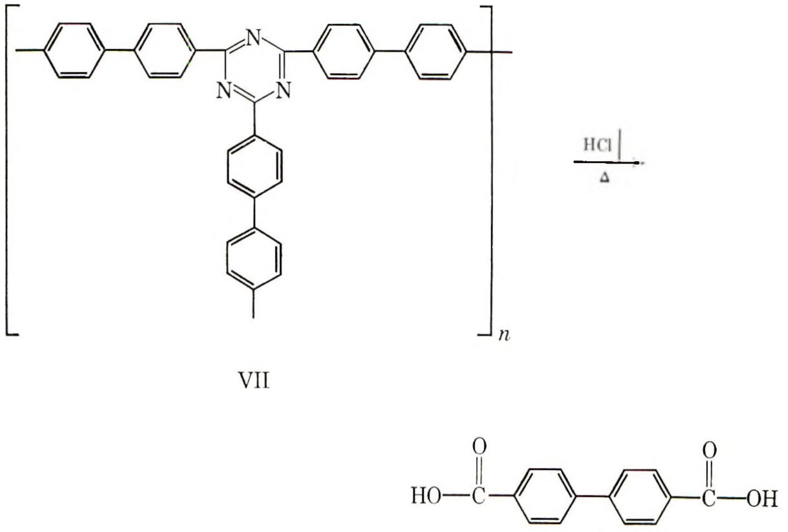


Fig. 1. Thermogravimetric curves of *s*-triazine polymers to 500°C. at 3°C./min. in air.

Infrared spectra of the polymers are somewhat less informative than usual, because absorption of both the aromatic monomer and the *s*-triazine "link" fall in approximately the same region. Because *s*-triazines prepared from monocyanoaromatic compounds will undergo hydrolysis, an attempt was made to hydrolize one polymer as representative of the series to indicate the *s*-triazine structure. The polymer chosen was poly-4,4′-dicyanobiphenyl (VII) because the physical properties of the 4,4′-diphenyldicarboxylic acid (VIII) are known.



VII

VIII

(2)

The conditions of hydrolysis were similar to those used by Smolin[10] for 2,4,6-triphenyl *s*-triazine, i.e., concentrated hydrochloric acid in a sealed tube at 250°C. From the hydrolysis, the expected 4,4′-diphenyldicarboxylic acid was obtained. From the hydrolysis and because the dark-colored polymers were insoluble (*s*-triazines are known to be very insoluble), the formation of the ring was indicated.

Differential thermal analyses (DTA) and thermal gravimetic analyses (TGA) to 500°C. in air and to 1000°C. in a nitrogen atmosphere were obtained. Spectra of three of the more promising polymers were then run to 1000°C. in air. From the TGA thermograms to 500°C. in air (Fig. 1), it was found that the polymer prepared from 4,4′-dicyanobiphenylmethylene (A) was the most stable, with only a 30% weight loss. The 4,4′-dicyanobiphenyl (B) and 4,4′-dicyanobiphenyl ether (F) were intermediate, with 35 and 43% weight loss, respectively. The other three, two copolymers (C) and (E) prepared with benzonitrile as a monofunctional monomer to attempt to decrease crosslinking and one homopolymer from terephthalonitrile (D), lost about 70% of their weight. Thus, polymers prepared from the extremely rigid terephthalonitrile are not as stable, possibly due to the internal stresses (steric) which develop upon polymerization or to incom-

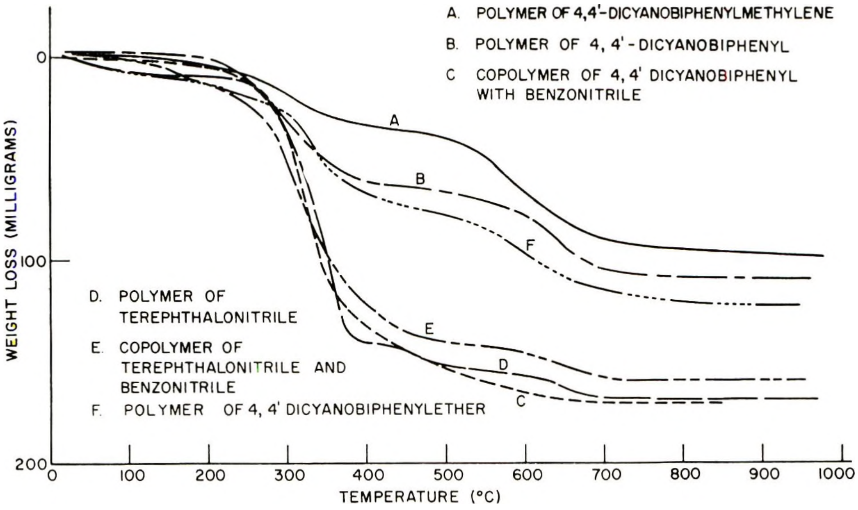


Fig. 2. Thermogravimetric curves of s-triazine polymers to 1000°C. at 3°C./min. in nitrogen.

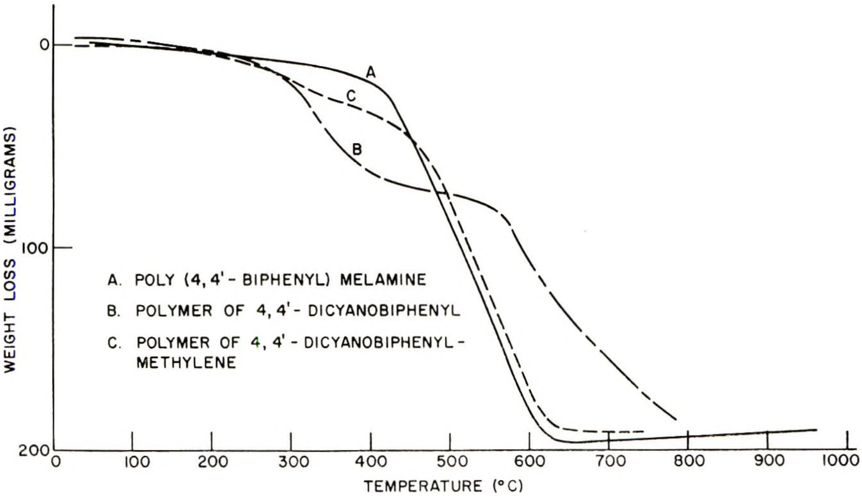


Fig. 3. Thermogravimetric curves of s-triazine and melamine polymers to 1000°C. at 3°C./min. in air.

plete trimerization or cyclization. Because the preparation of less highly crosslinked polymers was attempted by the addition of monofunctional to difunctional monomers in the ratio of $^1/_2$, the lower stability of the copolymers could result from a lower overall molecular weight.

It is interesting that polymer A (poly-4,4′-dicyanobiphenylmethylene) was the most stable, in that it contains a benzyl carbon which, it seems, would contain a lower energy path for decomposition and oxidation. The same order of stability was also observed for the five polymers in the

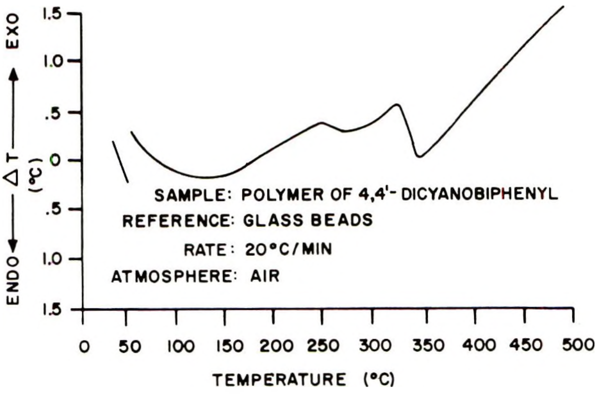


Fig. 4. Temperature differential thermogram of polymer of 4,4′-dicyanobiphenyl.

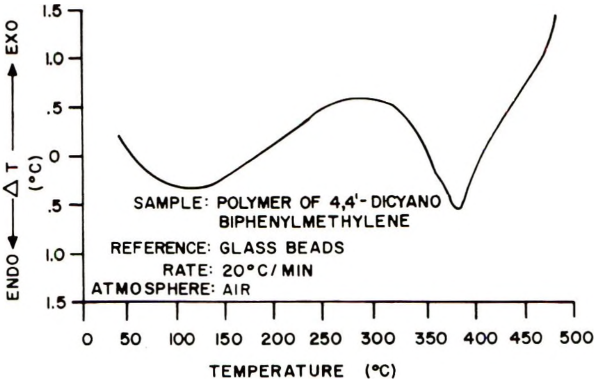


Fig. 5. Temperature differential thermogram of polymer of 4,4′-dicyanobiphenyl methylene.

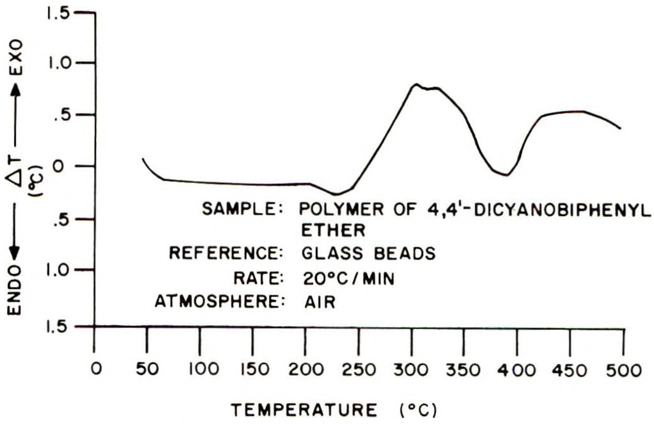


Fig. 6. Temperature differential thermogram of polymer of 4,4′-dicyanobiphenyl ether.

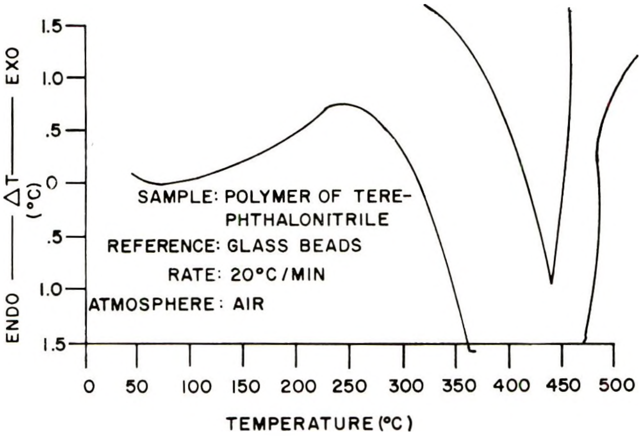


Fig. 7. Temperature differential thermogram of polymer of terephthalonitrile.

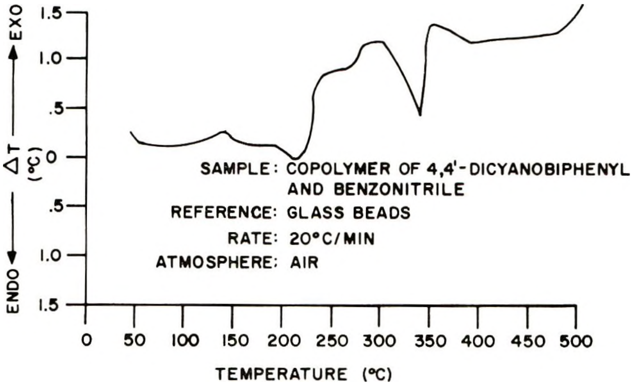


Fig. 8. Temperature differential thermogram of copolymer of 4,4′-dicyanobiphenyl and benzonitrile.

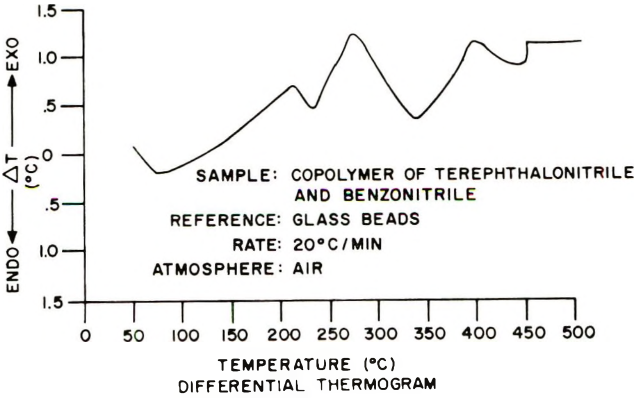


Fig. 9. Temperature differential thermogram of copolymer of terephthalonitrile and benzonitrile.

TGA spectra to 1000°C. in a nitrogen atmosphere (Fig. 2). Here again, the polymer containing the methylene bridge between phenyl rings (A) was several per cent more stable.

Figure 3 shows the stability in air to 1000°C. of the two most stable polymers picked from the previous data. Both polymers, however, had essentially 100% weight loss in an oxidative atmosphere. The polymer from 4,4′-dicyanobiphenyl (B) was at least 100°C. more stable than the one from 4,4′-dicyanobiphenyl methylene (C). This reversal in order at higher oxidative temperatures from the order found in the air to 500°C. and the nitrogen to 1000°C. could be due to the oxidation of the benzyl carbon at higher temperatures. The initially greater weight loss of B versus C could be due to the evaporation of the lower molecular weight portions of the polymer.

Figures 4–9 are thermograms of the six polymers tested in the DTA. The gentle exotherm in Figures 4 and 5 at 125°C. has been found to be due to incomplete removal of moisture from the sample. Because the TGA data of the polymers (both in air and in nitrogen) show a large weight loss between 350 and 450°C., the corresponding endothermic peak in the DTA can be explained via the evaporation of the lower molecular weight fractions of the polymer.

The exothermic slope in the spectra of most of the polymers above 450°C. can be attributed to the energy released in the air oxidation of the polymers. In Figure 4 the endothermic peak at 230°C. is due to the melting of part of the sample.

Attempts to prepare tri(pentafluorophenyl)-*s*-triazine as a model reaction for preparation of perfluoroaromatic *s*-triazine polymers by standard methods,[10] i.e., trimerization of nitriles and imidines, failed. When trimerization was attempted, starting material was recovered. Attempts to prepare the amidine resulted in an unexpected substitution reaction.

Aromatic Melamines

The aryl melamine polymers were prepared by a standard melamine preparation[10,12] which uses cyanuric chloride and an aryl diamine. Three of the four polymers in this group contained the same 4,4′-disubstituted aromatic monomers which were used in the *s*-triazine polymers. They are, 4,4′-diphenylmethylene, 4,4′-diphenyl ether, and 4,4′-biphenyl. The fourth polymer is an analog of 4,4′-biphenyl, with all the aromatic hydrogens replaced with fluorine.

Differential thermal analyses (DTA) and thermal gravimetric analyses (TGA) under like conditions to those of the triazines were obtained for the melamine polymers. From the TGA thermograms to 500°C. in air (Fig. 10), it was found that the polymer prepared from 4,4′-diaminobiphenyl (C) and that prepared from diphenylmethylene (A) lost 40–45%. The polymer prepared from 4,4′-diaminobiphenyl ether (B) was much inferior, with 75% weight loss.

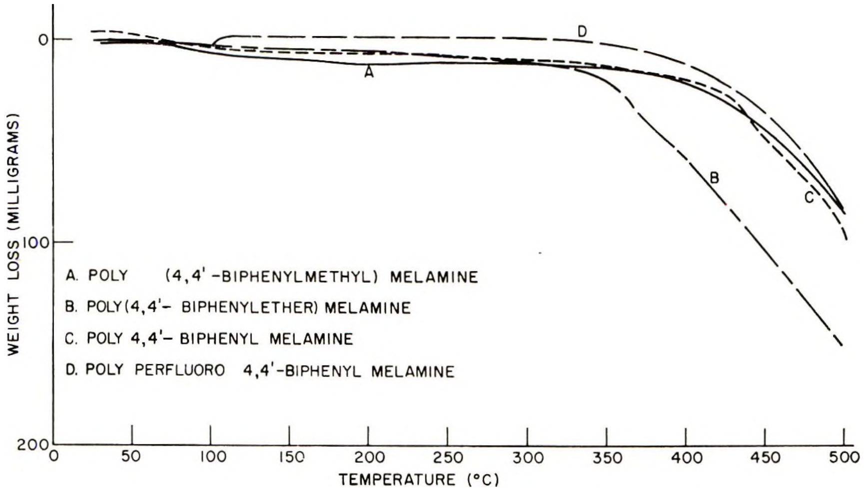


Fig. 10. Thermogravimetric curves of melamine polymers to 500°C. at 3°C./min. in air.

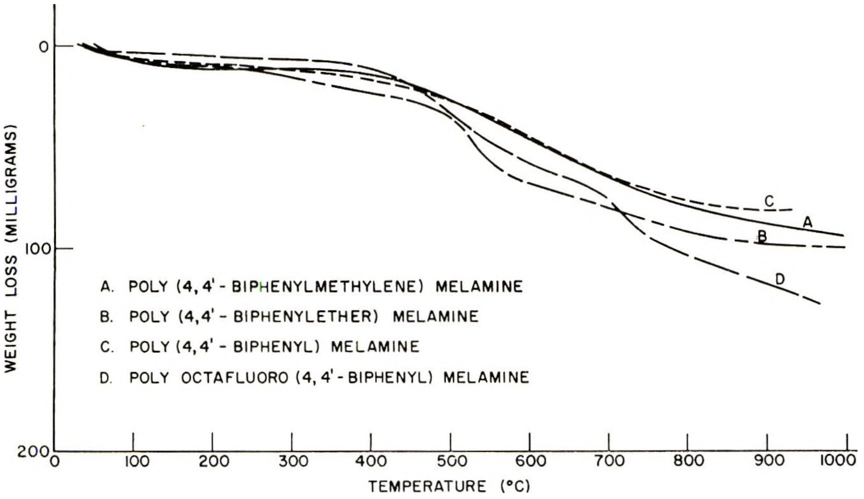


Fig. 11. Thermogravimetric curves of melamine polymers to 1000°C. at 3°C./min. in nitrogen.

When the polymers were heated to 1000°C. in a nitrogen atmosphere, the three polymers were much closer in stability, 40–50% (Fig. 11). Poly-(4,4′-biphenyl ether) melamine was found again to be the least stable of the three unfluorinated ones, with the poly(4,4′-biphenyl) melamine the most stable. The polymers (triazine and melamine) with biphenyl in the backbone were the more stable at 1000°C. in nitrogen, but were not as outstanding at 500°C. in air. This phenomenon may be explained by the larger amount of low molecular weight polymer which was removed from the sample during the first 500°C. Figure 3 shows the stability in air to 1000°C.

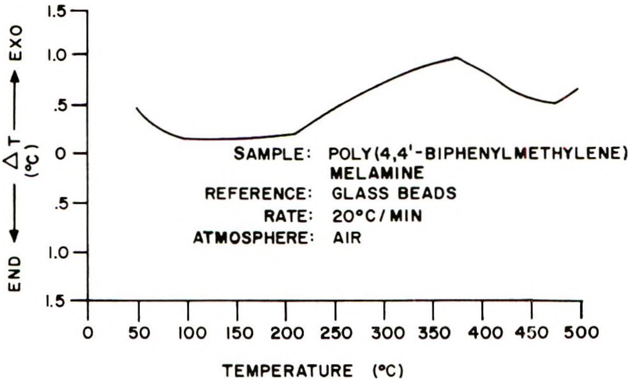


Fig. 12. Temperature differential thermogram of poly(4,4′-biphenylmethylene) melamine.

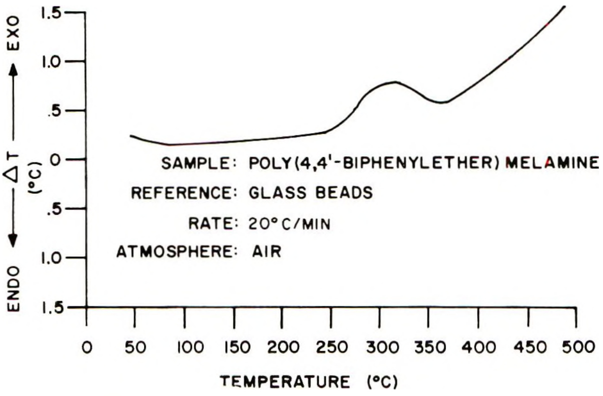


Fig. 13. Temperature differential thermogram of poly-(4,4′-biphenyl ether) melamine.

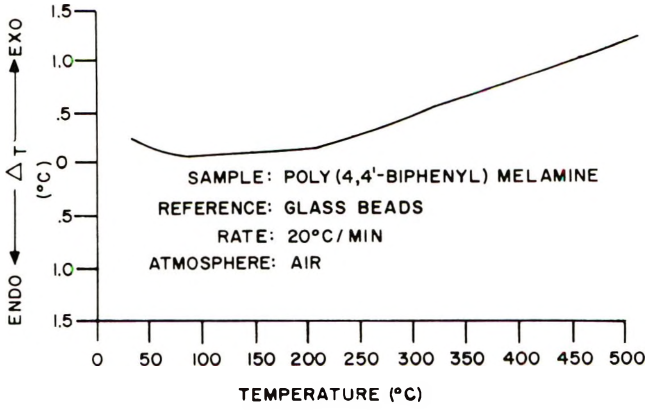


Fig. 14. Temperature differential thermogram of poly(4,4′-biphenyl) melamine.

of the two most stable *s*-triazine polymers and of one melamine polymer prepared from 4,4′-diaminobiphenyl. The melamine polymer was 100°C. less stable, with a 50% weight loss, than the structurally similar *s*-triazine polymer. Replacement of the remaining hydrogen on each amine group might enhance the stability.

Figures 12–14 are DTA thermograms of the three aromatic melamine polymers. The polymer prepared from 4,4′-diaminobiphenyl (Fig. 14) also indicated the greatest stability, in that there was only a gentle exothermic slope starting at about 250°C., whereas the other two had exothermic peaks at 325°C. for poly(4,4′-biphenyl ether) melamine and at 375°C. for poly(4,4′-biphenylmethylene) melamine.

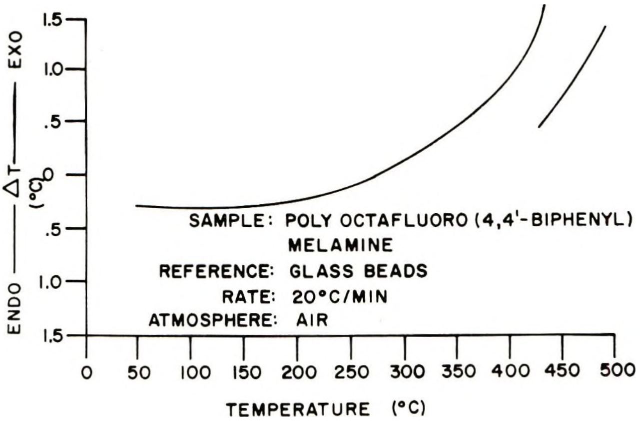


Fig. 15. Temperature differential thermogram of poly-octafluoro-(4,4′-biphenyl) melamine.

One perfluoroaromatic melamine polymer was prepared as above from 4,4′-diaminooctafluorobiphenyl. Figures 10 and 11 show the thermogravimetric curves of the polymer compared to those of the nonfluorinated aromatics.

This polymer was the most stable in air to 500°C. of all melamine polymers. Above 700°C. in nitrogen, it had lost enough weight (63%) to be the least stable. The DTA thermogram showed an increasing slope to the curve in the exothermic direction to 500°C.

EXPERIMENTAL

4,4′-Dicyanobiphenyl Ether. A solution of 30 g. (0.375 mole) of sodium nitrite in 100 ml. of water at 0°C. was slowly added to a solution of 25 g. (0.125 mole) of 4,4′-diaminobiphenyl ether in 100 ml. of concentrated hydrochloric acid at 0°C. Crushed ice was added throughout the course of the reaction to maintain the temperature at 0°C. After the addition was complete, the mixture was neutralized to litmus with sodium carbonate.

The above diazonium chloride solution was slowly added with stirring to a solution of 33 g. (0.75 mole) of sodium cyanide and 38 g. (0.5 mole) of cuprous cyanide in 300 ml. of water at 0°C. Crushed ice was added throughout the course of the reaction to minimize foaming. After stirring an additional 2 hr. at 0°C., the mixture was filtered and the residue was washed several times with water and then dried. The crude product was extracted with tetrahydrofuran, and the solvent was evaporated. The product was recrystallized from either glacial acetic acid or absolute ethanol m.p. 175–180°C. Infrared peaks: 1010, 1500, 1250, 840, 2200, 1180, 1160, 880, and 860 cm.$^{-1}$. Literature[13] reports m.p. 178–180°C.

4,4′-Dicyanobiphenylmethylene. A similar preparation by the Sandmeyer reaction and recrystallization from methanol yielded a tan solid, m.p. 159–160°C. Literature[14] reports 165–167°C. Infrared peaks: 3450, 2220, 1620, 1510, 1415, 875, 823, 812, and 760 cm.$^{-1}$.

4,4′-Dicyanobiphenyl. A similar preparation through the Sandmeyer reaction yielded a cream-colored sublimate, m.p. 239–240°C. Literature[16] reports m.p. 234°C. Infrared peaks: 3400, 2220, 1610, 1500, 1450, 1400, and 820 cm.$^{-1}$.

Preparation of Polymers

Copolymer of Cyanobenzene and Terephthalonitrile. To a mixture of 16 g. (0.55 mole) of benzonitrile and 20 g. (0.155 mole) of terephthalonitrile was slowly added, with stirring and ice-bath cooling, 100 ml. of chlorosulfonic acid. The mixture was allowed to stand 24 hr. at 0°C., after which it was poured onto cracked ice. The dark-colored polymer was isolated by filtration and was washed repeatedly with water and ethanol. Infrared peaks: 3400, 1520, 1370, 1630, 1460, 1230, 1110, 750, and 690 cm.$^{-1}$.

Copolymer of 4,4′-Dicyanobiphenyl with Benzonitrile. The dark-yellow polymer was prepared as above. Infrared peaks: 1530, 1380, 1620, 1600, 1450, 775, and 695 cm.$^{-1}$.

Polymer of Terephthalonitrile. To 12.4 g. (0.1 mole) of terephthalonitrile at 0°C. was slowly added 50 ml. of chlorosulfonic acid. The mixture was allowed to stand at room temperature for 48 hr. and was then poured onto cracked ice, filtered, and washed several times. The dark-tan polymer was obtained in essentially a 100% yield. Infrared peaks: 3450, 1700, 1510, 1410, and 1285 cm.$^{-1}$.

Polymer of 4,4′-Dicyanobiphenyl. The dark-yellow polymer, prepared as above, was isolated in a 100% yield. Infrared peaks: 1500, 1360, 3400, 1610, 1560, 1220, 1180, and 811 cm.$^{-1}$.

Polymer of 4,4′-Dicyanobiphenyl Ether. Prepared as above, the dark-yellow polymer was obtained in essentially a 100% yield. Infrared peaks: 3450, 1600, 1510, 1425, 1370, 1250, 1175, 1100, 1020, 880, and 825 cm.$^{-1}$

Polymer of 4,4′-Dicyanobiphenylmethylene. The yellow polymer was obtained in a 100% yield. Infrared peaks: 3400, 1490, 1660, 1620, 3190, 1280, 1240, 1080, 980, 930, and 725 cm.$^{-1}$.

Hydrolysis of the Polymer of 4,4′-Dicyanobiphenyl. A 10-g. portion of the polymer of 4,4′-dicyanobiphenyl and 75 ml. of concentrated hydrochloric acid were placed in a heavy-walled tube. The tube was sealed and placed in a metal shield. After being heated for 10 hr. at 250°C. the tube was opened and the crude product was isolated via filtration. After three water washes and two alcohol washes, the product was recrystallized from pyridine, m.p. >270°C.; literature m.p. >360°C.

ANAL. Calcd. for $C_{14}H_{10}O_4$: C, 69.5%; H, 4.1%. Found: C, 69.8%, H, 4.1%.

Poly-4,4′-biphenylmelamine. To a mixture of 6.15 g. (0.033 mole) of cyanuric chloride and 40 ml. of benzene was slowly added, over a 2-hr. period, 10.1 g. (0.05 mole) of benzidine. The mixture was then slowly heated to 300°C., during which time the benzene evaporated. The heating was continued until no hydrogen chloride gas was detected (5 days). The dark-brown residue was then washed two times with water and three times with hot benzene. The polymer was obtained in essentially 100% yield. The infrared spectrum was typical of highly polymeric materials, showing very broad, smooth curves without sharp peaks.

Poly(4,4′-biphenyl ether)melamine. The polymer, prepared as above, was obtained in 79% yield. The infrared spectrum was similar to that for poly-4,4′-biphenylmelamine.

Polyperfluoro(4,4′-biphenyl)melamine. The polymer was obtained in an 81% yield. The infrared spectrum was similar to that of poly(4,4′-biphenyl)melamine.

Poly(4,4′-biphenylmethylene)melamine. This polymer was obtained in an 80% yield. The infrared spectrum was similar to that of poly(4,4′-biphenyl)melamine.

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Résumé

Les dinitriles aromatiques cyclisent pour former des polymères aromatiques contenant des anneaux *s*-triaziniques. Dans ce manuscrit, ces polymères sont comparés thermiquement les uns aux autres et avec les polyméres aromatiques à base de mélamine preparés au moyen de diamines aromatiques et de chlorures de cyanure. Un polymère mélamine perfluoré aromatique a été préparé et comparé avec deux autres types de polymères. Les polymères (triazines et mélamines) qui utilisent le biphényle comme chaîne principale étaient stables jusqu'à 1000°C dans une atmosphère s'azote. Les polymères triaziniques, tels que, étaient les plus stables. Le polymère perfluoroaromatique était celui à base de mélamine le plus stable jusqu'a 500°C dans l'air mais était très instable au-dessus de 700°C.

Zusammenfassung

Aromatische Dinitrile zyklisieren unter Bildung aromatischer Polymerer mit einem *s*-Triazinring. In der vorliegenden Arbeit werden diese Polymeren in bezug auf ihre thermischen Eigenschaften miteinander und mit aromatischen, über das aromatische Diamin und Cyanursäurechlorid dargestellten Melaminpolymeren verglichen. Ein perfluor-aromatisches Melaminpolymeres wurde dargestellt und mit den anderen beiden Polymertypen verglichen. Die Polymeren (Triazine und Melamin) mit Biphenyl in der Hauptkette besassen die grössere Stabilität bis zu 1000°C unter Stickstoff. Die Triazinpolymeren waren als Gruppe die beständigsten. Das perfluor-aromatische Polymere war bis zu 500°C in Luft das beständigste Melamin, es war aber oberhalb 700°C sehr unbeständig.

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Homogeneous Ion-Exchange Membranes of Improved Flexibility

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Synopsis

Poly(styrenesulfonic acid)ion-exchange membranes having various degrees of porosity and flexibility have been prepared by using aliphatic and aromatic esters of *p*-styrenesulfonic acid. The membranes formed from the aliphatic ester monomers were found to exhibit an increase in water uptake, permeability, and flexibility with increase in the size of the alcohol group of the ester monomer. With membranes formed from the phenyl and β-naphthyl ester monomers the reverse trend was indicated. The flexibility of the membranes formed from the aromatic ester monomers was much greater than that obtained with the aliphatic esters.

Previous reports[1–4] have described sulfonated monomer ion-exchange membranes which are very selective for positive ion and of high ion transfer rates. Although these membranes are strong in tension,[1] they have proven to be very brittle and will not endure repeated flexing without fracture. In the preparation of poly(styrenesulfonic acid) ion-exchange membranes by polymerization of *p*-styrenesulfonic acid ester with styrene and divinylbenzene, the size of the ester grouping determines the spacing of the polymer chains.[5] The changes in the swelling of the resulting ion-exchange membranes, indicated by variations in moisture content, are dependent on the size of the ester grouping used during the polymerization. As a result, both mechanical and mass transfer properties of the membranes should be subject to variation by variation of the ester monomer.

The present work is an investigation of the effects of variation of the alcohol group in the ester monomer on the swelling, transfer behavior, and flexibility of the membranes formed. Fourteen poly(styrenesulfonic acid) ion-exchange membranes, having various degrees of porosity and flexibility, have been prepared from aliphatic and aromatic esters of *p*-styrenesulfonic acid. The membranes formed from the aliphatic ester monomers were found to exhibit an increase in water uptake, permeability, and flexibility with increase in the size of the alcohol group of the ester monomer. With membranes formed from the phenyl and β-naphthyl ester monomers

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the reverse trend was indicated. The flexibility of the membranes formed from the aromatic ester monomers was much greater than that obtained with the use of the aliphatic esters.

EXPERIMENTAL

Preparation of Monomers

The *n*-propyl ester of *p*-styrenesulfonic acid was prepared from β-bromoethylbenzene according to Metanomski's[6] variation on the method of Spinner et al.[7] The ethyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, phenyl, and β-naphthyl esters of *p*-styrenesulfonic acid were prepared from *p*-(β-bromoethyl)-benzenesulfonyl chloride by a sequence of esterification and dehydrobromination reactions by modifying the procedure used by Chen and Hammett.[8] The procedure used for the preparation of these ester monomers is described below.

A 25-g. portion (0.0875 g.-mole) of *p*-(β-bromoethyl)-benzenesulfonyl chloride and 0.0725 g.-mole of the designated alcohol were dissolved in 68 ml. of benzene. (In the case of β-naphthol more benzene was used.) The solution was heated to reflux temperature (above about 80°C.), 4.5 g. of powdered zinc oxide and 0.4 ml. of pyridine were added, and the solution was refluxed with vigorous stirring for 7 hr. (Reflux time was adjusted according to the alcohol used.) The mixture was cooled over an ice bath, benzene added to it, and the mixture filtered. The filtrate was washed twice with water and then dried with anhydrous sodium sulfate. (In the case of the phenyl and β-naphthyl derivatives, the filtrate was washed with 5% KOH, water, 2*M* HCl, and water in the order indicated.) The sodium sulfate was extracted with benzene. The excess benzene was removed with a flash evaporator until the solution had been reduced in volume to 100–150 ml. The solution was then heated to 55–60°C. and with vigorous stirring 39 ml. of alcoholic potassium hydroxide solution (representing a 33% excess), containing 25 g. of KOH in 150 ml. of 95% ethanol, was added dropwise over a period of 40–50 min. The solution was stirred for additional 15–20 min. at the same temperature. The resulting ester solution was then cooled over an ice bath, benzene added to it, washed three times with water, and dried with anhydrous sodium sulfate. A trace of *p*-*tert*-butylcatechol was added to the ester solution, and the volatile constituents were removed at room temperature on a flash evaporator and finally under high vacuum. The ester monomers formed by this method were used without further purification.

Membranes

The membranes used in this work were prepared by the bulk copolymerization of the esters of *p*-styrenesulfonic acid with styrene, divinylbenzene, and 1% by weight of benzoyl peroxide as catalyst and subsequent hydrolysis to produce poly(styrenesulfonic acid).[1,9,10] The membranes were formed at 110–120°C. in 4 hr. Hydrolysis of the membranes formed with the ali-

TABLE I
Membrane Characteristics and Properties

Membranes		Thickness, cm.(±0.0002)	Capacity, mequiv./g. of dry resin, H form	Moisture content, moles H_2O per equiv., H form	Range of flexibility measurements	$D_{\text{Na}^+ - \text{H}^+}$ at 25°C., cm.²/sec. × 10^6
Set no.[a]	Ester form					
2–4	Ethyl	0.0500	1.63	14.8		0.82
	n-Propyl	0.0450	1.68	16.8	3–9	1.23
	n-Hexyl	0.0973	1.84	17.6		1.74
	n-Octyl	0.0470	1.80	18.5	8–18	
	n-Decyl	0.0472	1.95	19.1	42–61	1.96
	n-Dodecyl	0.0475	1.89	19.7	49–63	
3–4	*n*-Propyl	0.0500	2.40	18.7		2.27
	n-Hexyl	0.0490	2.40	20.2		2.53
	n-Decyl	0.1052	2.39	23.3		2.59
	n-Dodecyl	0.0856	2.28	23.8		2.84
2–4	Phenyl	0.0472	1.65	16.6	150–201	1.13
	β-Naphthyl	0.0450	1.65	12.7		0.51
3–4	Phenyl	0.0158	2.37	20.2	176–210	1.94
	β-Naphthyl	0.0480	2.20	17.4	103–154	1.80

[a] The first digit represents the nominal exchange capacity of the membrane, while the second digit represents the mole per cent of divinylbenzene used in the preparation of the membrane.

phatic ester monomers to poly(styrenesulfonic acid) was carried out with 5% caustic soda solution.[1] The aqueous hydroxide was ineffective in hydrolyzing membranes formed with the aromatic esters, such as the phenyl and β-naphthyl derivatives of *p*-styrenesulfonic acid. These membranes were hydrolyzed in 5% ethanolic solution of potassium hydroxide at reflux temperatures for 4 days. In general, hydrolysis in 5% ethanolic solution of potassium hydroxide produced clearer membranes than that obtained with aqueous hydroxide. No marked difference in water uptake or transfer behavior was observed between pieces of a propyl membrane hydrolyzed by the two methods.

Membrane Moisture Content, Capacity, Thickness, and Flexibility Measurements

The methods used for the determination of membrane moisture content, exchange capacity, and thickness have been described previously.[1] In Table I are given the characteristics of the membranes used in this work and the moisture content of the membranes in the leached hydrogen form of the resin in 100% R.H. at 25°C.

The relative degree of flexibility of the membranes used was measured on surface-dried, hydrogen-form membrane samples, 0.64 cm. in width and 1.6 cm. long, which had been stored under 100% R.H. The test involved clamping the sample at one end in vertical position, leaving 0.95 cm. exposed. The end of a horizontal aluminum rod repeatedly moved the free end of the sample through an arc of 45°. The number of flexes required to fracture the sample was a measure of the flexibility of the membranes. Three samples were tested for each type of membrane. This procedure gave results of reasonable reproducibility using the small samples available.

Cation and Anion Diffusion Measurements

A two-compartment Lucite cell was used to measure the rates of sodium–hydrogen interchange and chloride-ion transfer across the ion-exchange membranes by the procedure described previously;[2,4,5] $0.1N$ solutions of $NaNO_3$ and HCl were used. The experimental data were used to calculate interdiffusion coefficients ($D_{Na^+-H^+}$) by using the relationship described previously.[4,5]

RESULTS AND DISCUSSION

The data obtained for water uptake, flexibility, and ion permeability of the ion-exchange membranes are given in Table I. It will be noted that the variation in ester size exerts a marked effect upon the moisture contents of the membranes. This effect is expected because of the much larger amount of material removed by the hydrolysis of the larger esters. There is thus provided an increased opportunity for moisture sorption without distortion of the polymer structure. Although these trends are quite regular within the aliphatic series of esters, the aromatic esters used result in a much lower moisture content than aliphatic esters of comparable size.

The variations in flexibility of the membranes which were observed also follow a similar pattern. Within the aliphatic series, increasing the size of the ester results in increasingly greater flexibility. The more bulky aromatic groupings proved to be particularly effective in increasing the flexibility. The chain spacing which is provided by the presence of the large group during polymerization is apparently largely retained after hydrolysis even though the water sorption in the void spaces is much less for the aromatic compounds than would be expected on the basis of the moisture content of the aliphatic series. The very large increase in flexibility indicated for the aromatic ester membranes permits much simpler handling of these materials. Much of the previous work on membranes of the ester monomer type has been done with propyl ester membranes which, while they could be handled, were quite brittle, requiring special care in cutting and the fabricating. The phenyl and β-naphthyl membranes, on the other hand, are flexible to touch and may be readily cut and fitted.

The cation interdiffusion coefficients listed in Table I illustrate that the new membranes possessing increased flexibility still retain mass transfer rates similar to those found for the earlier propyl membranes of comparable water content. It may also be noted within the aliphatic series that the variations in the mass transfer rates with the size of ester removed by hydrolysis are consistent with the variations described previously[5] for the lower ester monomers. For the aromatic esters, in both cases a reduced water content was obtained for the larger alcohol and the mass transfer rate is correspondingly smaller.

The increased flexibility of the aromatic membranes has also been obtained without sacrifice of the high selectivity of the earlier propyl ester membranes. Ratios of chloride ion to hydrogen ion flux across these membranes (set no. 2–4) have been measured at 1.7×10^{-3} for the β-naphthyl membrane and 1.8×10^{-3} for the phenyl membrane at an external solution concentration of 0.1 mole/l. Values for the relative transport for the earlier propyl membranes of comparable water content vary between 1.5×10^{-3} to 4.5×10^{-3}.

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Résumé

Des membranes échangeuses d'ions à base d'acide polystyrène-sulfonique présentant différents degrés de porosité ou de flexibilité, ont été préparées utilisant des esters aliphatiques ou aromatiques de l'acide *p*-styrènesulfonique. Les membranes formées au départ des monomères esters aliphatiques manifestent une augmentation en absorption d'eau, perméabilité et flexibilité avec une augmentation de la grandeur du groupe alcool du monomère ester. Avec des membranes formées au départ de monomères esters phényliques et β-naphthyliques la tendance inverse se manifeste. La flexibilité des membranes formées au départ d'esters monomériques aromatiques était beaucoup plus grande que celle obtenue au départ d'esters aliphatiques.

Zusammenfassung

Polystyrolsulfonsäureionenaustauschermembranen mit verschiedenem Porositäts- und Flexibilitätsgrad wurden aus aliphatischen und aromatischen *p*-Styrolsulfonsäureestern dargestellt. Die Membranen aus den aliphatischen Estermonomeren zeigten eine Zunahme der Wasseraufnahme, der Permeabilität und der Flexibilität mit steigender Grösse der Alkoholgruppe des Estermonomeren. Bei Membranen aus Phenyl- und β-Naphthylestermonomeren bestand die entgegengesetzte Tendenz. Die Flexibilität der Membranen aus den aromatischen Estermonomeren war bedeutend grösser als die bei aliphatischen Estern erhaltene.

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Polymerization of *n*-Octadecene-1 with Catalysts Derived from Titanium Tetrachloride and Triethylaluminum

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Synopsis

The effects of variation in Al/Ti mole ratio, catalyst concentration, reaction time, and temperature on the yield and some physical properties of polymers of *n*-octadecene-1 obtained with the use of Ziegler catalyst systems derived from titanium tetrachloride and triethylaluminum have been investigated. Results show many features similar to those obtained by other workers with lower olefins. In general, the yield of polymer shows a distinct maximum at an Al:Ti mole ratio of 2.8:1 and total catalyst concentration (at the stated mole ratio) of 4%, based on monomer; the yield increases sharply with polymerization temperature to a maximum at about 40°C. and with time up to about 12 hr. at 25°C. Polymer intrinsic viscosity also shows a strong dependence on Al:Ti mole ratio and catalyst concentration, increasing between Al:Ti mole ratios of 2.0–3.4, and showing a maximum at catalyst concentration of 3.5% on monomer. Polymer intrinsic viscosity shows a decrease with increasing reaction temperature and an increase with time of polymerization. The polymer densities, melting points, and fraction soluble in hexane (at 25°C.) appear to show much less dependence on the variables under consideration, and no firm conclusions are drawn. An important reaction concurrent with polymerization is the formation of a *trans* nonterminal isomer of octadecene. This certainly affects the yield (the nonterminal isomer not being polymerizable under the same conditions); the effect of the presence during polymerization of isomerized monomer on the physical characteristics of the polymer is less clear, and further work is proceeding.

INTRODUCTION

Although the Ziegler polymerization of α-olefins to polymers of highly stereoregular structure is now well known,[1] most of the published information relates to the polymerization of lower ($<C_8$) olefins. Considerably less work appears to have been carried out with higher α-olefins, the most comprehensive studies being those of Marvel and Rogers.[2]

In the present paper we are particularly concerned with the effects of some polymerization variables on the polymer yield and physical properties for a typical higher α-olefin, *n*-octadecene-1.

EXPERIMENTAL

Reagents

Good commercial grades of *n*-octadecanol-1, acetic anhydride, alcohols, and acetone were used as received.

n-Hexane, benzene, and cyclohexane (aromatic-free grade) were passed over anhydrous alumina, redistilled, and stored over clean sodium wire.

Aluminum trichloride was resublimed at 250°C. immediately before use.

Titanium tetrachloride was redistilled, the fraction boiling at 135°C. being delivered directly into pure cyclohexane.

Triethylaluminum was donated by I.C.I. Ltd. (Plastics Division), who also carried out the following analysis: $AlEt_3$, 88 mole-% (93 wt.-%); AlH_3, 9.5 mole-% (2.6 wt.-%); Al*i*-Bu_3, 1.6 mole-% (3.0 wt.-%); AlX_3 (X = halogen), 1.0 mole-% (1.5 wt.-%); concentration = 1685 mg.-atoms of aluminum/l.; solvent, (Lobase): paraffinic, aromatic-free, b.p. ~170°C. /atm. pressure.

n-Octadecene-1 was prepared by the pyrolysis of a mixture of *n*-octadecanol-1 (1.0 mole) and acetic anhydride (1.5 mole) in a manner previously described.[3] Only the pure, homolog-free monomer (b.p. 210°C./70 mm., m.p. 17.8°C., n_D^{20} 1.4450, d_4^{20} 0.7893, iodine no. 100.8) was used for polymerizations.

Analytical Procedures

Titanium Tetrachloride. Titanium tetrachloride was estimated, as titanium dioxide, by hydrolyzing a measured volume of solution with ammonium hydroxide, separating the precipitated titanium dioxide, and heating at 600°C. to constant weight.

Iodine Number. Iodine numbers were determined by Hanus' method.[4]

Infrared Spectra. Infrared spectra were recorded as liquid films on a Grubb Parsons S3A spectrometer with sodium chloride optics, or on a Grubb Parsons Spectromaster fitted with diffraction gratings. The *trans* nonterminal olefin was estimated from its absorbance at 965 cm.$^{-1}$, *trans*-7-octadecene being used as a reference reagent.

Vapor-Phase Chromatography. Analysis by chromatography was carried out with a Pye argon chromatograph fitted with a 4-ft. column, closed magnetic injection system, and a Sunvic 10s recorder. The column packing used for all analyses was Apiezon L grease on Celite.

Polymerization Procedures

Monomer and catalyst components were stored in a dry box, through which a slow stream of oxygen-free nitrogen passed at all times. Phosphorus pentoxide was used as a drying agent and was changed whenever its surface became discolored and tacky.

Apparatus for polymerization was left in the unopened dry box for at least 3 days before use. Polymerizations were carried out in 15-ml. screw-cap bottles fitted with neoprene sealing washers. These bottles were dried at 70°C./60 mm. for 24 hr., then placed in the dry box. Monomer and solutions of catalyst components were delivered, in the dry box, from pipets graduated in 0.01 ml., and it is estimated that an accuracy of at least ±0.0025 ml. was obtained. After sealing, the screw-cap reaction vessels were removed from the dry box and maintained at the required temperature for the required time. Samples polymerized at −35, −20, and 0°C. were placed in refrigerators, samples at 25°C. were placed in a water bath, and samples polymerized at temperatures higher than 25°C. were placed in ovens at the appropriate temperatures. All temperature readings were accurate to ±1°C.

Isolation of Polymer and Residual Monomer

After the specified reaction time, polymerization mixtures were added to acetone (excess) and allowed to stand for 2 hr. Insoluble material (polymer and inorganic matter) was filtered off and heated, under reflux (bath temperature 100°C.), for 1 hr. with *n*-hexane. The hot viscous mixture was centrifuged, and the clear supernatant liquid poured into excess of acetone, giving a bulky white precipitate which was filtered off, dried at 50°C./60 mm. for 2 hr., and weighed.

Distillation of the filtrate afforded acetone, catalyst solvents, and higher fractions containing alkanes, terminal alkenes, and nonterminal alkenes, which were examined by infrared spectroscopy and gas–liquid chromatography.

Polymer Properties

Intrinsic Viscosity. Intrinsic viscosities were determined by plotting graphs of η_{sp}/c against concentration and extrapolating to zero concentration. As a check on the results, intrinsic viscosities were also calculated by plotting graphs of $\ln(\eta_{rel}/c)$ against c and extrapolating to zero concentration.[5]

Specific (or relative) viscosities were determined by using an Ostwald viscometer (type B) in benzene at 25 ± 0.1°C.

Solutions of differing concentrations were made up by successive dilutions of solutions containing approximately 1% (w/v) of polymer.

Crystalline Melting Point. Polymer melting points were determined on an electrically heated micro-melting point apparatus fitted to a microscope stage. The heating rate was approximately 1.5°C./min.

The crystalline melting point was taken as that temperature at which the polymer granules became clear and coalesced. Results were reproducible to ±0.5°C.

Solubility in Hexane at 25°C. Solubility in hexane at 25°C. was determined by adding *n*-hexane (20 ml.) to a known weight of finely divided polymer (about 0.05 g.) and maintaining the stoppered vessels at 25°C. for 5 days. Insoluble matter was removed by filtration and dried to constant weight at 50°C./60 mm. Care was taken to ensure that samples being tested for hexane solubility all had the same thermal history. Results were found to be reproducible to within at least 3% of the percentage weight of polymer soluble in hexane.

Density. Density was determined by a flotation method, with the use of methanol–water mixtures. Both solvents were boiled before use, and the polymer was degassed *in vacuo* at 80°C. Samples for density measurements were maintained at 70°C. for 48 hr. and then allowed to cool to room temperature for about 1 hr. Densities of the mixtures containing known volumes of water and methanol were taken from a previously plotted calibration curve of density against the ratio of water to methanol. Measurements of density were reproducible to ±0.001 g./cc.

RESULTS AND DISCUSSION

General Considerations

Viscosity–Molecular Weight Relationship. Intrinsic viscosity measurements carried out in benzene at 25°C. have been used to show molecular weight differences in polymers prepared in this study. Molecular weight is related to intrinsic viscosity by the Kuhn-Mark-Houwink equation, $[\eta] = KM^\alpha$ where $[\eta]$ is intrinsic viscosity, M is molecular weight, and K and α are constants for a particular polymer–solvent system.

No values of K and α are at present available for solutions of polyoctadecene in benzene, but work on another system (C_{12}–C_{18} poly-α-olefins in hexadecene) in which molecular weights were determined by light-scattering methods, suggests $K = 2.1 \times 10^{-4}$ and $\alpha = 0.61$.[6] Application of these values to the present work indicates that polyoctadecene prepared with a titanium tetrachloride–triethylaluminum catalyst has a molecular weight ranging from about 500,000 ($[\eta] = 0.6$) to 1,500,000 ($[\eta] = 1.3$).

However, Marvel and Rogers have calculated molecular weights of polyoctadecene by measuring, by Hanus' method, the amount of unsaturation in a polymer sample, and have reported values differing greatly from those given above (Table I).

Due to the large differences in the above two sets of results, no attempt has been made to calculate the molecular weights from intrinsic viscosity results reported in this work.

TABLE I
Molecular Weights and Intrinsic Viscosities of Polyoctadecene[a]

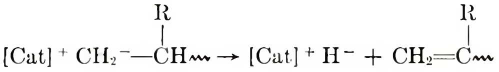
Molecular weight	Intrinsic viscosity
840	0.064
1150	0.061
1240	0.070
2030	0.760
7850	1.52
9880	1.37

[a] Data of Marvel and Rogers.[2]

Reactions Affecting Polymer Molecular Weight. It could be reasoned that the factors favoring a high molecular weight bear little relationship to those favoring a high polymer yield. The latter requires that monomer, having reached the catalyst surface, should either add to a growing polymer chain or start a new one; both processes give the same yield of polymer. A high molecular weight polymer, however, requires that the monomer should add to a growing polymer chain rather than start a new one.

Natta[7] has proposed that chain termination in a Ziegler polymerization takes place by three main reactions.

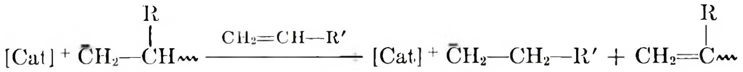
(*1*) Transfer of a hydride ion from the growing polymer chain to the catalyst leaves a polymer terminated by a vinylidene group and a catalyst site which reacts only slowly with monomer.[10]



$$[\text{Cat}]^+\,CH_2^-{-}\overset{\overset{R}{|}}{C}H\!\sim\; \rightarrow [\text{Cat}]^+\,H^- + CH_2{=}\overset{\overset{R}{|}}{C}\!\sim \qquad (1)$$

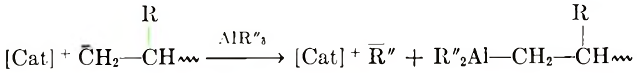
The more electropositive the alkyl group (R), the easier it becomes for the transfer to occur, and Natta thinks that this is the reason why poly-α-olefins generally have a lower molecular weight than polyethylene.[9]

(*2*) Transfer of a hydride ion from a growing polymer chain to a monomer molecule, gives, as before, a vinylidene compound.



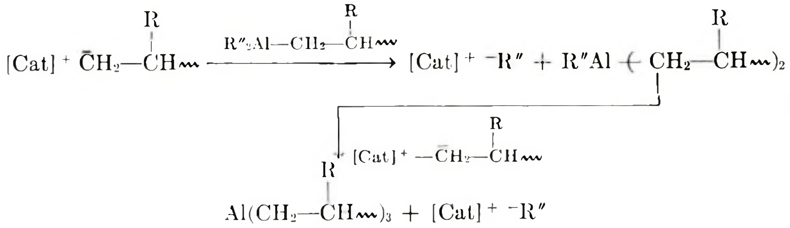
$$[\text{Cat}]^+\,\bar{C}H_2{-}\overset{\overset{R}{|}}{C}H\!\sim\; \xrightarrow{CH_2=CH-R'} [\text{Cat}]^+\,\bar{C}H_2{-}CH_2{-}R' + CH_2{=}\overset{\overset{R}{|}}{C}\!\sim \qquad (2)$$

(*3*) Reaction of a growing polymer chain with aluminum alkyl leaves an active catalyst site and a long-chain aluminum alkyl.



$$[\text{Cat}]^+\,\bar{C}H_2{-}\overset{\overset{R}{|}}{C}H\!\sim\; \xrightarrow{AlR''_3} [\text{Cat}]^+\,\bar{R}'' + R''_2Al{-}CH_2{-}\overset{\overset{R}{|}}{C}H\!\sim \qquad (3)$$

It is possible that the aluminum alkyl formed by this reaction further reacts with a growing polymer chain as shown in eq. (4).



$$\begin{aligned}&[\text{Cat}]^+\,\bar{C}H_2{-}\overset{\overset{R}{|}}{C}H\!\sim\; \xrightarrow{R''_2Al-CH_2-\overset{\overset{R}{|}}{C}H\sim} [\text{Cat}]^+\,{}^-R'' + R''Al\,(CH_2{-}\overset{\overset{R}{|}}{C}H\!\sim)_2\\ &\xrightarrow{[\text{Cat}]^+\,-\bar{C}H_2-\overset{\overset{R}{|}}{C}H\sim} Al(CH_2{-}\overset{\overset{R}{|}}{C}H\!\sim)_3 + [\text{Cat}]^+\,{}^-R''\end{aligned} \qquad (4)$$

where R, R′, R″ are *n*-alkyl.

In the present instance, the situation is further complicated by the presence of *trans* nonterminal olefin formed as a by-product. The latter, although not copolymerizing with the terminal olefin, could well interact with catalyst sites by the reaction (2) above, where an inactive site would probably result, or by reaction (2) followed by reaction (3), where a polymeric trisubstituted ethylene would be eliminated. Evidence for the occurrence of these reactions has been presented elsewhere.[11]

Reproducibility of Results. Difficulty in obtaining reproducibility of results with Ziegler catalysts has often been encountered by other workers,[8] and similar problems have arisen during the present work. It has always proved possible to reproduce the general form of the graphs obtained, but it has been found that the actual polymer yield for similar catalyst conditions can vary by as much as 10%.

Similarly, it did not always prove possible to reproduce intrinsic viscosity results accurately on polymers prepared at different times. Because of this, polymerizations were always carried out in batches, and the above considerations were taken into account when comparing results from different batches.

Polymerizations were allowed to reach equilibrium before products were isolated and examined. No kinetic studies have been attempted, but experiments were carried out to check that yields were in fact at equilibrium after 30 hr. (Table II).

For those conditions giving maximum polymer yield, the actual time for polymer yield and viscosity to reach equilibrium was found to be about 12 hr. (Table III).

TABLE II
Variation in Polymer Yield with Time for Different Polymerization Conditions

Polymerization conditions			Polymer yield, %		
Al:Ti mole ratio	$TiCl_4$:monomer mole ratio	Temp., °C	30 hr.	100 hr.	160 yr.
2.2:1	0.035:1	25	28	28	25
2.8:1	0.035:1	25	50	53	51
3.2:1	0.035:1	25	34	38	36
2.8:1	0.025:1	25	24	24	24
2.8:1	0.050:1	25	47	51	48
2.8:1	0.035:1	40	62	57	59
2.8:1	0.035:1	60	50	44	48

TABLE III
Variation of Polymer Yield and Properties with Time for the Polymerization of *n*-Octadecene-1 with $TiCl_4/AlEt_3$[a]

Reaction time, hr.	Polymer yield, %	Melting point, °C.	[η]	Hexane solubility at 25°C., %	Density, g./cc.
1	23	66	0.64	43	0.908
4	34	66	0.75	39	0.905
6	39	65	0.75	41	0.905
8	47	64	0.86	40	0.905
12	55	66.5	0.93	39	0.905
24	57	66	0.95	40	0.908
30	56	67	0.95	37	0.908

[a] Al:Ti mole ratio 2.8:1; $TiCl_4$:terminal olefin mole ratio 0.035:1.

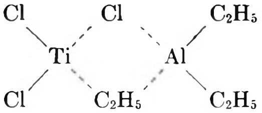
Effect of Al:Ti Mole Ratio on Polymer Yield

At 25°C. and constant titanium tetrachloride concentration, maximum yield of polyoctadecene is obtained at an Al:Ti molar ratio of 2.8:1 (Fig. 1).

Using similar catalysts, other workers have reported similar optimum values of Al:Ti molar ratio (between 2.5:1 and 3.0:1), for the polymerization of ethylene, propylene,[12] and 4-methyl-1-pentene.[13] An optimum ratio of Al:Ti = 1.7:1 has been reported for the polymerization of *n*-butene-1 with titanium tetrachloride–triethylaluminum.[14]

Triethylaluminum reacts readily with traces of oxygen or moisture present in the polymerization system, and hence small variations in reported Al:Ti ratio probably cannot be regarded as significant. What is more important is that most reported results indicate that a maximum is obtained in the graph of percentage yield against Al:Ti molar ratio, the optimum ratio being about 2.8:1.

According to Natta[9] triethylaluminum reduces titanium tetrachloride to crystalline lower chlorides, hence giving a solid lattice for heterogeneous catalysis. He regards the bridge complexes, such as



as the active catalyst sites.

An increase in Al:Ti molar ratio could therefore be expected to (*a*) reduce all available titanium tetrachloride to trichloride and then to lower valency states, and/or (*b*) provide more triethylaluminum to form bridge complexes, and/or (c) compete with monomer molecules for adsorption at the catalyst surface.

Medalia et al.[14] are of the opinion that polymer yield increases to a maximum as enough triethylaluminum becomes available for bridge complex formation after reduction of titanium tetrachloride, and decreases again as triethylaluminum competes with monomer for adsorption on the catalyst surface.

Ludlum[15] suggests that catalytic activity is directly related to the average valency state of the titanium in the catalyst, and has demonstrated the latter to have a value of 2 for maximum polymer yield. Increase of Al:Ti molar ratio is thought by Ludlum gradually to decrease the average valency state of titanium in the catalyst, the catalytic activity increasing as the average valency state of titanium approaches 2, then decreasing as the titanium average valency state falls below this value. Ludlum also shows that the addition of mild oxidizing agents, such as *n*-butyl chloride, restores activity to a spent Ziegler catalyst.

Schnecko et al.[12] report that, for the polymerization of propylene with a titanium trichloride–triethylaluminum catalyst, the graph of polymer yield against Al:Ti molar ratio does not show a maximum, whereas a maximum is obtained when a titanium tetrachloride–triethylaluminum catalyst is used.

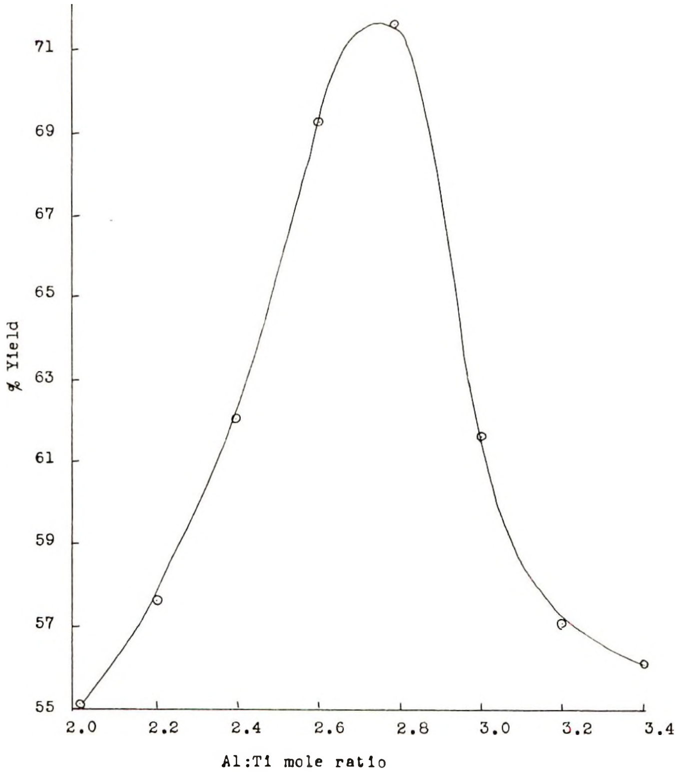


Fig. 1. Variation of polymer yield with Al:Ti mole ratio for the polymerization of *n*-octadecene-1 with $TiCl_4$–$AlEt_3$; 30 hr., 25°C., $TiCl_4$:monomer mole ratio 0.035:1.

It would seem reasonable to assume that the arguments of Ludlum, Medalia, et al. could be applied to both titanium tetrachloride–triethylaluminum and titanium trichloride–triethylaluminum systems, both involving active catalyst sites situated on a solid surface. Similarly, it appears likely that reduction of Ti(III) to lower than Ti(II) would occur in the titanium trichloride–triethylaluminum system, as could be deduced from Ludlum's ideas. It would therefore seem that the titanium trichloride–triethylaluminum and titanium tetrachloride–triethylaluminum systems function in different ways. On the other hand, when ethylene is polymerized at 50°C. with titanium tetrachloride–triethylaluminum, the graph of percentage yield against Al:Ti molar ratio shows no maximum.[13]

Natta has pointed out that the surface of the crystalline support is of great importance in Ziegler polymerization,[7] and that different behavior may be observed, depending on whether titanium trichloride exists as the α (violet), β (brown), γ (violet), or δ (violet) crystalline form.

Since the $TiCl_3$ formed by reduction of $TiCl_4$ with Et_3Al is likely to be mainly of the β variety, whereas $TiCl_3$ used as starting reagent is usually α, γ, or δ, this could well account at least partly for the observed difference in behavior of the two types of catalysts.

Further, the catalyst-forming reactions in systems involving $TiCl_4$ are notoriously complex, $TiCl_4$ showing a much greater ease of reduction and alkylation than $TiCl_3$. Thus, in the present instance, the drop in yield at high Al:Ti mole ratios might well be due to such reactions.

During the current work it has been found that an increase in Al:Ti molar ratio causes an increase in the amount of internal isomer present in the residual materials from olefin polymerization. Internally unsaturated *n*-octadecene will not polymerize under the conditions prevailing in this work, and monomer isomerization is therefore a factor in determining polymer yield (unless the isomerization is considered to be reversible). If yield were dependent only on the amount of monomer isomerization that takes place during polymerization, then an increase in Al:Ti molar ratio would always cause a decrease in polymer yield. This is not the case, and it is probable that the peak on the graph of polymer yield against Al:Ti molar ratio (Fig. 1) merely indicates the stage at which reactions such as monomer isomerization, adsorption of triethylaluminum on catalyst sites, and reduction of titanium below its optimum valency state become more significant than chain initiation and/or growth.

Effect of Al:Ti Mole Ratio on Polymer Intrinsic Viscosity

For the polymerization of *n*-octadecene-1 with titanium tetrachloride–triethylaluminum, polymer intrinsic viscosity increases with Al:Ti mole ratio (Fig. 2), even after polymer yield has started to decrease (Fig. 1).

Reported results for other α-olefins differ greatly. For instance, Medalia[14] reports that, for the polymerization of *n*-butene-1 with titanium tetrachloride–triethylaluminum, intrinsic viscosity is at a maximum at an Al:Ti molar ratio of 2.5:1, whereas Kodamas et al.[16] have shown that, for the polymerization of propylene with a similar catalyst, polymer molecular weight reaches a constant value at an Al:Ti molar ratio of 3:1.

In the present work, results seem to indicate that an increase in Al:Ti molar ratio either decreases the number of catalyst sites available and/or hinders the chain termination processes.

The increase in intrinsic viscosity throughout the entire Al:Ti molar ratio range studied suggests that the cause is related to some factor which also changes consistently throughout the range. According to Ludlum[15] the average valency state of titanium decreases as Al:Ti molar ratio increases. Therefore, if chain termination depends on the concentration of, say Ti(III) or Ti(IV) in the polymerization mixture, molecular weight would be expected to increase with Al:Ti molar ratio.

Natta[7] has suggested that, for the polymerization of propylene with titanium trichloride–triethylaluminum, there is a termination process which depends on the concentration of titanium trichloride, molecular weight decreasing with an increase in the latter. This reaction could be applicable to the present studies. It can also be considered that, after Al:Ti molar ratio 2.8:1, polymer yield decreases, hence suggesting that

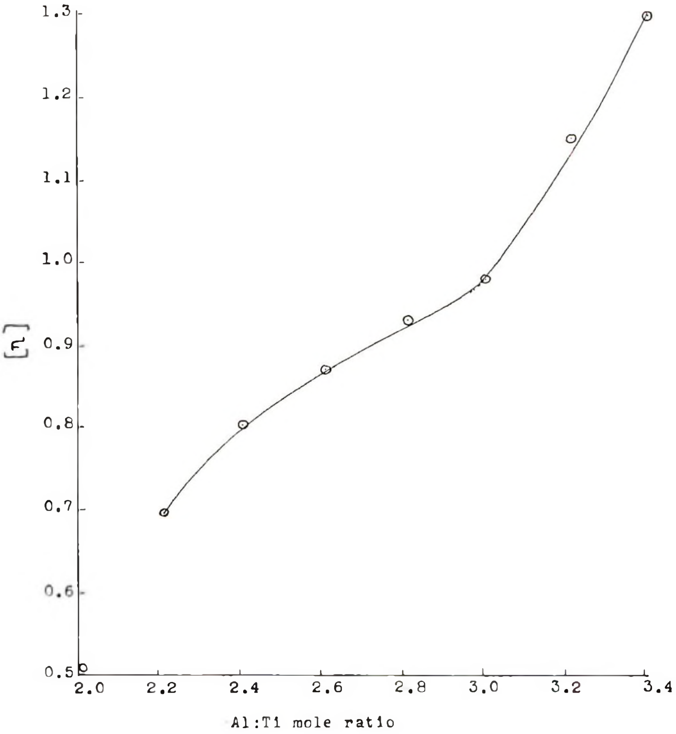


Fig. 2. Variation of polymer intrinsic viscosity with Al:Ti mole ratio for the polymerization of *n*-octadecene-1 with $TiCl_4$–$AlEt_3$; 30 hr., 25°C., $TiCl_4$:monomer mole ratio 0.03:1.

fewer catalyst sites are available. As explained above, this could be another factor in determining polymer molecular weight.

Effect of Catalyst Concentration on Polymer Yield

A graph of polymer yield against catalyst ($TiCl_4$) concentration (at constant Al:Ti ratio) was found to have a maximum at about $3^1/_2\%$ titanium tetrachloride. (Fig. 3). The actual position of the peak on the graph could be subject to variation with polymerization conditions, since the catalyst and catalyst components react readily with nucleophilic impurities, such as oxygen or moisture, which may be present in the polymerization system.

It would be reasonable to conclude that an increase in catalyst concentration gives more available sites, and the observed reduction in yield at high catalyst concentrations would therefore at first sight seem surprising.

It is possible that, up to the maximum on the above curve (Fig. 3), an increased number of catalyst sites gives an increased polymer yield. After the maximum it would seem that the addition of catalyst somehow decreases the number of active sites and/or decreases the concentration of

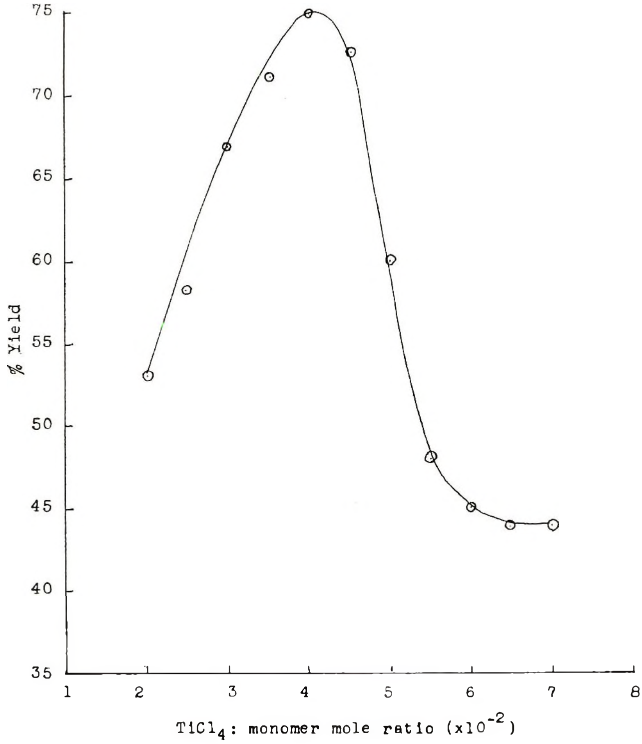


Fig. 3. Variation of polymer yield with catalyst concentration for the polymerization of *n*-octadecene-1 with $TiCl_4$–$AlEt_3$; 30 hr., 25°C., Al:Ti mole ratio 2.8:1.

polymerizable monomer. This latter possibility certainly appears to be relevant in the present polymerizations, as it has been shown that an increase in catalyst concentration causes an increase in the amount of non-terminal isomer in unpolymerized olefin, (Table IV).

The monomer isomerization figures would appear to indicate that the low yield at high catalyst concentration is probably due to loss of monomer by isomerization, whereas the low yield at low concentrations (where much 1-olefin is still apparently available for polymerization) is due to deactivation of the catalyst sites in some way. It is possible that deactivation of the few sites available at low catalyst concentrations could occur through reactions of the type described earlier in the discussion.

Effect of Catalyst Concentration on Polymer Intrinsic Viscosity

Intrinsic viscosity of the polymer was found to pass through a maximum as the concentration of titanium tetrachloride increases (Fig. 4).

Similar results have been obtained for the polymerization of propylene with titanium tetrachloride–triethylaluminum, the maximum intrinsic viscosity being obtained when the mole ratio of $TiCl_4$: monomer is 0.025:1.[16]

With up to about $3^1/_2\%$ (on monomer) titanium tetrachloride, it could be that the few catalyst sites available become surrounded so quickly by

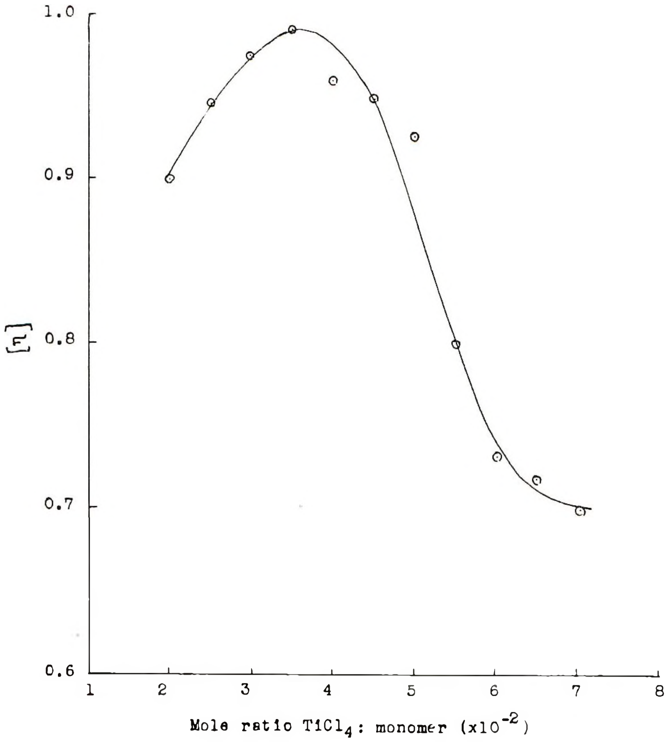


Fig. 4. Variation of polymer intrinsic viscosity with catalyst concentration for the polymerization of *n*-octadecene-1 with $TiCl_4$–$AlEt_3$; 30 hr., 25°C., Al:Ti mole ratio 2.8:1.

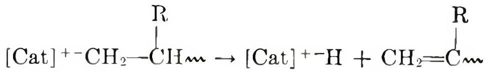
polymer that yield and molecular weight of the latter remains low, since diffusion of monomer through the (possibly crystalline) polymer would be a slow process. Under these conditions chain termination by hydride ion

TABLE IV

Variation of Monomer Isomerization and Polymer Yield with Catalyst Concentration

$TiCl_4$, mole/100 mole monomer	Nonterminal isomer in residual olefin, %	Polymer yield, %
2.0	5	44
2.5	35	58
3.0	55	67
3.5	62	71
4.0	70	75
4.5	68	73
5.0	76	60
5.5	74	48
6.0	85	45
6.5	90	44

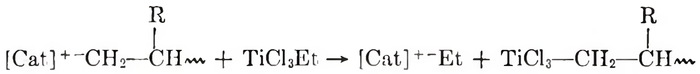
transfer from polymer chain to catalyst might become an important reaction [eq. (5)].



$$[\mathrm{Cat}]^{+-}\mathrm{CH_2}{-}\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{H}\!\sim\!\sim \rightarrow [\mathrm{Cat}]^{+-}\mathrm{H} + \mathrm{CH_2}{=}\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\!\sim\!\sim \qquad (5)$$

At higher catalyst concentrations it is reasonable to assume that, besides extra catalyst sites, an increasing number of compounds such as ethyltitanium trichloride, $TiCl_3Et$, ethyltitanium dichloride, $TiCl_2Et$, diethylaluminum chloride, $AlClEt_2$, and ethylaluminum dichloride, $AlCl_2Et$, become available in solution, and it could be these that cause chain termination.

It has already been suggested that the latter is favored by an increased concentration of Ti(III) or Ti(IV). For instance, it may be that ethyltitanium trichloride, $TiCl_3Et$, undergoes redistribution reactions in such a manner that the ethyl group from the titanium starts the next chain, as shown in eq. (6).



$$[\mathrm{Cat}]^{+-}\mathrm{CH_2}{-}\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{H}\!\sim\!\sim + \mathrm{TiCl_3Et} \rightarrow [\mathrm{Cat}]^{+-}\mathrm{Et} + \mathrm{TiCl_3}{-}\mathrm{CH_2}{-}\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{H}\!\sim\!\sim \qquad (6)$$

That intrinsic viscosity increases with Al:Ti molar ratio seems to indicate that chain termination is favored by the presence of high valency state titanium compounds, as has been suggested by Natta for the polymerization of propylene with titanium trichloride–triethylaluminum.

An increase in titanium tetrachloride concentration has been shown to cause an increase in monomer isomerization, and the low viscosity at higher catalyst concentrations could in part be due to the increasing importance of transfer reactions of the type described in earlier discussion, but involving isomerized monomer.

Effect of Polymerization Temperature on Polymer Yield

The yield of polymer was found to increase with reaction temperature up to about 45°C. and then fall off rapidly (Fig. 5).

Ludlum[15] has obtained similar results for the polymerization of ethylene with titanium tetrachloride–alkylaluminum catalysts, and has shown that the optimum temperature for polymer yield depends on the nature of the organometallic compound and the Al:Ti molar ratio. He proposed that an increase in temperature causes an increase in alkylation of the titanium, with consequent reduction of its average valency state and increase in polymer yield. Further increase in temperature is thought by Ludlum to assist in the reduction of titanium below its optimum valency state for catalytic activity, and polymer yield consequently falls.

In current work the amount of nonterminal olefin in unpolymerized material recovered from polymerizations carried out between −35 and 80°C. increases very sharply (15% to 95%) between 10 and 30°C. The sudden increase does not coincide with the reaction temperature (45°C.) giving highest polymer yield, and it would therefore seem that some factor

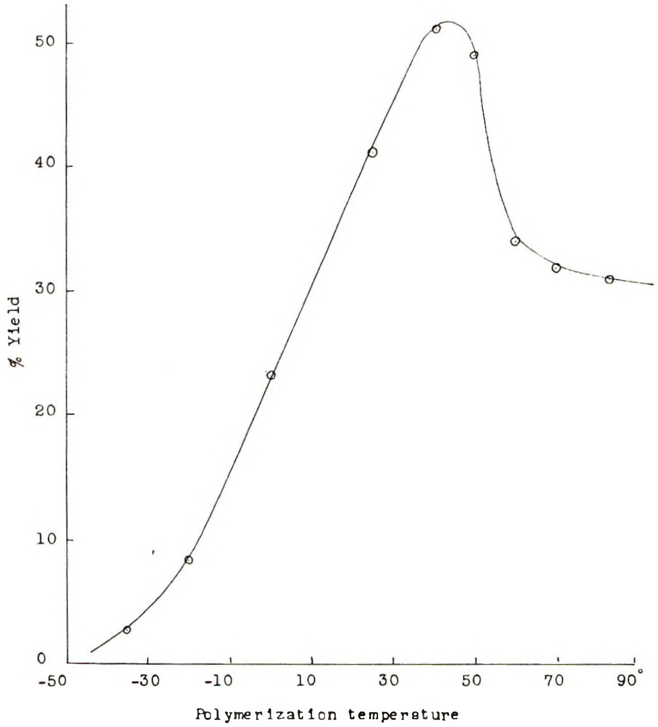


Fig. 5. Variation of polymer yield with polymerization temperature for the polymerization of *n*-octadecene-1 with $TiCl_4$–$AlEt_2$; 72 hr., Al:Ti mole ratio 2.8:1, $TiCl_4$:-monomer mole ratio 0.035:1.

more important than monomer isomerization is responsible for the drop in polymer yield at temperatures greater than 45°C. It could be that Ludlum's idea of increased temperature favoring reduction of titanium below its optimum valency state is applicable in this case.

Effect of Polymerization Temperature on Polymer Intrinsic Viscosity

This work has shown that an increase in reaction temperature causes a decrease in polymer intrinsic viscosity (Fig. 6).

It could be that increased temperature favors the formation of alkylated titanium compounds such as ethyltitanium trichloride, $TiCl_3Et$, which have already been suggested as a factor favoring chain termination. If this is so, increased temperature reduces the amount of triethylaluminum in the catalyst system, and previous work has shown that a decrease in polymer molecular weight would therefore be expected.

Effect of Polymerization Variables on Polymer Density, Melting Point, and Solubility in Hexane

Polymer density, melting point, and hexane solubility at 25°C. showed only small changes with variation in polymerization variables over the range studied (Tables V–VII).

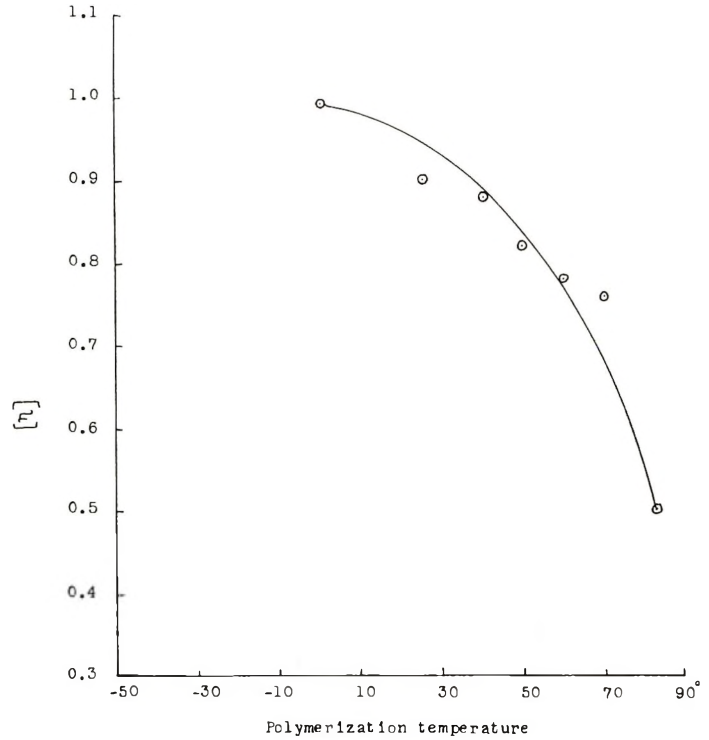


Fig. 6. Variation of polymer intrinsic viscosity with polymerization temperature for the polymerization of *n*-octadecene-1 with $TiCl_4$–$AlEt_3$; 72 hr., Al:Ti mole ratio 2.8:1, $TiCl_4$:monomer mole ratio 0.03:1.

Since all three properties are related to polymer crystallinity, which is more dependent on the microstructure than on molecular weight, results seem to indicate that very little variation in specific stereoregulating activity of the catalytic sites has been brought about by changing polymerization conditions. Since very little work has so far been carried out on the structural characterization of higher poly-α-olefins, it is not possible to

TABLE V
Effect of Al:Ti Ratio on Polymer Density, Melting Point, and Hexane Solubility

Al:Ti mole ratio	Polymer density at 25°C., g./cc.	Polymer m.p., °C.	Hexane-soluble at 25°C., %
2.0	0.901	68.5	42.2
2.2	0.901	69.5	—
2.4	0.901	74.0	50.0
2.6	0.902	75.0	50.7
2.8	0.899	75.0	51.1
3.0	0.900	72.0	52.7
3.2	0.900	69.0	48.0
3.4	0.898	66.5	48.0

TABLE VI
Effect of Catalyst Concentration on Polymer Density, Melting Point, and Hexane Solubility

$TiCl_4$, mole/100 mole monomer	Polymer density at 25°C., g./cc.	Polymer m.p., °C.	Hexane-soluble at 25°C., %
2.0	0.890	71.5	50
2.5	0.897	71.0	51
3.0	0.898	71.5	49
3.5	0.901	71.0	49
4.0	0.903	71.0	46
4.5	0.894	71.0	48
5.0	0.893	68.5	55
5.5	0.893	67.5	51
6.0	0.891	67.0	46
6.5	0.892	67.0	49
7.0	0.883	68.0	51

TABLE VII
Effect of Polymerization Temperature on Polymer Density, Melting Point, and Hexane Solubility

Polymerization temperature, °C.	Polymer density at 25°C., g./cc.	Polymer m.p., °C.	Hexane-soluble at 25°C., %
−35	0.900	62	58
−20	0.903	63	59
0	0.890	64	57
25	0.902	68	49
40	0.898	68	48
50	0.908	68	43
60	0.891	69	44
70	0.900	68	40
83	0.904	68	38

correlate physical properties with stereoregularity or microstructure. Further work is proceeding in an investigation of the structure and crystalline behavior of these polymers. For the present the following observations appear pertinent.

(*1*) Polymer melting point and hexane solubility both show a maximum with Al:Ti mole ratios in the range about 2.6–3.0.

(*2*) Polymers prepared at temperatures of 0°C. and below show a distinctly lower melting point and higher hexane-soluble content than all other polymers.

(*3*) The hexane solubility of the polymers decreases with increasing reaction temperature.

The third feature appears to be at variance with the observations of other workers using lower olefins. For example, Medalia showed that, in the polymerization of *n*-butene-1 with titanium tetrachloride–triethylaluminum catalysts, polymer solubility in isooctane at 25°C. remained approximately constant with increasing temperature.[14] Natta has demonstrated that, in the polymerization of propylene with Ziegler catalysts, polymer solubility increases with increasing polymerization temperature.[17] However it must be borne in mind that whereas only main-chain crystallization can occur in polypropylene and poly-1-butene, both side-chain and main-chain crystallization is possible with poly-1-octadecene.[18]

CONCLUSIONS

Variation in Al:Ti mole ratio, catalyst concentration, and polymerization temperature within the ranges studied produce marked changes in the yield and viscosity of poly-*n*-octadecene-1 prepared with Ziegler-type catalysts based on titanium tetrachloride and triethylaluminum. Only slight variation in polymer density, melting point, and hexane solubility occurs.

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Résumé

En utilisant un système de catalyseur du type Ziegler dérivé du tétrachlorure de titane et du triéthyl-aluminium, les effets de variation du rapport molaire Al/Ti, de la concentration en catalyseur, du temps de réaction et de la température sur le rendement et sur certaines propriétés physiques des polymères de *n*-1-octadécène ont été étudiés.

Les résultats montrent de nombreux phénomènes semblables à ceux obtenus par d'autres auteurs avec des oléfines plus basses. En général, le rendement en polymères montre un maximum net à un rapport molaire Al/Ti de 2.8:1 et une concentration totale en catalyseur au rapport molaire indiqué à 4% par rapport au monomère; le rendement croît fortement avec la température de polymérisation jusqu'à un maximum d'environ 40°C et avec le temps jusqu'à environ 12 heures à 25°C. La viscosité intrinsèque du polymère montre également une forte dépendance du rapport molaire Al/Ti et de la concentration en catalyseur, croissant avec les rapports molaires Al/Ti de 2.0 à 3.4, et montrant un maximum à une concentration en catalyseur de 3,5% par rapport au monomère. La viscosité intrinsèque du monomère montre une diminution avec une température de réaction croissante et un accroissement avec la durée de polymérisation. Les densités du polymère, les points de fusion et la fraction solubles dans l'hexane à 25°C montrent une moins forte dépendance des variables considérées et aucune conclusion ferme n'a pu être tirée. Une reaction importante concurrente avec la polymérisation est la formation de l'isomère de l'octadécène trans-non terminal. Ceci certainement affecte le rendement (l'isomère non terminal n'étant pas polymérisable) dans les mêmes conditions); l'effet de la présence du monomère isomérisé en cours de polymérisation sur les caractéristiques physiques du polymère est moins clair et nécessite encoce du travail ultérieur.

Zusammenfassung

An von Titantetrachlorid und Triathylaluminium abgeleiteten Zieglerkatalysatorsystemen wurde der Einfluss der Variation des Al:Ti-Molverhältnisses, der Katalysatorkonzentration, der Reaktionsdauer und -temperatur auf die Ausbeute und auf einige physikalische Eigenschaften der Polymeren aus *n*-1-Octadecen untersucht. Die Ergebnisse weisen viele gemeinsame Züge mit denjenigen von anderen Autoren an nied rigeren Olefinen erhaltenen auf. Im allgemeinen zeigt die Polymerausbeute eine ausgeprägtes Maximum bei einem Molverhältnis Al:Ti von 2,8:1 und einer Gesamtkatalysatorkonzentration (bei obigem Molverhältnis) von 4% bezogen auf Monomeres; die Ausbeute nimmt mit der Temperatur scharf zu einem Maximum bei etwa 40°C zu und mit der Dauer zu etwa 12 Stunden bei 25°C. Die Viskositätszahl des Polymeren zeigt ebenfalls eine starke Abhängigkeit vom Molverhältnis Al:Ti und von der Katalysatorkonzentration; sie steigt zwischen Molverhältnissen Al:Ti von 2,0–3,4 an und zeigt bei einer Katalysatorkonzentration von 3,5% in bezug auf das Monomere ein Maximum. Die Visnahme mit steigender Reaktionstemperatur und eine Zunahme mit der Polymerisationsdauer. Die Polymerdichte, der Schmelzpunkt und die in Hexan lösliche Fraktion (bei 25°C) scheinen eine viel geringerer Abhängigkeit von den betrachteten Variablen zu zeigen, und es können daher keine sicheren Schlüsse gezogen werden. Eine wichtige Konkurrentreaktion zur Polymerisation ist die Bildung eines trans-Isomeren von Octadecen mit nichtendständiger Doppelbindung. Dadurch wird sicher die Ausbeute beeinflusst (das Isomeren mit nichtendständiger Doppelbindung ist unter den gleichen Bedingungen nicht polymerisierbar); der Einfluss der Gegenwart eines isomerisierten Monomeren während der Polymerisation auf die physikalischen Charakteristik des Polymeren ist weniger klar, und weitere Versuche werden ausgeführt.

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Ordered Structures of Styrene-Butadiene Block Copolymers

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Synopsis

Anionically prepared block copolymers of butadiene and styrene exhibit solution properties which result from a two-dimensional ordering of the polymer molecules. The most notable of these properties is the iridescent colors of toluene solutions which are dependent on concentration and abruptly change on mechanical deformation. Electron micrographs of the surface of cast films indicate that the ordered structure is retained to some degree in the solid state.

Ordered structures of molecules in solution and in melts have been known for some time.[1] These ordered structures, commonly termed "liquid crystals," are usually two-dimensional in nature and lead to interesting flow and optical properties. The most notable of these properties are the "stringy" appearance when the solution is poured, resulting from two-dimensional ordering, and the colors of certain liquid crystal structures due to interference of reflected light waves from multiple layers.

The materials which have shown ordered arrangements in the fluid state have generally been of the low molecular weight variety, with the exception of polypeptides[2] and polystyrene-ethylene oxide block copolymers.[3] Recently we have found that solutions of block copolymers of styrene and butadiene in toluene anionically polymerized with butyllithium are similar to cholesteric liquid crystals in exhibiting iridescent colors which are dependent on concentration and change on mechanical deformation.[4]

Anionic polymerization of styrene and butadiene mixtures with the use of butyllithium as an initiator[5] produces a block copolymer structure nearly identical to that of two homopolymer chains joined at one end. This leads to a very peculiar situation, as the two polymers are normally incompatible. Therefore, we can picture the homopolymer portions in a situation where they would like to separate but cannot.

The incompatibility of the homopolymer segments results in ordered arrangements, as shown by the work of Sadron,[3] much the same way as soap molecules undergo an ordering when present in solution above a critical micelle concentration.[6] In fact, a critical copolymer concentration is found below which the solution is colorless and above which a reflection maximum occurs. Typical reflection spectra for several concentrations of a copolymer having an inherent viscosity of 2.0 are shown in Figure 1.

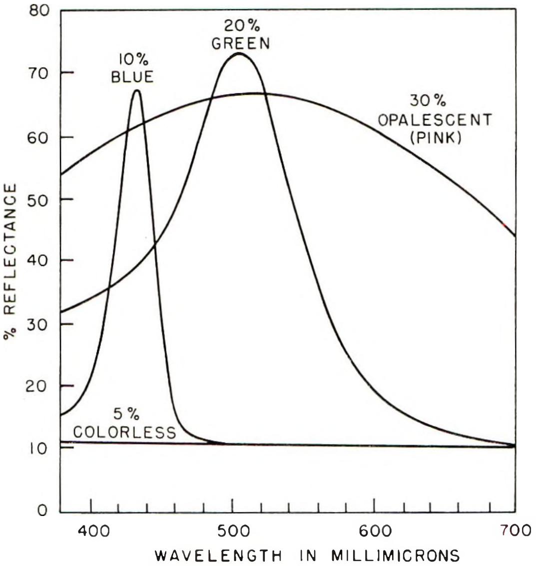

Fig. 1. Visible spectrum of styrene–butadiene block copolymer at various concentrations in ethylbenzene.

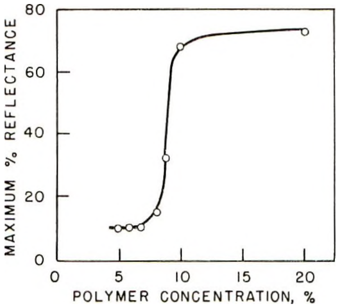

Fig. 2. Effect of polymer concentration on maximum reflectance in the visible spectrum.

Figure 2 shows the change in the reflection maximum with concentration and indicates a critical concentration of approximately 9% copolymer.

As the concentration is increased, the reflectance maximum moves from the initial blue into the green region and becomes somewhat broader. At 30% copolymer concentration this particular sample becomes opalescent with the spectral curve very broad, indicating a wide variety in the spacings of the ordered structures.

Dried films made from these solutions generally retain a blue color, and, if dried under carefully controlled conditions, the blue-green iridescent colors of the more concentrated solution may be preserved. It might be expected that such ordered arrangements should give a distinct film structure and, in fact, electron micrographs of surface replicas do show very regular patterns. These patterns vary according to the monodispersity of the copolymer chain size and the method of sample preparation.

Figure 3 shows some of the surface structures found. The regular spacings should correlate with molecular weight; however, difficulty in preparing monodisperse copolymer samples has prevented any meaningful studies

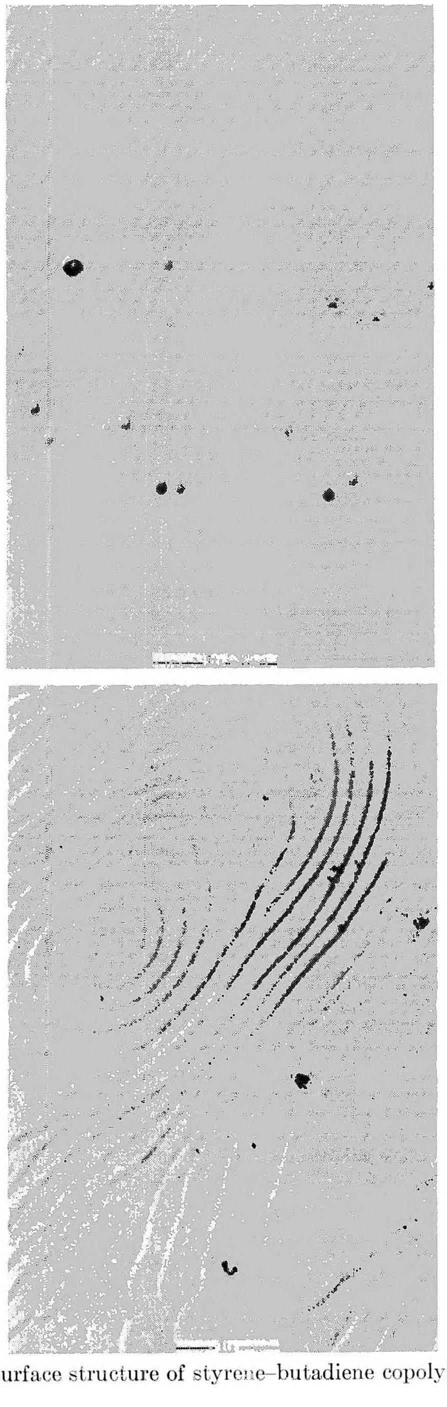

Fig. 3. Surface structure of styrene–butadiene copolymer film.

along this line. It is interesting to note that the regular spacings observed (1000–1200 A.) are not out of line with the dimensions attributed to randomly coiled polymer molecules.[7]

Similarity to cholesteric liquid crystals is pointed out by the vivid colors of thin films on a black background which change with concentrations, angle of viewing, and mechanical deformation.

In conclusion, it does not seem unreasonable to propose an ordering arrangement for the copolymer molecules in solution very similar to the one proposed for soap molecules in aqueous solutions. At low concentrations, the polymer molecules are dispersed in the solvent. Above some critical concentration, the interactions between the copolymer segments cause an aggregation into spherical micelles. At even higher concentrations these spherical micelles may coalesce into "laminar" structures which can be oriented in thin films to form regular layers. Such films exhibit vivid colors which are very similar to those observed in cholesteric liquid crystals.

The author wishes to thank F. Kristal for preparation of the polymers, E. Bradford for the electron micrographs, and B. Mildner for the color spectra.

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Résumé

Des copolymères à bloc préparés anioniquement au départ de butadiène et de styrène montrent des propriétés en solution qui résultent de l'ordre bidimensionnel existant au sein de ces molécules de polymères. La plus notable de ces propriétés est l'irisation des couleurs de solutions toluéniques qui dépendent de la concentration et changent brutalement par déformation mécanique. Les micrographies électroniques de la surface de films coulés indiquent que la structure ordonnée est maintenue jusqu'à un certain degré à l'état solide.

Zusammenfassung

Anionisch dargestellte Blockcopolymere aus Butadien und Styrol zeigen Lösungseigenschaften, welche durch eine zweidimensionale Ordnung der Polymermoleküle bedingt sind. Die bemerkenswertesten Eigenschaften sind die Schillerfarben der Toluollösungen, welche von der Konzentration abhängen und bei mechanischer Deformation sich plötzlich ändern. Elektronenmikroskopische Aufnahmen der Oberfläche gegossener Filme zeigen, dass die Ordnungsstruktur im festen Zustand zu einem gewissen Grad beibehalten wird.

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Polymerization of Cyclic Ethers in the Presence of Maleic Anhydride. Part I. Polymerization of Trioxane and 3,3-Bis(chloromethyl)oxetane by γ-Rays, Ultraviolet Light, and Benzoyl Peroxide

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Synopsis

Cyclic ethers such as trioxane and 3,3-bis(chloromethyl)oxetane have been polymerized easily in the presence of maleic anhydride by the irradiation of γ-rays and ultraviolet light. The polymer formed is a homopolymer of cyclic ether. The rate of polymerization is accelerated by suitable amounts of oxygen which is required to form some active species at the initiation step. The polymerization is inhibited by the addition of a small amount of radical scavenger, thus suggesting a radical initiating mechanism. In addition, the polymerization is easily initiated by benzoyl peroxide even *in vacuo* at or above 50°C. Diaroyl and diacyl peroxides are also effective, and polymerization also proceeds in the presence of chloromaleic anhydride, exactly in the same manner as in maleic anhydride. On the other hand, it is well known that polymerization of these cyclic monomers rarely occurs with radical catalysts and easily with cationic catalysts in the absence of maleic anhydride. From these results, it may be concluded that the polymerization is brought about by means of a radical–cationic species.

INTRODUCTION

It was previously reported that cyclic ethers, such as trioxane (TOX) and 3,3-bis(chloromethyl)oxetane (BCMO), could be polymerized only in the solid state by ionizing radiation to form well-oriented polymer crystals.[1] It is well known that these monomers can be polymerized by a strong cationic catalyst, such as BF_3 etherate or $SnCl_4$. However, no polymerization occurs at all by radical initiators as far as we know.

During our recent studies on the radiation-induced solid-state polymerization of binary monomer systems, it was found that the polymerization of these monomers could be markedly accelerated by the addition of suitable amounts of maleic anhydride (MAH), and moreover, the polymerization of this system took place even in the liquid state. Furthermore, it was discovered that polymerization of these cyclic ethers easily occurred by benzoyl peroxide (BPO) in the presence of MAH. The preliminary results of such polymerization phenomena have recently been reported.[2]

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The present paper is concerned with a detailed study of these polymerizations. In the following paper (Part II),[3] the investigation made in an attempt to elucidate the polymerization mechanism is described.

EXPERIMENTAL

Trioxane (TOX) was purified by sublimation or recrystallization from methylene chloride solution. Cyclic ethers such as BCMO were dried over calcium hydride and distilled twice under reduced pressure. Commercial grade MAH (Tokyo Kasei Co. Ltd., G. R. grade) was purified by recrystallization from chloroform solutions or by vacuum sublimation. The purified sample was confirmed to have no detectable amount of impurities such as metal ions from the emission spectrochemical analysis. Benzoyl peroxide (BPO) was used as received (Nakarai Chemicals, Ltd., G. R. grade). All other organic peroxides and α,α'-azobisisobutyronitrile (AIBN) were of the purest grade commercially available and used without further purification. All other reagents were purified according to the standard procedures.

Unless otherwise noticed, the radiation polymerizations were carried out in air in sealed glass ampules (diameter 11 mm., length 10–14 cm.) by using ^{60}Co γ-rays. For ultraviolet irradiation, a 100-w. Toshiba SHL 100 ultraviolet high-pressure mercury lamp and a quartz glass ampule (diameter 11 mm.) were used. The polymerization by the use of BPO was carried out *in vacuo* at 50°C. Immediately after stopping the reaction, the reaction mixture was poured into a large excess of methanol and the isolated polymer was washed thoroughly to remove the unreacted monomer, the remaining MAH and a small amount of poly(MAH), if any, then filtered, dried, and weighed. For chemical analysis and infrared absorption measurement, the polymers obtained were furthermore purified by reprecipitation from the dilute solutions with excess methanol. Viscosity measurement was performed in p-chlorophenol containing 2% α-pinene at 60°C. and in cyclohexanone at 40°C. for poly (TOX) and poly(BCMO), respectively. The degree of polymerization of poly(BCMO) was calculated from the relationship[4]:

$$\bar{P}_n = 1503[\eta].^{0.91}$$

RESULTS AND DISCUSSION

Polymerization of Trioxane Induced by γ-Radiation

The phase diagram for the TOX–MAH system is illustrated in Figure 1. The melting points of the monomer mixtures were determined by means of both capillary tube method and polarizing light microscope. This system forms a eutectic mixture.

In Figure 2 is shown the radiation-induced polymerization of trioxane in the presence of various amounts of MAH, together with the phase diagram. Polymerization occurs at 50°C. in the liquid state and at 20°C. in the

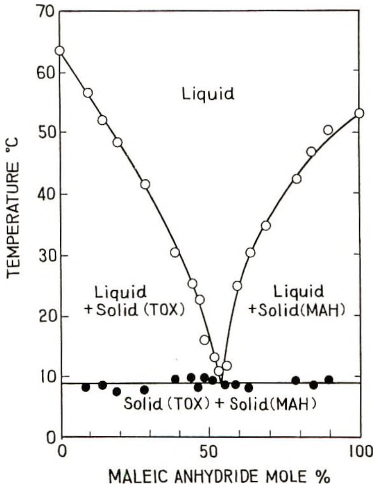

Fig. 1. Phase diagram of TOX–MAH binary system.

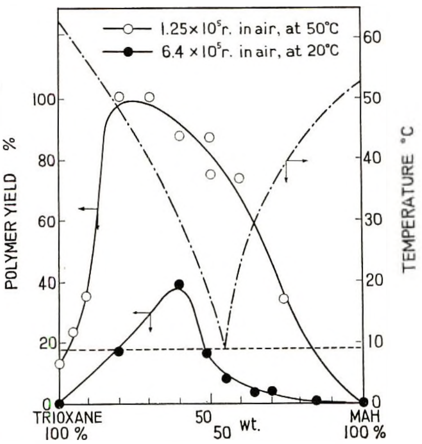

Fig. 2. Relationship between polymer yields and compositions of TOX–MAH binary system for the radiation-induced polymerization of trioxane: (-—-) liquidus; (--) solidus. Total monomer mixture, 0.6 g.; yield is based on initial trioxane.

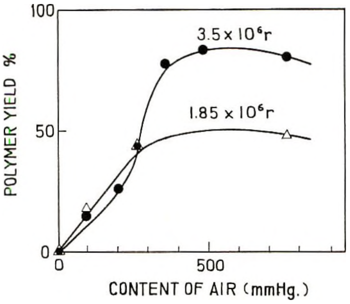

Fig. 3. Effect of air on polymer yields of TOX–MAH binary system (1:1, w/w) at 23°C. in the liquid state. ^{60}Co γ-rays, $I = 8.5 \times 10^4$ r/hr.

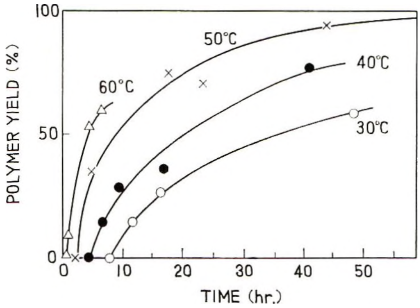

Fig. 4. Time–conversion curves for polymerization of trioxane at different temperatures in the TOX–MAH binary system (1:1, w/w) in the liquid state. ^{60}Co γ-rays, $I = 8.0 \times 10^3$ r/hr., in air.

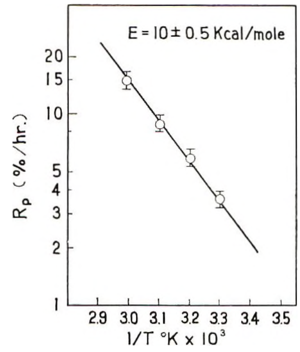

Fig. 5. Effect of temperature on the initial rate of polymerization of trioxane in the TOX–MAH binary system (1:1, w/w).

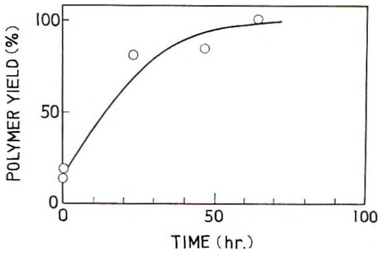

Fig. 6. Post-polymerization of trioxane in the TOX–MAH binary system (1:1, w/w) in air at 24°C. Preirradiation with ^{60}Co γ-rays, 2.1×10^6 r, in air, 22°C.

liquid or liquid–solid state. No polymer is obtained below the eutectic temperature, 9°C. on the solid state. There is an optimum monomer composition around a TOX content of 80–50%. It was found that although MAH was necessary for inducing polymerization of trioxane, most of the MAH remained unaltered after polymerization was completed. The polymer obtained is a white powder which is confirmed to be a polyether structure, as will be described below.

Figure 3 shows the effect of air on polymerization. It is one of the characteristic features of this polymerization that suitable amount of oxygen is necessary. In the complete absence of air, no polymerization took place. The course of polymerization of trioxane at various temperatures is shown in Figure 4 where the initial TOX–MAH (1:1) monomer mixture is liquid. However, the system turned purple in color during irradiation and after a definite induction period the polymer precipitated out. Polymerization proceeds heterogeneously up to higher conversion (nearly 100% based on the initial amount of trioxane). As the temperature was raised, the rate of polymerization increased and the induction period became short. From the conversion curves, it appears that the rate of polymerization is first-order with respect to monomer concentration, since the plot of $\ln([M_0]/[M])$ against time gives a straight line. The overall activation energy calculated from the Arrhenius plot in Figure 5 is 10 kcal./mole.

Figure 6 shows a typical example of the post-polymerization. It is very interesting to note that even when the irradiation was stopped before polymer formation, polymerization subsequently occurred to a considerable extent.

This suggests that some relatively stable initiating species is produced by irradiation. When the pre-irradiated monomer system was evacuated, and once again irradiated or allowed to stand without irradiation at 50°C., polymerization occurred, while no polymerization occurred for the system irradiated throughout *in vacuo*. The conditions and results are summarized in Table I.

TABLE I

Post-Polymerization of Trioxane[a]

	Irradiation temp., °C.	Atmosphere	Dose, r	Conversion, %
Sample 1[b]	40	Air	2×10^4	0
	50	Vacuum	10^5	94
Sample 2[c]	40	Air	2×10^4	0
	50	Vacuum	0	51
Sample 3	50	Vacuum	7×10^5	0

[a] Monomer mixture TOX–MAH = 3:2 (by weight).

[b] Irradiated (at 40°C.), deaerated, and again irradiated *in vacuo* (at 50°C.) for 14 hr.

[c] Irradiated (at 40°C.), deaerated, and allowed to stand *in vacuo* (at 50°C.) for 14 hr.

This indicates that oxygen is required at the initiation step to form some active species. Therefore, oxygen seems to be one of the essential components for the polymerization, polymerization *in vacuo* did take place in the presence of BPO, as shown in Table II.

The specific features of this polymerization are summarized in Table II. It is noted that the polymerization was inhibited by the addition of a small amount of radical scavenger such as hydroquinone or 1,1-diphenyl-2-picryl hydrazyl (DPPH) suggesting a radical initiation, and hardly any polymerization occurred in the presence of the common solvents.

TABLE II
Specific Features of the Polymerization of Trioxane[a]

No.	Radiation	Additive or solvent	Atmosphere	Temperature, °C.	Polymerization[b]
1	γ-rays	None	Air	>9	Yes
2	γ-rays	None	Vacuum	10–60	No
3	γ-rays	Hydroquinone	Air	33	No
4	γ-rays	DPPH	Air	33	No
5	γ-rays	BPO	Vacuum	33	Yes
6	None	BPO	Vacuum	50	Yes
7	Ultraviolet light	None	Air	28	Yes
8	γ-rays	Chloroform	Air	50	No
9	γ-rays	Acetone	Air	50	No
10	γ-rays	Methylene chloride	Air	50	No

[a] TOX–MAH = 1:1 (by weight).
[b] Polymerization of trioxane.

Spontaneous polymerization often occurs to an appreciable extent, when the monomer mixture is allowed to stand for a long time without irradiation above room temperature. However, under the present conditions, this spontaneous polymerization was scarcely observed.

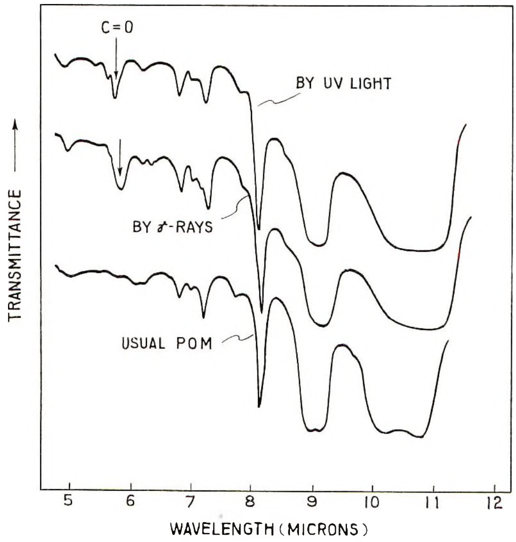

Fig. 7. Infrared spectra of polymers obtained by three different initiation methods: ultraviolet light irradiation (Toshiba SHL-100 UV Hg lamp, TOX–MAH = 1:1, w/w, 28°C.; γ-ray irradiation (TOX–MAH = 1:1, w/w, 20°C., dose = 4.0×10^6 r, conversion = 76%); POM (HCHO, γ-rays).

The polymer obtained was a white powder and was confirmed to be a polyether structure on the basis of the elementary analysis, its x-ray diffraction pattern and its infrared spectra.

ANAL. Calcd. for polytrioxane: C, 39.99%; H, 6.72%. Found: C, 39.66%; H, 6.54%.

In Figure 7 are shown the infrared spectra of the polymers. The spectrum of the polymer obtained is identical with that of polyoxymethylene except that there is a small absorption at 5.7–5.8 μ due to the carbonyl group. The intrinsic viscosities were relatively low, being in the range of 0.05–0.3 dl./g.

Polymerization of BCMO Induced by γ-Rays and Ultraviolet Light

Similar studies have been made for the BCMO–MAH system. The polymerization behavior is almost the same as observed for trioxane. Very little spontaneous polymerization occurred under the experimental conditions studied.

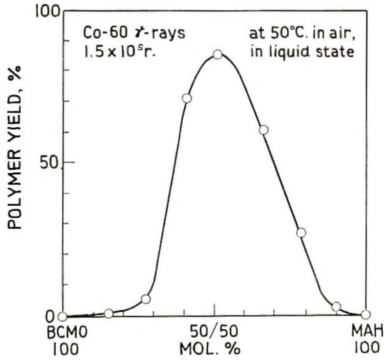

Fig. 8. Effect of monomer composition on radiation-induced polymerization of BCMO in the BCMO–MAH binary system.

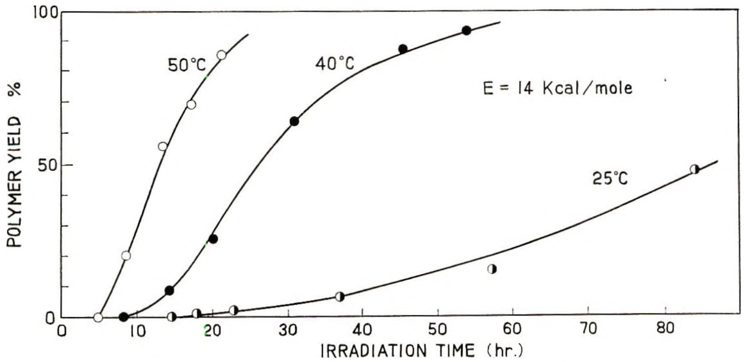

Fig. 9. Time–conversion curves for polymerization of BCMO at different temperatures in the BCMO–MAH binary system (1:1, molar) in the liquid state. ^{60}Co γ-rays, $I = 7.0 \times 10^3$ r/hr., in air.

Figure 8 shows the effect of monomer composition on radiation polymerization of the BCMO–MAH system in the liquid state. Although the monomer mixtures were always liquid at 50°C., the polymerization system became inhomogeneous and was completely solidified at higher polymer yields. The highest polymer yield was obtained for the equimolar mixture

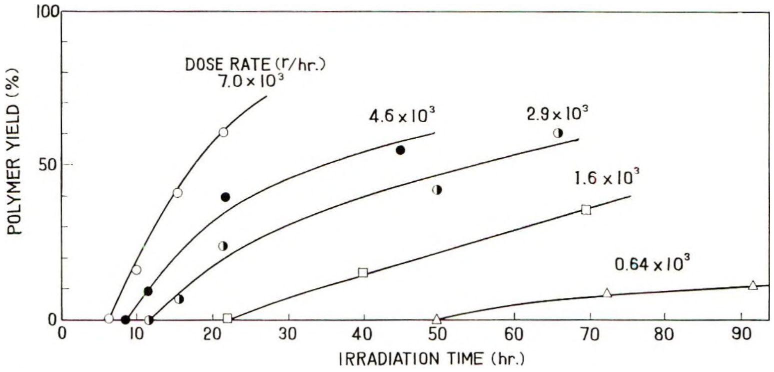

Fig. 10. Time–conversion curves for polymerization at different dose rates in BCMO–MAH binary system (1:1, molar) in the liquid state. ^{60}Co γ-rays, 50°C., in air.

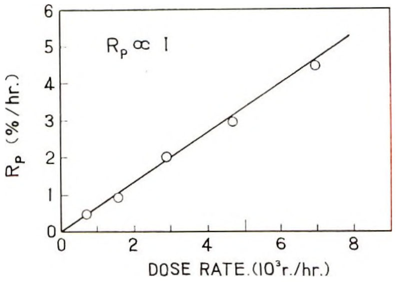

Fig. 11. Effect of dose rate on the initial polymerization rate of the BCMO–MAH binary system (1:1) in the liquid state; cf. Fig. 10.

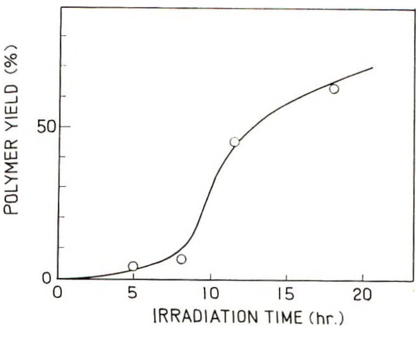

Fig. 12. Ultraviolet-induced polymerization of BCMO in the BCMO–MAH binary system (61:39, molar) in the liquid state. Irradiation with a Toshiba SHL-100 UV high-pressure lamp, 36°C., in air.

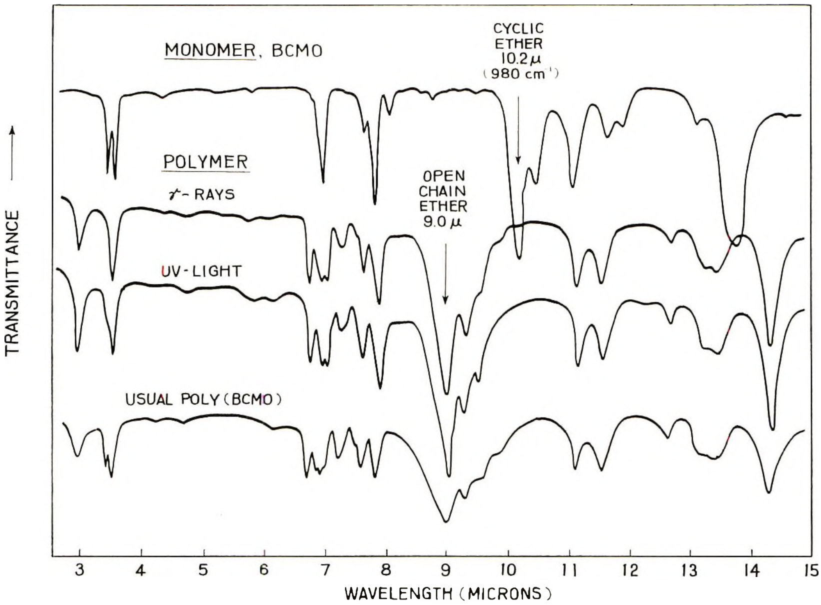

Fig. 13. Infrared spectra of the polymers obtained in the BCMO–MAH binary system compared with those of BCMO monomer and conventional poly(BCMO).: for γ-ray polymer, BCMO/MAH = 4:3; air, 24°C., dose = 1.4×10^6 r, conversion 91%; for the ultraviolet light-initiated polymer, BCMO/MAH = 61:39, 36°C., conversion 46.3%, $[\eta]$ = 0.05 dl./g.; for the conventional polymer, γ-ray polymerization in the solid state, 0°C.

of BCMO and MAH, as in the TOX–MAH system. This fact suggests that the highest concentration of an active species formed may be obtained at an equimolar mixture, or MAH may participate in the propagation step as well as in the initiation. The effect of air was also pronounced.

Figure 9 shows the course of polymerization of equimolar MAH–BCMO mixtures at different temperatures. The activation energy was calculated to be 14 kcal./mole. The rate of polymerization was found to be first-order with respect to monomer concentration from the time–conversion curves.

Figures 10 and 11 show the effect of dose rate on the polymerization. The induction period was found to be inversely proportional to the dose rate. As seen in Figure 11 the initial rate was proportional to the dose rate, in spite of the heterogeneous character of the polymerization.

In Figure 12 is shown an example of ultraviolet-induced polymerization, in which the monomer mixture was irradiated in a quartz glass ampule by ultraviolet light from a Toshiba SHL-100 UV ultra high-pressure mercury lamp at the distance of 15 cm.

In general, the polymer obtained was a white powder and was confirmed to be poly(BCMO) from chemical analysis, its x-ray diffraction, its infrared spectrum and its melting point.

Anal. Calcd. for poly(BCMO): C, 38.74%; H, 5.20%; Cl, 45.74%. Found: C, 38.75 ± 0.07%; H, 5.50 ± 0.03%; Cl, 45.0%.

Figure 13 shows the infrared spectra of the polymers obtained. The spectra were almost identical with that of the poly(BCMO) obtained by radiation-induced solid-state polymerization. The intrinsic viscosities were in the range of 0.05–0.3 dl./g. (P_n = 25–500), and melting points were in the range of 162–172°C. for the polymers obtained under the various conditions.

Polymerization TOX and BCMO Induced by BPO *in Vacuo*

In view of the fact that either the oxygen–γ-rays or the oxygen–ultraviolet light combination was very effective for inducing the polymerization of cyclic ethers in the presence of MAH, we attempted to carry out the polymerization *in vacuo* by using a small amount of BPO instead of air. Although it is well known that no polymerization of these monomers occurs by radical initiation, the BPO-catalyzed polymerization easily took place in the presence of MAH, in almost the same manner as with radiation. Typical polymerization curves for BCMO and trioxane are shown in Figures 14 and 15, respectively, where the initial MAH–cyclic ether monomer mixtures (1:1) were liquid. At first, the system turned purple and after a definite induction period the polymer precipitated out. Polymerization proceeded heterogeneously up to high conversion (nearly 100% based on the initial amount of cyclic ethers). The polymerization behavior is exactly the same as observed with radiation. With increasing initial BPO concentration, the purple color in the system was intensified, the induction period was shortened, and the rate of polymerization increased. As is shown in Figure 14, the degree of polymerization increased as a function of

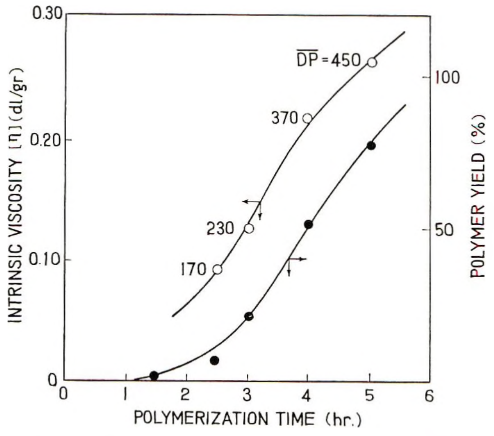

Fig. 14. BPO-catalyzed polymerization of BCMO in the BCMO–MAH system (1:1, molar) in the liquid state; BPO = 1 wt.-% based on the total monomer mixture, *in vacuo*, 50°C.

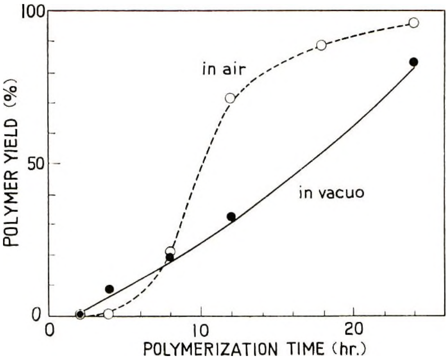

Fig. 15. BPO-catalyzed polymerization of trioxane in the TOX–MAH system (1:1 w/w) in the liquid state; BPO = 1.43 wt.-% based on the total monomer mixture; 50°C.

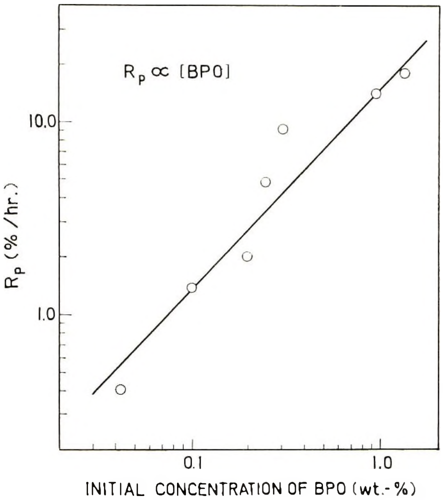

Fig. 16. Effect of BPO concentration on the initial rate of BCMO polymerization in the BCMO–MAH binary system (1:1, w/w). BPO based on the total monomer mixture, *in vacuo*, 50°C.

polymerization time. This suggests that the polymerization proceeded successively.

In order to study the polymerization behavior in detail, the following kinetic study has been made for the BCMO–MAH system. Figure 16 shows the dependence of the rate of BCMO polymerization on the initial catalyst concentration at 50°C. At constant monomer mixture (1:1 by weight) the concentration of BPO was varied over a wide range. The order of the reaction with respect to BPO is approximately 1, as is seen in Figure 16. Figure 17 shows the effect of MAH concentration in the monomer mixture on the polymerization. The monomer alone could not polymerize with BPO under the conditions used. Polymerization occurred

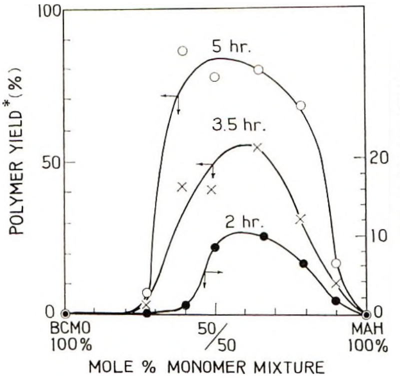

Fig. 17. Relationship between polymer yields and composition of the BCMO–MAH binary system in the polymerization of BCMO induced by BPO (1 wt.-%), *in vacuo*, 50°C. (liquid state). Polymer yield based on the initial amount of BCMO.

more favorably when the monomer mixture was nearly 1:1, as was observed in the radiation polymerization. Table III indicates the relation between the initial MAH concentration on the monomer mixture and the intrinsic viscosity of the polymer obtained. With increase in the MAH content, the intrinsic viscosity tended to decrease.

The overall activation energy calculated from the Arrhenius plot in Figure 18 was 23 kcal./mole. The value was somewhat higher than the energy determined by Penczek[4] for the polymerization catalyzed by gaseous BF_3 in methylene chloride (18.0 kcal./mole).

The polymer obtained was a powder and was confirmed to be a polyether by means of the chemical analysis, its x-ray diffraction pattern, and its infrared spectrum. The cationic polymerization of BCMO initiated by BF_3-OEt_2 occurred easily in the presence of MAH as well as in methylene chloride. The infrared spectrum of the purified polymer is illustrated in Figure 19, together with that of the polymer obtained in the MAH by use of a BF_3 etherate catalyst. These spectra are almost identical with that of the poly(BCMO) obtained by radiation-induced solid-state polymerization.

Finally, we examined briefly the effects of various organic peroxides as catalyst for the present polymerization. Among them, diaroyl peroxides

TABLE III
Relation between MAH Content and the Intrinsic Viscosity in the Polymerization of BCMO for the BCMO–MAH System

MAH, mole-%	Conversion, %	[η], dl./g.[a]
28.3	7.0	0.10
40.4	15.5	0.25
50.0	12	0.11
66.0	16.8	0.06
78.6	15	0.04

[a] [η] in cyclohexanone, 40°C.

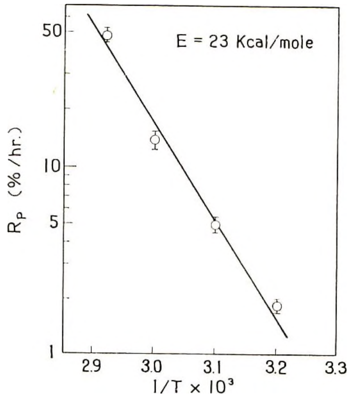

Fig. 18. Effect of temperature on the rate of BCMO polymerization in the BCMO–MAH binary system (1:1, molar) induced by BPO (1 wt.-%), *in vacuo*, at 50°C. (liquid state).

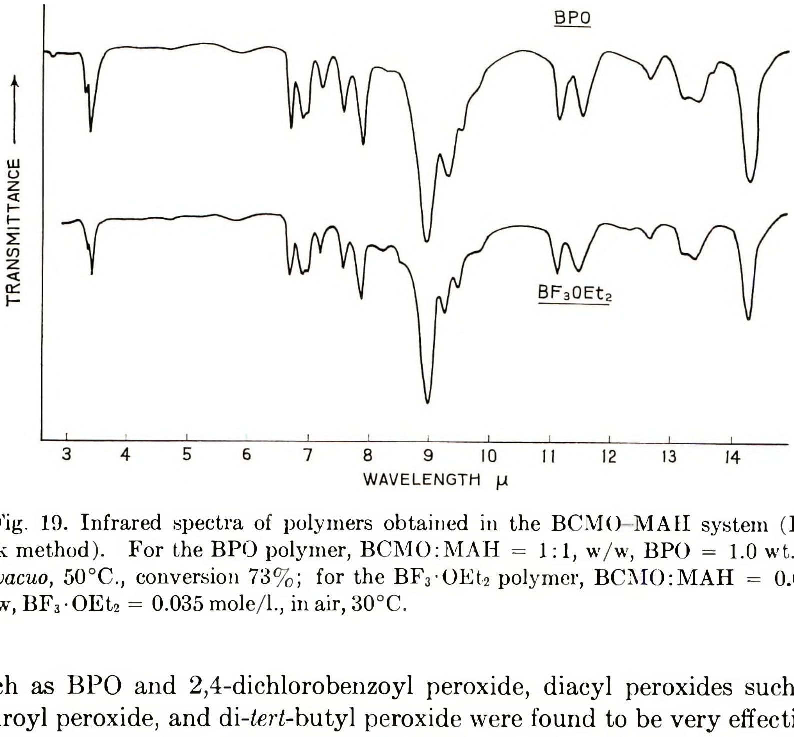

Fig. 19. Infrared spectra of polymers obtained in the BCMO–MAH system (KBr disk method). For the BPO polymer, BCMO:MAH = 1:1, w/w, BPO = 1.0 wt.-%, *in vacuo*, 50°C., conversion 73%; for the $BF_3 \cdot OEt_2$ polymer, BCMO:MAH = 0.6:1, w/w, $BF_3 \cdot OEt_2$ = 0.035 mole/l., in air, 30°C.

such as BPO and 2,4-dichlorobenzoyl peroxide, diacyl peroxides such as lauroyl peroxide, and di-*tert*-butyl peroxide were found to be very effective. α,α'-Azobisisobutyronitrile failed to initiate such polymerization. The polymerization also occurred readily in the presence of chloromaleic anhydride exactly in the same manner as in MAH, but failed to occur in the other acid anhydrides examined.

On the basis of the results obtained, it may be suggested that an active species such as a cationic intermediate is at first formed from the combination of MAH and cyclic ethers with a free-radical reaction, and then this species would initiate the polymerization by a cationic mechanism. In the radiation-induced polymerization, oxygen is considered to be converted to some peroxidic compound which would decompose to yield a free radical in the same way as BPO. The radicals arising from these peroxides are characterized by their strong hydrogen abstraction ability for the cyclic ethers. The hydrogen abstraction of cyclic ethers and an electron-accepting property of MAH seem to play an important role in producing a species sufficiently active to initiate cationic polymerization.[3] During the induction period observed in each case, such an active species is expected to be formed and accumulated. Detailed investigation of the reaction mechanism and some evidences for a radical-induced cationic mechanism will be described in the following paper (Part II).[3]

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Résumé

Des éthers cycliques tels que le trioxane et le 3,3-bis(chlorométhyl) oxétane peuvent être aisément polymérisés en présence d'anhydride maléique par irradiation aux rayons-γ ou à la lumière ultraviolette. Le polymère formé est un homopolymère d'éther cyclique. La vitesse de polymérisation est accélérée par une quantité adéquate d'oxygène qui est requise pour former des espèces actives au cours de l'étape d'initiation. La polymérisation est inhibée par l'addition de faibles quantités de capteurs de radicaux ce qui suggère un mécanisme par radicaux initiateurs. En outre, le polymérisation est facilement initiée par le peroxyde de benzoyle, même sous vide à une température de 50°C. Les peroxides de diaroyle et de diacyle sont également effectifs et la polymérisation progresse également en présence d'anhydride chloromaléique, exactement de la même façon qu'en présence d'anhydride maléique. Par ailleurs, il est bien connu que la polymérisation de ces monomères cycliques se passe difficilement en présence d'un catalyesur radicalaire et facilement en présence d'un catalyseur cationique en absence d'anhydride maléique. Il résulte que la polymérisation s'effectue au moyen d'espèces cationiques–radicalaires.

Zusammenfassung

Zyklische Äther wie Trioxan und 3,3-Bis(chlormethyl)oxetan konnten in Gegenwart von Maleinsäureanhydrid durch Bestrahlung mit γ-Strahlen und UV-Licht leight zur Polymerisation gebracht werden. Das gebildete Polymere ist ein Homopolymeres des zyklischen Äthers. Die Polymerisationsgeschwindigkeit wird durch eine geeignete Sauerstoffmenge, welche zur Bildung einer aktiven Spezies beim Startschritt erforderlich ist, erhöht. Die Polymerisation wird durch Zusatz einer kleinen Menge von Radikalfängern inhibiert, was für einen Radikalmechanismus spricht. Ausserdem wird die Polymerisation durch Benzoylperoxyd sogar im Vakuum bei oder oberhalb 50°C leicht gestartet. Die Diaroyl- und Diacylperoxyde sind gleichermassen wirksam und die Poly-

merisation verläuft auch in Gegenwart von Chlormaleinsäureanhydrid in genau der gleichen Weise wie mit Maleinsäureanhydrid. Andererseits ist gut bekannt, dass die Polymerisation dieser zyklischen Monomeren in Abwesenheit von Maleinsäureanhydrid kaum durch Radikalstart, aber leicht mit kationischen Katalysatoren verläuft. Aus diesen Ergebnissen kann man schliessen, dass die Polymerisation durch ein Radikalkation eingeleitet wird.

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Polymerization of Cyclic Ethers in the Presence of Maleic Anhydride. Part II. Investigation of the Polymerization Mechanism

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Synopsis

In order to elucidate the reaction mechanism of both the radiation-induced and benzoyl peroxide-catalyzed polymerizations of cyclic ethers in the presence of maleic anhydride, the development of color during reaction and copolymerization of oxetane derivatives were investigated. Upon addition of a small amount of the γ-ray or ultraviolet-irradiated equimolar solution of a cyclic ether and maleic anhydride to isobutyl vinyl ether, a rapid polymerization took place, and the resulting polymer was confirmed to be a homopolymer of isobutyl vinyl ether. A heated solution of dioxane, maleic anhydride, and a small amount of benzoyl peroxide can initiate the polymerization of isobutyl vinyl ether in the same manner. The electrical conductivity of a 1:1 mixture of maleic anhydride and dioxane is increased by about a factor of ten after ultraviolet irradiation. These results indicate that some cationic species are actually formed in the system by irradiation or the decomposition of added benzoyl peroxide. The mechanism of formation of the cationic species responsible for the initiation may be explained as follows. A free radical of an ether is formed by abstraction of a hydrogen atom attached to the carbon adjacent to oxygen atom, followed by a one-electron transfer from the resulting radical to maleic anhydride, an electron acceptor, to yield the cationic species of the ether and the anion-radical of maleic anhydride, respectively. The resulting cationic species as well as the counteranion-radical are resonance-stabilized. Therefore, the present polymerization may be designated a radical-induced cationic polymerization.

INTRODUCTION

In the preceding paper (Part I), experimental results on both the radiation- and BPO-induced polymerization of trioxane (TOX) and 3,3-bis(chloromethyl)oxetane (BCMO) in the presence of maleic anhydride (MAH) were reported in detail.[1] It was suggested that the polymerization is brought about by means of some cationic species which is produced by a radical process in the binary system of cyclic ether and MAH by irradiation in air or by decomposition of BPO. The present paper is concerned with the investigation which was undertaken in order to elucidate the initiation mechanism of the polymerization.

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EXPERIMENTAL

3-Ethyl, 3-chloromethyloxetane (ECMO) which was prepared by H. Watanabe[2] in our laboratory was dried over calcium hydride and distilled under low pressure (67°C., 19 mm. Hg) before use. Chloromaleic anhydride (ClMAH) (Tokyo Kasei Co., Ltd. G. R. grade) was purified by distillation under reduced pressure (72°C., 8 mm. Hg). Other acid anhydrides used were of G.R. grade and purified by distillation of recrystallization. Boron trifluoride etherate (BF_3OEt_2) was obtained from Nakarai Chemicals, Ltd. and was used without purification. All other cyclic ethers and reagents were purified according to usual procedures.

The polymerization procedures were the same as already described in the preceding paper.[1] Copolymer compositions were determined by means of infrared spectroscopy (KBr disk method). The electrical conductivity of the mixture solution of cyclic ether and MAH was measured by the use of a drum-shaped glass cell equipped with two platinum plates.

RESULTS AND DISCUSSION

Development of Color in the Reaction System

It is of great interest to note that a purple color always developed in the nearly equimolar mixture of MAH and the cyclic ethers prior to the polymer formation, both in the radiation- and BPO-catalyzed polymerization. The absorption spectra of the reaction systems for several cyclic ethers are

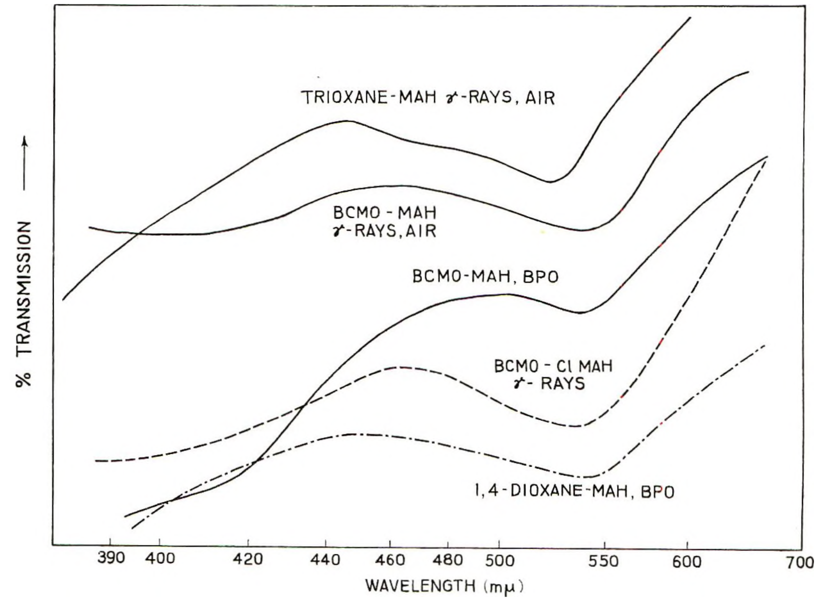


Fig. 1. Absorption spectra of the reaction systems. Polymerization with γ-rays at room temperature, with BPO at 50°C.; MAH–cyclic ether system (1:1, molar).

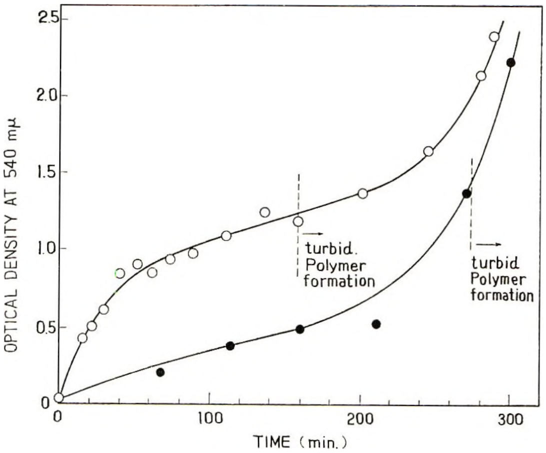


Fig. 2. Relationship between absorption at 540 mμ and reaction time with BCMO–MAH (1:1, molar): (○) BPO, 50°C., in air, 0.8%; (●) γ-rays, $I = 7.0 \times 10^3$ r/hr., in air. Quartz glass cell, 2 mm. thickness, reference dioxane.

shown in Figure 1; in all of these systems, an equimolar quantity of MAH and cyclic ethers was irradiated in air or heated in the presence of small amounts of BPO *in vacuo*. In each case, a broad absorption maximum appeared at 500–550 mμ. No absorption was observed in the visible range until these mixture solutions were irradiated or heated. On the other hand, in the infrared spectra of these reaction systems no change was observed after irradiation, indicating that the concentration of the colored species formed was quite low. The development of color in the reaction system was followed spectrophotometrically until polymer was formed. The results are shown in Figure 2. The coloration is markedly dependent upon the mixture ratio of MAH to cyclic ether. Color varied from deep purple to light reddish brown with decreasing amount of MAH in the mixture system, and at lower concentrations (MAH < 10%), no coloration was visible. The intense color of the reaction system, as is seen Figures 1 and 2, seems to be associated with an interaction between MAH and cyclic ether such as a complex formation, caused by irradiation or decomposition of added BPO. In general, the more intense the coloration of the system, the greater the extent of polymerization. Hence, the colored complex formed may be considered to be closely related to the active species which would initiate the polymerization. An apparently similar phenomenon is that the polymerization of *N*-vinylcarbazole in the presence of suitable π-complex-forming electron acceptors such as *p*-chloranil is accompanied by the development of color, and a cationic radical mechanism is proposed.[3,4]

The polymerization and coloration were briefly examined for systems with various cyclic ethers and MAH (1:1). 1,3-Dioxolane, 1,4-butanediol cyclic formal, and other oxetane derivatives could polymerize, accompanied by color formation in a similar manner as BCMO. The preliminary study indicated that the higher the basicity of cyclic ethers, the more intense the color developed; this suggests that the color formation may be correlated with the basicity of cyclic ethers, although it does not reveal whether or not the color formation is due to the complex between MAH and cyclic ether.

Evidence for the Formation of Cationic Species in the Ether–Maleic Anhydride Systems

Anticipating that some cationic species may be formed in the cyclic ether–MAH system on irradiation or decomposition of BPO, we attempted to use a small amount of ultraviolet light- or γ-ray-irradiated equimolar solution of BCMO and MAH or trioxane and MAH as a catalyst for the polymerization of isobutyl vinyl ether (IBVE). As briefly reported previously,[5] it was found that IBVE polymerized explosively by the use of such a catalyst system in air at room temperature. From the infrared spectra, the polymer thus obtained was confirmed to a homopolymer of IBVE, rather than a copolymer with MAH. A nonirradiated solution or MAH or maleic acid alone could not initiate such polymerization. Therefore, it is demonstrated that some cationic species were formed in the irradiated system, since IBVE is known to polymerize only by cationic initiations.

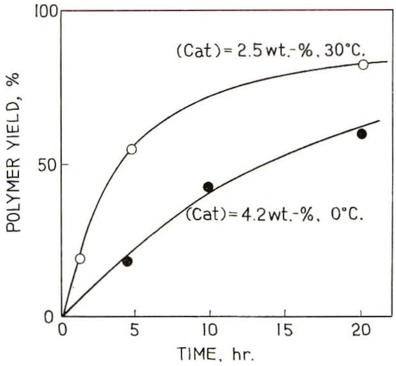


Fig. 3. Bulk polymerization of IBVE in air by use of a heated solution of MAH, dioxane, and BPO as catalyst. A solution of 3.0 g. MAH, 3.1 g. dioxane, and 0.1 g. BPO was heated *in vacuo* at 50°C. for 46 hr. and was then used as catalyst. The catalyst concentration is based on amount of IBVE.

Besides these polymerizable cyclic ethers, a variety of cyclic ethers, such as dioxane or paraldehyde, as well as chain ethers were found to be successfully used for this purpose. The preliminary results are shown in Table I. In the case of the polymerizable cyclic ethers the irradiation was stopped immediately before polymer formation. Thermal decomposition of added BPO also produced active species in the ether–MAH system. Typical results of bulk polymerization of IBVE by the use of this catalyst system are shown in Figure 3. The ethereal solution of MAH thus treated usually developed a purple or reddish-brown color. Bryce-Smith et al.[6] reported

TABLE I
Bulk Polymerization of IBVE Initiated by the Species Derived from Irradiated Ethereal Solutions of MAH

Catalyst systems			Polymerization conditions[b]		
Ether	Ether:MAH mole ratio	Irradiation conditions[a]	Catalyst concn., wt.-%[c]	Time, min.	Conversion, %
BCMO	1.0/1.0	γ-rays (2.0 × 10^4 r), 50°C.	≥20	Explosive	
BCMO	1.0/1.0	Nonirradiated, 30°C.	≥20	60	~0
Dioxane	1.75/1.00	UV, 35°C.	10	25	43
	0.87/1.00	UV, 35°C.	4	30	68
	0.87/1.00	UV, 35°C.	10	60	98
	0.87/1.00	UV, 35°C. or γ-rays (4.0 × 10^5 r), 30°C.	>20	1, explosive	
Diethyl ether	2.0/1.0	UV, 30°C.	≥20	Explosive	
Toluene		UV, 30°C.	20	120	0
MAH		Nonirradiated	10	1440	0
Maleic acid			15	1440	0

[a] UV irradiation: 100-w. Toshiba high-pressure mercury lamp at a distance of 15 cm. in air for 60 min., γ-rays: 1000 curie ^{60}Co source.

[b] Polymerizations were carried out in air at 20°C. The reaction mixtures were poured into a large excess of methanol, and the polymers obtained were purified by reprecipitation with methanol from chloroform solutions.

[c] Catalyst concentration based on amount of IBVE.

TABLE II
Electrical Conductivity of 1,4-Dioxane–Maleic Anhydride Solution Mixture before and after Ultraviolet Irradiation[a,b]

	Current, amp.			
Irradiation time, hr.	At 10 v. applied voltage	At 50 v. applied voltage	Relative resistance,[c] v./amp. × 10^{-5}	Color of irradiated system
0	1.3	6.7	77.0	Colorless
2	11.0	64.0	8.4	Brown
4	15.0	80.5	6.4	Reddish brown

[a] Mixture dioxane 54 mole-%, MAH 46 mole-%.

[b] Irradiation in quartz glass ampule, by using a Toshiba SHL 100 UV high-pressure mercury lamp at a distance of 10 cm., in air, 25°C.

[c] Ω measurement in air at 15°C. by use of a drum-shaped glass cell; Pt plate: 12 mm. diameter disk; distance of the plate, 20 mm.

that similar coloration was observed when MAH was irradiated in diethyl ether solution with sun light.

Figure 4 shows the polymerization of *N*-vinylcarbazole (VCZ) in toluene by the use of a catalytic quantity of the ultraviolet-irradiated solution of MAH in dioxane. This is further evidence to indicate that some ionic species had actually been formed in this system.

Table II shows the electrical conductivity of a nearly 1:1 solution of MAH and dioxane before and after ultraviolet irradiation.

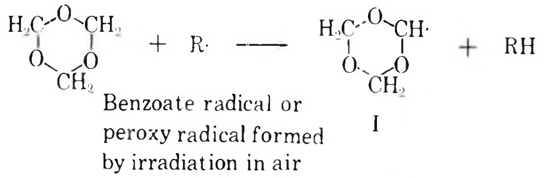
As is seen in Table II, the electrical conductivity of the mixture solution increased about tenfold on irradiation. From these results, it is evident that an active species responsible for a cationic initiation is actually formed in the MAH–cyclic ether reaction system by irradiation or decomposition of BPO.

Copolymerization of ECMO and BCMO

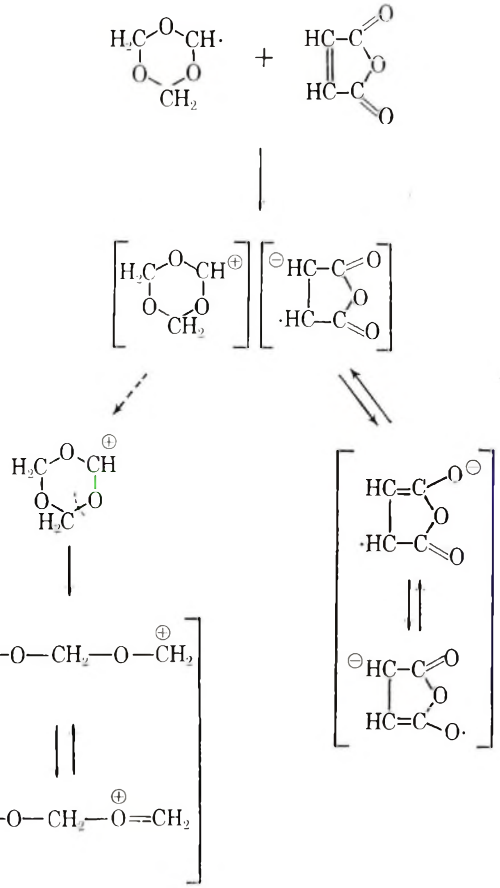
In another attempt to elucidate the polymerization mechanism, the copolymerization of ECMO and BCMO was carried out in the presence of MAH by using the three different catalysts. The copolymer compositions were calculated from the ratio of the absorbance at 14.3 μ (C—Cl), which is a characteristic band of poly(BCMO), to that at 3.45 μ (CH_2) in the infrared spectra of copolymers, by the base-line method. The copolymerization was stopped at low conversion ($<5\%$). The rate of polymerization increased in each case with increase in ECMO content in the monomer mixture. Figure 5 shows the relationship between monomer and copolymer compositions. As is seen in Figure 5, the results obtained with γ-rays and BPO catalyst are identical within experimental error with those obtained with BF_3OEt_2. This indicates that the polymerizations induced by both γ-rays and BPO are substantially propagated by a cationic mechanism. A purple color also developed during the copolymerization with both γ-rays and BPO, whereas with BF_3OEt_2 the system remained entirely colorless. The monomer reactivity ratios, r_1 (ECMO) and r_2(BCMO) calculated from the Fineman and Ross relationship were 8.0 ± 0.20 and 0.07 ± 0.04, respectively. These values are in agreement with those previously obtained by BF_3OEt_2 for the same monomer system in methylene chloride at 30°C. ($r_1 = 6.5, r_2 = 0.05$).[2]

Tentative Proposal of Initiation Mechanism

On the basis of the results hitherto obtained, it may be concluded that the polymerization is brought about by means of some cationic species formed by irradiation in air or by decomposition of BPO in the mixture of MAH and cyclic ether through a radical process. Therefore, a radical-induced cationic mechanism seems to be probable for the present polymerization. The proposed mechanism for the polymerization of trioxane in the presence of MAH is shown in eqs. (1) and (2).



(1)



(2)

At first, the radical R·, which may be a benzoyl radical or peroxy radical formed by irradiation, abstracts a hydrogen atom from trioxane to form a trioxane radical (I). The resulting radical I, which is of nucleophilic character may form a charge-transfer type complex with MAH, an electron acceptor, followed by one-electron transfer from the radical I to MAH to yield the cationic species of the ether and the anion-radical of MAH, respectively. Then the trioxane cation would undergo ring-opening to become a cationic species with a formate endgroup. The resulting cationic species as well as gegenanion-radical are resonance-stabilized. There have recently been several reports concerning the free-radical reactions of cyclic ethers.[7-9] A hydrogen atom attached to the carbon adjacent to oxygen atom of a cyclic ether is abstracted preferentially in a free-radical

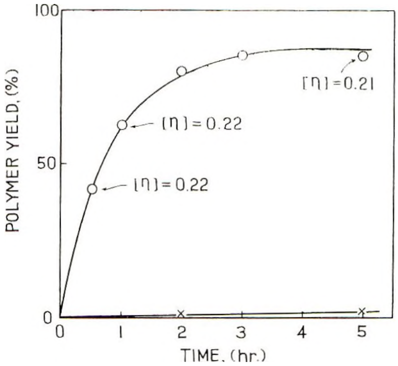


Fig. 4. Solution polymerization of *N*-vinylcarbazole initiated by the cationic species derived from the ultraviolet-irradiated solution of MAH in dioxane: (O) after irradiation; (X) before irradiation. Catalyst system: a solution of MAH–dioxane (46:54, molar) irradiated by ultraviolet light in air at 25°C. for 4 hr. at a distance of 10 cm. Polymerization conditions: VCZ monomer = 2 g. in 10 ml. toluene; [catalyst] = 5 wt.-% on amount of VCZ; in air; 30°C. Intrinsic viscosity is in deciliters per gram, in benzene at 30°C.

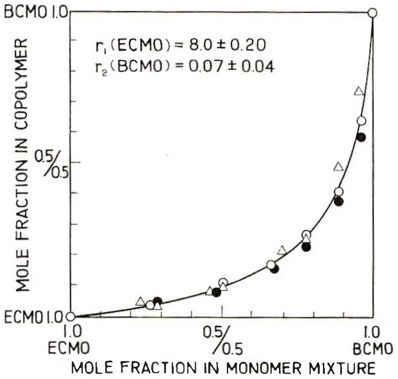


Fig. 5. Copolymerization composition curve for the ECMO–BCMO system: (O) $BF_3 \cdot OEt_2$ = 0.035 mole/l., in air, 30°C.; (●) ^{60}Co γ-rays, in air, 26°C.; (Δ) BPO = 1 wt.-%, in N_2, 50°C.

reaction. Jacobs et al.[9] reported that free radicals (BPO) initiate a reaction between tetrahydrofuran and MAH to form (tetrahydro-2-furyl)-succinic anhydride in higher yield. However, this reaction appears to be specific with respect to five-membered cyclic ethers. They did not mention at all the formation of the acidic product which is responsible for a cationic initiation of polymerization. The electron donation from a free radical of ether to an electron acceptor was very recently reported by Buley and Norman.[10] The electron acceptor property of MAH seems essential for the polymerization. The fact that chloromaleic anhydride could be successfully used in place of MAH[1] is easily understood in terms of its stronger acceptor property due to an electron deficiency in the ring caused by the inductive effect of the Cl atom. These highly electronegative substituents may be considered to be effective in withdrawing charge from the ethylenic groups to enhance the electron affinity, while the methyl-substituted compound, i.e., citraconic anhydride, has a reduced electron affinity and, in fact, was not effective for the present polymerization. The inhibition of the polymerization by a radical scavenger[1] is satisfactorily explained by the suppression of the formation of cationic species via a radical process. In the infrared spectra of the polymers obtained, there was a weak absorption peak due to the carbonyl group, as shown in the preceding paper.[1] This small amount of carbonyl group presumably is attributed to incorporation of a formate group of the initiating cationic species into the polymer chain.

All the results obtained are satisfactorily interpreted by the mechanism proposed here. However, it is still an open question as to the exact nature of the active species responsible for the initiation, and more quantitative studies are required in near future.

Effect of MAH as Solvent for the Cationic Polymerization

Finally, the $BF_3 \cdot OEt_2$-initiated polymerization of BCMO was carried out in the presence of different amounts of MAH, in order to examine the effect of MAH as solvent for the polymerization of cyclic ether in the binary system of MAH and cyclic ether. The preliminary results are shown in Table III.

TABLE III
$BF_3 \cdot OEt_2$-Initiated Polymerization of BCMO in the Presence of Different Amounts of MAH[a]

Monomer system		
BCMO, mole-%	MAH, mole-%	Polymer yield, %
100	0	8.0
60	40	62.0
38	62	89.5
17	83	30.2

[a] Polymerization conditions: $BF_3 \cdot OEt_2 = 1.4 \times 10^{-2}$ mole/kg., 30°C., air, 20 min.

It was found that the polymerization was markedly enhanced in the presence of MAH. The highest yield was obtained at a nearly equimolar mixture, as observed[1] in the radiation-induced polymerization of BCMO in the presence of MAH. This acceleration may be due to the higher dielectric constant of MAH, since cationic polymerization, in general, is enhanced in the solvents of high dielectric constant. From this result, it is suggested that in the radiation- and BPO-induced polymerization, MAH would participate not only in the initiation process, but also in the cationic propagation as a favorable solvent. More detailed study is required to investigate the effect of MAH on the cationic propagation.

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Résumé

En vue d'élucider le mécanisme de réaction de la polymérisation induite par radiation et induite en présence de peroxyde de benzoyle d'éthers cycliques en présence d'anhydride maléique, on a suivi le développement de la couleur en cours de réaction et la copolymérisation de dérivés de l'oxétane. On a ajouté une faible quantité d'une solution préalablement irradiée aux rayons-γ ou à la lumière ultraviolette d'un mélange équimoléculaire d'éther cyclique et d'anhydridemaléique à de l'éther isobutyl-vinylique; une polymérisation rapide a lieu et le polymère en résultant est un homopolymère d'ether isobutyl-vinylique. La solution chauffée de dioxanne, d'anhydride maléique et d'une faible quantité de peroxyde de benzoyle peut initier la polymérisation de l'éther isobutyl-vinylique de la même façon. La conductivité électrique de la solution du mélange 1:1 d'anhydride maléique et de dioxanne est accrue par environ un facteur de 10 après irradiation ultraviolette. Au départ de ces résultats, on prouve que certaines espèces cationiques sont actuellement formées dans les systèmes par irradiation ou par décomposition du peroxyde de benzoyle additionné. Le mécanisme de formation de ces espèces cationiques, responsables de l'initiation, peut être expliqué de la façon suivante: un radical libre d'un éther est formé par abstraction de l'atome d'hydrogène attaché au carbone adjacent à l'atome d'oxygène, suivi d'un transfert d'électrons au départ d'un radical résultant de l'anhydride maléique, accepteur d'électrons, de façon à fournir une espèce cationique de l'éther et un radical anion de l'anhydride maléique, respectivement. Les espèces cationiques résultantes, aussi bien que l'anion radical de charge opposée sont stabilisés par résonance. C'est ainsi, que la présente polymérisation a été désignée comme une polymérisation cationique induite par les radicaux.

Zusammenfassung

Zur Aufklärung des Reaktionsmechanismus der strahlungsinduzierten und der Benzoylperoxyd-katalysierten Polymerisation zyklischer Äther in Gegenwart von Maleinsäureanhydrid wurde die Farbentwicklung während der Reaktion und die Kopolymerisation von Oxetanderivaten untersucht. Bei Zusatz einer kleinen Menge der γ-ode UV-bestrahlten äquimolaren Lösung eines zyklischen Äthers und Maleinsäureanhydrid zu Isobutylvinyläther findet eine rasche Polymerisation statt und das entstehende Polymere kann als ein Homopolymeres von Isobutylvinyläther identifiziert werden. Die erhitzte Lösung von Dioxan, Maleinsäureanhydrid und einer kleinen Menge von Benzoylperoxyd kann die Polymerisation von Isobutylvinyläther in gleicher Weise starten. Die elektrische Leitfähigkeit einer 1:1 Mischung von Maleinsäureanhydrid und Dioxan wird durch UV-Bestrahlung um einen Faktor von etwa 10 erhöht. Diese Ergebnisse zeigen, dass durch Bestrahlung oder durch die Zersetzung von Benzoylperoxyd in dem System tatsächlich eine kationische Spezies gebildet wird. Der Bildungsmechanismus,

der für den Start verantwortlichen kationischen Spezies kann in folgender Weise erklärt werden: ein freies Ätherradikal wird durch Abstraktion eines Wasserstoffatoms von dem dem Sauerstoff benachbarten Kohlenstoff gebildet: darauf folgt ein Einelektronenübergang von dem gebildeten Radikal zu Maleinsäureanhydrid, einem Elektronenacceptor, unter Bildung der kationischen Ätherspeizies bzw. des Maleinsäureanhydridanionenradikals. Die gebildete kationische Spezies und das anionische Radikalgengenion sind resonanzstabilisiert. Die vorliegende Polymerisation kann daher als "radikalinduziert kationische Polymerisation" bezeichnet werden.

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Degradation of Pectin by γ-Radiation under Various Moisture Conditions

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Synopsis

By using D_{50} and D_{37} doses for 50 and 63% decreases in the solution viscosity of pectin, an evaluation was made of the effectiveness of radiation at different moisture levels. The relation between radiation effectiveness, as measured by the D_{50} value, and the pectin:water ratio was expressed in a simplified empirical equation. The indirect effect of radiation in dilute aqueous solutions decreased progressively with increasing pectin concentration. On the other hand, a protective effect was produced by small additions of water to dry pectin and a minimum in degradation (i.e., maximum D_{50} and D_{37} values) was attained at about the 20% moisture level.

The relation between the intrinsic viscosity of dilute aqueous solutions of pectin irradiated air-dry and the number-average molecular weight and D_{37} values was determined. By using the former relation, the number of chain scissions per unit of absorbed energy was measured at different moisture levels.

The importance of moisture control in comparative radiation studies was emphasized. An approximately 26-fold increase in the radiation sensitivity of pectin was produced by an increase in the moisture content from the 20 to the 99% level. Varying the moisture content therefore provides a good means of altering the sensitivity of pectin and similar materials to radiation damage.

Introduction

Pectin is an essentially linear polyionic molecule which is sensitive to oxidative and hydrolytic scission by radiation[1,2] and chemical means.[3,4] Like other polysaccharides, it undergoes degradation upon exposure to a source of ionizing radiation.[2,5] It possesses several properties which make it useful as a model system in studies of radiation action, such as the relatively high viscosity of its dilute aqueous solutions and the absence of crosslinking upon irradiation at various moisture levels.[6] Its sensitivity to oxidative degradation and the absence of an "oxygen effect" during irradiation, except at very low moisture levels,[7] reduce to a minimum any possible oxidative effects which do not result in chain scission. Although solution viscosity may be used as an index of pectin degradation, the exact relation between viscosity and number-average molecular weight of irradiated pectin has not as yet been established.

Most biological materials including polymers are more readily degraded by irradiation in an aqueous solution than in the dry form.[8] This "sensitizing" effect of moisture has been reported for both pectin[2] and dextran.[9] On the other hand, whereas small additions of water have been found to decrease the sensitivity of dry starch to radiation,[10] with cellulose the radiation effect is reported to be independent of moisture content.[11]

Experimental Procedure

Highly refined samples of NF pectin (11.6% moisture and 9.8% methoxyl content), obtained from Sunkist Growers, Ontario, California, were used in this study. Moisture levels were adjusted by either drying in vacuum over phosphorus pentoxide or exposure to atmospheres of predetermined relative humidities or by the direct addition of the appropriate volumes of distilled water. Following adjustment, all samples were allowed to stand for at least 24 hr. in order to attain moisture equilibrium. Moisture content was determined on an aliquot by oven drying for 12 hr. at 55°C. and under a reduced pressure of 100 mm.

Irradiation of samples was conducted in sealed glass ampules under vacuum at room temperature (20°C.). The radiation dose was administered with a 4000-curie ^{60}Co source by varying both dose rate and exposure time. Since in preliminary experiments, the degree of degradation was found to be independent of pH and the rate of viscosity loss exhibited a first-order dependence with respect to dose rate, no attempt was made to control solution pH or radiation dose rate.

Viscosity measurements were made within 5 hr. following the irradiation treatment. Charge and aggregation or surface effects were controlled in these measurements by determining the viscosity of dilute aqueous solutions at a pH of 6.0 and in the presence of 0.8% sodium chloride to depress the electroviscous effect and 0.2% sodium hexametaphosphate (Calgon) to reduce the aggregating action of residual polyvalent cations.[13,14] The determinations were performed at 30.00 ± 0.03°C. in Ostwald-Cannon-Fenske viscometers and at pectin concentrations of 0.4, 0.2, 0.1, and 0.05 g./100 ml. Intrinsic viscosity was calculated in the usual method of extrapolating the reduced specific viscosity to zero concentration. No kinetic energy correction was found necessary, since the fractional error arising from this source was negligible.

Since the viscosity of dilute solutions of irradiated pectin cannot be used directly as a measure of the effectiveness of radiation under different moisture conditions, an indirect method was employed. This involved a comparison of equi-effective doses, i.e., the doses giving the same residual activity (in this case, the same per cent decrease in intrinsic viscosity) at different moisture levels. In this study, a 50% and a 63% decrease in the original intrinsic viscosity were chosen for comparison purposes and the corresponding extinction doses were designated D_{50} and D_{37}.

Viscosity data do not yield molecular weight values directly. Therefore, the relation between intrinsic viscosity $[\eta]$ and molecular weight $\bar{M}_n$ was established with duplicate air-dry pectin samples (11.6% moisture), each irradiated with three successive D_{37} doses for a decrease in $[\eta]$ and

$\bar{M}_n$, respectively. $\bar{M}_n$ was determined by both the chlorous acid oxidation procedure involving the reaction of an aldehyde group with sodium chlorite as an acid medium[15–18] and by another method in which the mass of "target volume" is derived from the D_{37} value for the loss of a specific property.[19]

Results and Calculations

Plotting log D_{50} and log D_{37} (for a decrease in $[\eta]$) versus the $[\eta]$ of the sample at a specific dose give parallel lines for during-irradiation moisture levels between 1.5 and 99.5% as indicated in Figure 1. This indicates that the pattern of pectin degradation is essentially the same under different moisture conditions, notwithstanding the differences in the rates of degradation. The regularity of both plots indicates that, if those chemical effects which do not result in chain scission are moisture-dependent, their relative influence on viscosity changes is negligible or constant.

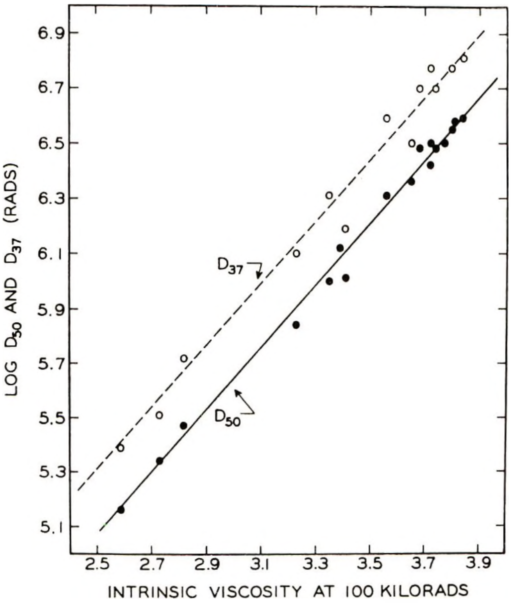

Fig. 1. Dependence of the D_{50} and D_{37} values of a pectin sample (for a decrease in $[\eta]$) on its radiation sensitivity or its rate of degradation (as reflected by its solution viscosity at a specific radiation dose) irrespective of moisture content.

Log D_{50} and the log of the corresponding D_{37} values were determined and plotted in Figure 2 as a function of pectin concentration (per cent by weight) over the whole moisture range. From the nature of the curves obtained, it is seen that the net degradation of pectin is at a minimum when the moisture content is about 20–23%. A pronounced "protective" effect of water is exhibited below this moisture level and a "sensitizing" effect in dilute solutions (above 90% moisture). In the intermediate moisture range (20–90% water), the "sensitizing" effect of water is relatively small, as indicated by the slope of the curves within this moisture range.

In an "indirect" radiation effect energy is absorbed primarily by the solvent. Therefore, the number of solute molecules affected should be independent of their concentration while the proportion of the solute molecules affected should diminish with increasing concentration.[20] As indicated in Table I, the radiation dose/solute concentration ratios at different moisture levels for a specific decrease in intrinsic viscosity is fairly constant for pectin concentrations of 0.5–5.0%. This points to the predominating or exclusive indirect action of radiation at these low pectin concentrations.

TABLE I

Effect of Moisture Content on the D_{50}/C_p and D_{50}/C_w Ratios[a]

C_p	C_w	$D_{50} \times 10^4 / C_p$	$D_{50} \times 10^4 / C_w$
0.5	99.5	15.2	—
1.0	99.0	14.5	—
1.5	98.5	14.6	—
2.0	98.0	14.8	—
5.0	95.0	13.8	—
96.7	3.3	2.3	68.2
97.4	2.6	1.7	63.4
98.5	1.5	1.0	65.6

[a] C_p, C_w = pectin and water concentrations, respectively, in weight per cent. D_{50} is for a decrease in $[\eta]$.

In dilute aqueous solutions of pectin where the direct effect of radiation is insignificant, the indirect effect of radiation E_i may be expressed as a function of the per cent pectin concentration C_p and the per cent water content C_w as $E_i = K_1C_w/C_p$. In dilute solutions C_w/C_p will approximate $100/C_p$, and, since as shown above, the D_{50}/C_p ratio is fairly constant, the above equation may also be expressed as $E_1 = K_a/D_{50}$, or $D_{50} = K_3C_p/C_w$.

In the case of a direct effect of radiation, at first consideration the number of substrate molecules affected should be proportional to their concentration while the fraction affected should be independent of concentration.[20] Therefore, in relatively dry material, the radiation effect should be independent of the moisture content. However, as indicated in Table I, D_{50} and the D_{50}/C_p ratio vary approximately in proportion to the water content, indicating that an indirect effect is in operation also in this case. Therefore in this case, the effect of radiation may be expressed as $E_d = K_4C_p/C_w$, or $E_d = K_5/D_{50}$, and $D_{50} = K_6C_w/C_p$.

From the previous analysis, it may be reasonably assumed that, at intermediate moisture levels (10–90%) both effects are in operation and both contribute substantially, although not necessarily equally, to the total effect of radiation.

TABLE II

Relation between D_{37}, $\bar{M}_n$, and $[\eta]$ for a Pectin Sample Irradiated Three Successive Times in the Air-Dry State (11.6% Moisture) with D_{37} Doses[a]

Sample	D_{37}, Mrad.	$\frac{D_{37,0}}{D_{37,f}}$	$\bar{M}_n$ (mol. wt. units)[b]	$\frac{\bar{M}_{n,f}}{\bar{M}_{n,0}}$	$D_{37}\bar{M}_n \times 10^{-4}$	M (mol. wt. units)[c]	$[\eta]$	$\frac{\bar{M}_n^{0.6}}{[\eta]}$
0	2.2	—	75,210	—	16.5	318,000	4.10	206
f_1	6.4	0.34	27,830	0.37	17.8	109,000	2.34	199
f_2	16.4	0.13	10,300	0.137	16.9	43,000	1.31	195

[a] For a decrease in $\bar{M}_n$.

[b] Determined by reducing endgroup analysis.

[c] Determined by the equation $D_{37}M = 0.7 \times 10^{12}$.

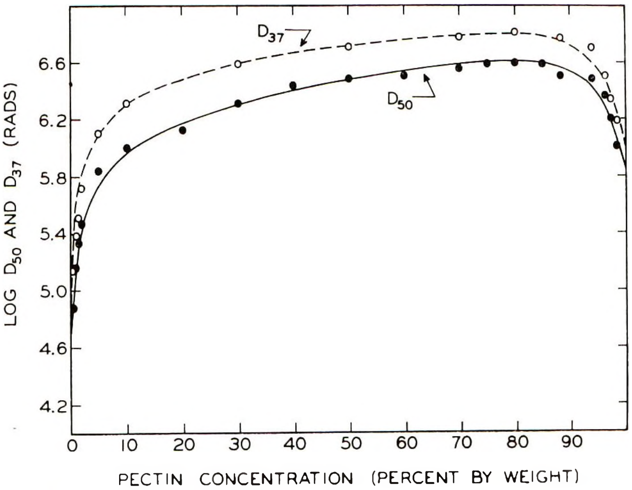

Fig. 2. Effectiveness of radiation in pectin degradation at various moisture levels as determined by the D_{50} and D_{37} values for a decrease in $[\eta]$.

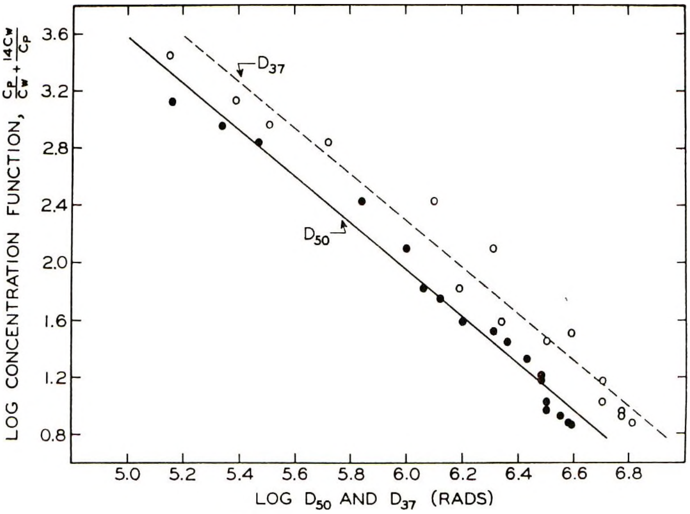

Fig. 3. Relation between the D_{50} and D_{37} values for a decrease in $[\eta]$ and the concentration function $(C_p/C_w) + (14C_w/C_p)$, where C_p and C_w are the relative concentrations of pectin and water, respectively.

An approximation of the ratio of the "sensitizing" effect of water in solution to the net "protective" effect of water in the dry material may be obtained by extrapolating the data in Figure 2 to 100% pectin and 100% water. This ratio has a value of approximately 14. Therefore the relation between the D_{50} value and the relative concentration of pectin and water over the whole moisture range may be expressed as

$$D_{50} = f\left(\frac{C_p}{C_w} + \frac{14C_w}{C_p}\right)$$

TABLE III

Relation between D_{37}, $\bar{M}_n$, and $[\eta]$ for a Pectin Sample Irradiated Three Successive times in the Air-Dry State (11.6% Moisture) with D_{37} Doses[a]

Sample	D_{37}, Mrad	$\frac{D_{37,0}}{D_{37,f}}$	$[\eta]$	$\frac{[\eta]_f}{[\eta]_0}$	$\left(\frac{[\eta]_f}{[\eta]_0}\right)^{1/1.2}$	$(D_{37})^{1.2}[\eta]$	$\bar{M}_n$ (mol. wt. units)[b]	$\frac{\bar{M}_n^{0.6}}{[\eta]}$
0	5.5	—	4.10	—	—	31.7	75,210	206
f_1	11.7	0.47	1.52	0.37	0.44	29.1	13,300	196
f_2	26.2	0.21	0.56	0.137	0.19	28.2	2,410	191

[a] For a decrease in $[\eta]$.

[b] Determined by reducing endgroup analysis.

or

$$\frac{C_p}{C_w} + \frac{14C_w}{C_p} = \frac{K}{D_a}$$

Log–log plots of this concentration function versus D_{50} and D_{37} are indicated in Figure 3. From this it was determined that the value K is determined by the degradation or reduction in intrinsic viscosity which is used as a basis for comparison of the equi-effective doses, and a is equal to 1.6 for this system.

The relationship between intrinsic viscosity and molecular degradation was investigated utilizing the relationship between D_{37} and the mass M of the target volume established by Pollard et al.[19] as $D_{37}M = 0.7 \times 10^{12}$. Tables II and III give the D_{37} values for a reduction in $M\delta$ and $[\eta]$, respectively, for two air-dry pectin samples (11.6% moisture) irradiated progressively with D_{37} dose. It will be noted that the product $D_{37}\bar{M}_n$ is fairly constant in this instance. The relation between $[\eta]$ and its respective D_{37} value for a specific moisture content is more complex, since the $[\eta]$ of a polymer solution is known to respond relatively more to changes in the size of the larger molecules. It is seen from Table III that this relation is exponential and may be expressed in a simplified form as $(D_{37})^{1.2}[\eta] = 29.7$.

Estimation of the molecular weight of pectin in aqueous solution was possible by utilizing the relation[21] $[\eta] = 5 \times 10^{-3}\bar{M}_n^{0.6}$. Assumption of this relationship permits the use of $[\eta]$ and D_{37} data (for a decrease in $[\eta]$) for the indirect measurement of the effectiveness of radiation (number of chain scissions per unit of absorbed energy) at different moisture levels. These data are presented in Table IV. Up to 20% moisture, the number of chain scissions per ion pair produced is fairly close to that obtained with amylose,[10] indicating that, at these low moisture levels, the radiation sensitivity of these two polysaccharides is somewhat similar.

TABLE IV
Effectiveness of Radiation at Different Moisture Contents for Pectin Irradiated with D_{37} Doses (3.75×10^{19} chain scissions/g.[a]

Water content, %	Number of chain scissions per ion pair produced (32.5 e.v. of absorbed energy)
5.0	4.3
11.6 (air-dry)	3.3
20	3.1
50	3.9
80	6.4
90	9.7
99	80.6

[a] D_{37} for a decrease in $[\eta]$.

Discussion

As indicated by this study, the radiation sensitivity of pectin is affected appreciably by its moisture content. Any measurement of molecular weight based on the D_{37} value should take into consideration the water content of the sample. Viscosity determination is the commonest method presently in general use for measurement of degradation. It offers the advantage of simplicity and reproducibility. Although viscosity is known to be a function of polymer chain length, interpretation of data is complicated by the fact that, in a homologous series, the higher molecular weight samples will show a greater relative decrease in viscosity than those of lower molecular weights for the same average number of chain scissions. Further, the weight-average molecular weight and viscosity-average molecular weight should be affected more by random chain scission along the polymer backbone than by fractures close to the extremities of the molecules. The radiation-induced degradation of air-dry pectin has been shown to proceed by random fissure of the glycosidic linkages,[22] and it is probable that this pattern of degradation is exhibited at other moisture levels.

Because of the ionic nature of pectin, charge effects might be expected to alter the size and shape of the polymer molecules in solutions, and therefore their sensitivity to radiation, as has been demonstrated in the case of the x-ray irradiation of poly(methacrylic acid).[23] In pectin, however, change in ester content as a result of irradiation has been shown to be minor as compared to changes in the degree of polymerization.[2,22,23] Furthermore, pectin is a fairly rigid, rodlike molecule[13] possessing little opportunity for rotation around the glycosidic bond. Also, the negligible influence of charge effects on the radiation sensitivity of pectin is indicated by the negligible effect that is produced on pectin degradation by low concentrations of NaCl (1%) and by changes in pH of 1.5–6.0.[6]

The effect of radiation on dry materials is considered to be mostly or exclusively "direct" in contrast to the "indirect" effect of radiation in dilute aqueous solutions. The radiation-induced hydrolytic fissure of glucosidic linkages in dry pectin may result from an internal arrangement within the polymer radicals or excited molecules. In aqueous solution[24,25] degradation is produced presumably through an attack on the solute molecules by the radiolytic products of water. As in the case of sucrose[26] and dextran,[27] chain scission in pectin by the indirect action of radiation is probably both hydrolytic and oxidative.

Many substances can be expected to be less affected by irradiation in the dry state than in aqueous solution since the cage effect in dry materials may lead to a recombination of some of the free polymeric radicals produced by the direct dissociation of the excited molecules. Some recombination of polymer fragments in solution has also been reported in the case of poly(methacrylic acid).[28] Because of such recombination reactions, changes in viscosity or molecular weight do not give true value for the real effectiveness of radiation. Furthermore, a decrease in viscosity reflects only a decrease in molecular weight as resulting from hydrolytic and oxidative scission of the glycosidic bonds. Ring scission, loss of substituent groups, and other less well-defined chemical changes (such as oxidative effects) which do not result in main-chain fracture are known to be produced by the irradiation of various polysaccharides and sugars.[26] These other effects have been found, in the case of starch[10] and pectin,[2] to show relatively little dependence on moisture content and radiation dose or not to respond to the same degree as viscosity to differences in moisture content during irradiation.

The decrease in the effect of radiation with increasing moisture content at the lower moisture levels does not conform with the commonly accepted view that water "sensitizes" substances to radiation damage or with the view that, in dry material, the fraction of the substrate molecules affected by a specific radiation dose is independent of their concentration.[4] However, the radiation sensitivity of a few other substances, including hydrophilic colloids, has been found to be slight at very low moisture levels and to decrease with increasing water content until a minimum is reached at about 12–20% moisture.[29] Although the protective effect of water against radiation damage in dry materials is still not clearly understood, it is presumed that in the presence of water there is less internal rearrangement following excitation of the polymer molecules due to charge, electron and/or excitation transfer between polymer and water molecules. Such a stabilizing effect can be produced if the excited polymer molecules or radicals are sufficiently long-lived. There are a number of instances in which it has been shown that extremely long-lived free radicals are produced in dry materials by ionizing radiation, such as those involved in the "after-effect" (post-radiation degradation) in the case of dry cellulose.[30] Part of the protection provided by water under low moisture conditions may also be attributed, at least in part, to the decreasing proportion of the total radiation that is directly absorbed by the polymer molecules with increasing moisture content. However, if according to the "target" theory of radiation action, the target volume comprises a substrate molecule plus a surrounding water layer, than an increase in moisture content or degree of hydration (particularly at the lowest moisture levels) should increase the target volume and should therefore increase the rate of degradation of the polymer molecules.

A study of the effect of moisture on the radiation-induced degradation of pectin should take into account that some of its degradation products, while contributing little or nothing to the viscosity of the resulting admixture, may provide appreciable radiation protection to the surviving macromolecules.[6] We are therefore dealing at each moisture level with a system consisting of a substrate and radiation protectants in ratios which vary progressively with dose. Further, since the effect of radiation on pectin has been shown to be dependent on the pectin/water ratio, it would be expected that substances in general, when added in high enough concentrations to alter appreciably the solvent/solute ratio, will provide "apparent" protection whether or not they possess "true" protective qualities. For example, the reported protective effect of high concentrations of various sugars against the radiation-induced degradation of pectin in aqueous solution[2] may be attributed, at least in part, to the concentration effect of the added sugars.

The calculation of the molecular weight of the target volume from the corresponding D_{37} value presumes that only ionization or electron removal is responsible for each inactivating event, the effect or excitation being minor. The relatively large size of the ion cluster formed in an inactivating event results in high "target" molecular weights for the lower size molecules.[31] This may explain the relatively large values obtained from M (mass of the target volume) as compared to the $\bar{M}_n$ values obtained for both irradiated and nonirradiated samples (Table II).

The treatment and simplified empirical equation relating the viscosity-reduction dose (D_{50}) to moisture content and substrate concentration may possibly apply to radiation studies of various biological polymers such as enzymes, starch, proteins, and nucleic acids, where a similar protective effect of water has been reported.[10,29] The pronounced effect of water on the response of these substances to radiation points to the possibility of using moisture control as a means of controlling the radiation damage. From Figure 2 and Table IV it is estimated that an approximately 50% reduction in pectin degradation is produced by increasing the pectin concentration from the 10 to 20% level or by raising the moisture content from the 5 to the 20% level.

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Résumé

Utilisant des doses D_{60} et D_{37} pour une diminution de 50 et 63% de la viscosité en solution de la pectine nous avons évalué l'efficacité de la irradiation à différents taux d'humidité. La relation entre l'efficacité de l'irradiation telle qu'elle a été mesurée à la valeur D_{50} et le rapport pectine/eau était exprimée par une équation empirique simplifiée. L'effet indirect de l'irradiation sur des solutions aqueuses et diluées décroît progressivement avec une concentration croissante en pectine. Par ailleurs, un effet de protection était introduit par l'addition de faibles quantités d'eau à la pectine sèche et un minimum de dégradation (c.à.d. les valeurs maximum D_{50} et D_{37}) était atteint à un niveau d'humidité d'environ 20%. La relation entre la viscosité intrinsèque de solutions diluées aqueuses de pectine irradiée à l'air sec et le poids moléculaire moyen en nombre et les valeurs D_{37} a été déterminée. En utilisant la première relation nous avons mesuré le nombre de scissions de chaîne par unité d'énergie absorbée pour différents niveaux d'humidité. L'importance du controle de l'humidité dans des études d'irradiation comparative a été soulignée. Un accroissement approximativement de 26 fois dans la sensibilité à l'irradiation de la pectine a été produite par une augmentation de teneur en humidité de 20 à 99%. Une variation de teneur en humidité entraîne par conséquent un moyen facile de modifier la sensibilité de la pectine et de matériaux semblables à l'égard de dommages du à la radiation.

Zusammenfassung

Mit D_{50}- und D_{37}-Dosen für eine 50 und 63%ige Abnahme der Lösungsviskosität von Pectin wurde die Wirksamkeit der Strahlung bei verschiedenem Feuchtigkeitsgehalt ermittelt. Die Beziehung zwischen der durch den D_{60}-Wert gemessenen Strahlungswirksamkeit und dem Pectin:Wasser-Verhältnis wurde durch eine vereinfachte em pirische Gleichung ausgedrückt. Der indirekte Strahlungseffekt nahm in verdünnten wässrigen Lösungen mit steigender Pectinkonzentration stetig ab. Andrerseits wurde durch kleinen Wasserzusatz zu trockenem Pectin ein Schutzeffekt erzeugt und ein Abbauminimum (d.h. maximale D_{50}- und D_{37}-Werte) wurde bei einem Feuchtigkeitsgehalt von etwa 20% erreicht. Die Beziehung zwischen der Viskositätszahl verdünnter wässriger Lösungen von in trockener Luft bestrahltem Pectin und dem Zahlenmittelmolekulargewicht sowie den D_{37}-Werten wurde bestimmt. Mit dieser Beziehung wurde die Anzahl der Kettenspaltungen pro absorbierter Energieeinheit bei verschiedenem Feuchtigkeitsgehalt ermittelt. Die Wichtigkeit der Feuchtigkeitskontrolle bei vergleichenden Strahlungsuntersuchungen wurde betont. Eine etwa 26-fache zunahme der Strahlungsempfindlichkeit von Pectin wurde durch eine Zunahme des Feuchtigkeitsgehalts von 20 auf 99% erzeugt. Eine Variierung des Feuchtigkeitsgehalts liefert daher ein gutes Mittel zur Änderung der Empfindlichekit von Pectin und ähnlichen Stoffen gegen Strahlungsschädigung.

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Studies on Polymers Containing Functional Groups. II. Polymerization Behavior of *o*-Hydroxystyrene

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Synopsis

The polymerization behavior of *o*-hydroxystyrene with free-radical and cationic initiators and without an initiator was examined. The structures thus obtained were estimated. Although polymerization behavior of *o*-hydroxystyrene was rather complicated, according to the results, it appeared that each polymerization more or less might simultaneously follow the two types of mechanisms: normal vinyl polymerization and polymerization through the addition to benzene nuclei. The proportion of addition to benzene nuclei was considered to be highest in the polymerization with $BF_3 \cdot (OEt)_2$ and lowest in that with azobisisobutyronitrile. Degrees of polymerization of these polymers were low in all cases (42–82). Some brief experiments on copolymerization of *o*-hydroxystyrene were carried out.

INTRODUCTION

The aim of the present work was to synthesize polymers containing hydroxystyrene so as to obtain chemically reactive polymers. It is expected that, if phenol groups are present in the polymers, these polymers will easily undergo such reaction as hydroxymethylation, sulfonation, azocoupling and will lead to three-dimensional and ion-exchange resins, dye polymers, and other interesting polymers.

In the first part of this series, *o*-hydroxystyrene was selected as a monomer and its polymerization behavior was investigated. The polymerization behavior of *o*-hydroxystyrene has been investigated by several groups.[1-3] Their data however, differ considerably, and a consistent mechanism for polymerization has not yet been obtained.

In this paper, thermal, free-radical, and cationic polymerizations of *o*-hydroxystyrene and copolymerizations with methyl acrylate, methyl methacrylate, and styrene are examined, and the structures of the polymers thus obtained are compared in order to obtain clearer information on the polymerization behavior of *o*-hydroxystyrene.

EXPERIMENTAL

Materials

o-Hydroxystyrene. *o*-Coumaric acid was prepared by the method of Ebert.[4] From 100 g. (0.68 mole) of coumarin and 32 g. (1.4 mole) of so-

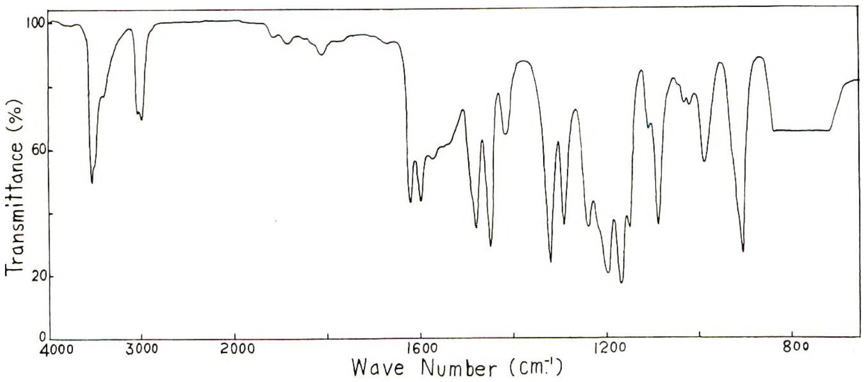


Fig. 1. Infrared absorption spectrum of *O*-hydroxystyrene (CCl$_4$ solution).

dium dissolved in 500 ml. of absolute ethanol, there was obtained 84 g. (75%) of almost colorless product after recrystallization from water; m.p. 207–208°C. (lit.:[4] 208°C.). The acid was decarboxylated according to the procedure of Fries and Fickwirth[5] under reduced pressure (ca. 5 mm.). From 70 g. (0.43 mole) of *o*-coumaric acid, there was obtained 30 g. (58%) of colorless oil after redistillation, b.p. 58–59°C./1 mm.), which solidified upon standing to a white crystalline mass, m.p. about 28°C.

o-Hydroxystyrene thus obtained was stored at −10°C. in the dark place.

The infrared absorption spectrum of *o*-hydroxystyrene (CCl$_4$ solution) is shown in Figure 1. It is found that there are four bands due to the vinyl group at 1415, 1290, 987, and 905 cm.$^{-1}$, three bands due to the aromatic ring at 1600, 1480, and 1450, cm.$^{-1}$, and a band due to the hydroxyl group at 3530 cm.$^{-1}$. A band near 1320 cm.$^{-1}$ may be attributable to the phenol group.

Monomers for Copolymerization. Methyl acrylate, methyl methacrylate, and styrene (commercially obtained) were purified by distillation just before use to remove stabilizers.

Solvents. Tetrahydrofuran was refluxed with sodium for several hours and then, distilled over lithium aluminum hydride. Methylene chloride was distilled over phosphorus pentoxide. Methanol, acetone, and ligroin were commercial products.

Initiators. Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Benzoyl peroxide (BPO) was purified by reprecipitation according to the method of Nozaki and Bartlett.[6] Boron trifluoride etherate, a typical cationic initiator, was of the highest purity commercially available.

Polymerizations

Thermal and Free-Radical Polymerizations. *o*-Hydroxystyrene or its tetrahydrofuran solution and an initiator (except for thermal polymerizations) were put into a Pyrex tube. The tube was cooled with Dry Ice, evacuated, filled with nitrogen gas, and thawed. This operation was repeated three times, after which the tube was sealed off under vacuum.

Polymerizations were carried out in a thermostat regulated at 50 and 75 ± 0.1°C. After 20 hr., the tube was removed from the thermostat, cooled, and opened. The contents were diluted with methanol containing a small amount of hydroquinone, and then the solution was poured into an excess of ligroin in the centrifuge tube. After centrifugation, the sticky mass left in the tube was dissolved in methanol, and the solution was poured into a large excess of water to isolate the polymer, which was then filtered with a glass filter (IG No. 4) and dried over sodium hydroxide under reduced pressure at 50°C.

Cationic Polymerization. *o*-Hydroxystyrene (2 g.) was dissolved in 4 g. of methylene chloride. The solution was put into a 10-ml. flask, which was then sealed with serum stopper and cooled to −15°C. in the refrigerator. Boron trifluoride etherate (0.17 g.) was injected through the stopper into the flask, and the mixture was stirred and allowed to stand 15 hr. at this temperature. After being allowed to stand, the contents were treated in almost the same way as in the free-radical polymerization.

Free-Radical Copolymerizations. Approximately equimolar quantities of *o*-hydroxystyrene and methyl acrylate (MA), *o*-hydroxystyrene, and methyl methacrylate (MMA), or *o*-hydroxystyrene and styrene (St), and AIBN were put into glass tubes. The tubes being then sealed as described above. The *o*-hydroxystyrene used here was in the form of a 50% solution in tetrahydrofuran. Polymerizations were carried out at 70°C. for 25 min. In the case of the *o*-hydroxystyrene–MA and *o*-hydroxystyrene–St systems, the contents in the tubes were treated by the same procedure as in the free-radical polymerization; in the case of the *o*-hydroxystyrene–MMA system, the contents were diluted with acetone and then poured into an excess of ligroin. A fluffy polymer was obtained.

Preparation of a Model Polymer of *o*-Hydroxystyrene

Poly(*o*-vinylphenol Benzoate). *o*-Hydroxystyrene (7 g., 0.05 mole) was dissolved in 23 ml. of ice-cooled pyridine. To the mixture, 0.081 mole of benzoyl chloride was added dropwise with stirring. After the addition was completed, the mixture was stirred for 30 min., then allowed to stand overnight at 0°C. The oily product thus formed was washed with 23 ml. of water containing 4 ml. of concentrated hydrochloric acid, and then the product layer was removed with a separatory funnel with the use of 20 ml. of ether. The ether extract was washed with 10 ml. of 0.1*N* sodium hydroxide followed by 10 ml. of 0.1*N* hydrochloric acid, finally washed with water three times and then dried over anhydrous sodium sulfate. While the solvent of the product was being removed under reduced pressure, the product became highly viscous, and *o*-vinylphenol benzoate monomer was not obtained. However, when the viscous substance was dissolved in benzene and poured into an excess of ethanol, a white fluffy polymer was

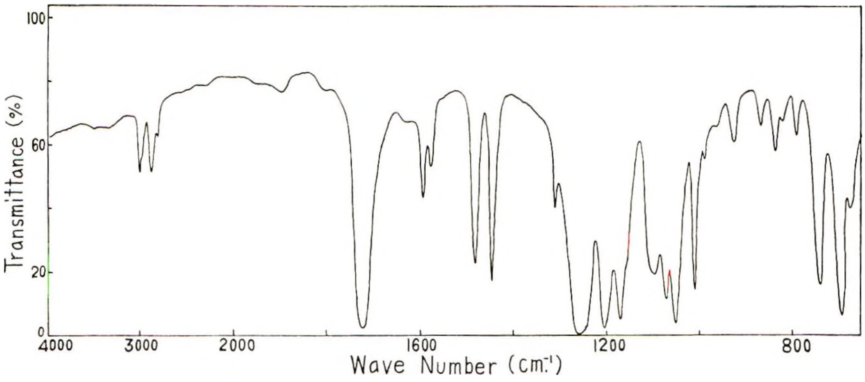


Fig. 2. Infrared absorption spectrum of poly(*o*-vinylphenol benzoate) (KBr disk). Absorption bands at 2870 and 1725 cm.$^{-1}$ are due to the methylene and carbonyl groups, respectively, and those at 1592, 1580, 1482, and 1445 cm.$^{-1}$ to the aromatic ring.

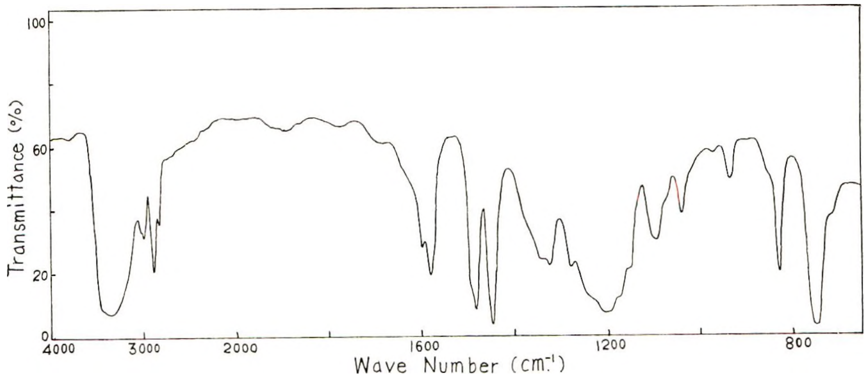


Fig. 3. Infrared absorption spectrum of poly-*o*-hydroxystyrene (KBr disk). Absorption bands at 3350 and 2890 cm.$^{-1}$ are due to the hydroxyl group and the methylene group, respectively, and those at 1600, 1582, 1485, and 1450 cm.$^{-1}$ to the aromatic ring.

isolated. This polymer is identified as poly(*o*-vinylphenol benzoate) from the results of analysis and the infrared spectrum (Fig. 2).

ANAL. Calcd. for $(C_{15}H_{12}O_2)_n$: C, 80.34%; H, 5.39%. Found: C, 78.88%; H, 5.44%. $[\eta]$ = 2.51 in benzene at 30 ± 0.05°C.

Another experiment was carried out under the same conditions except that the alkali washing was omitted. Similarly, a white polymer ($[\eta]$, 1.57) was obtained. Unfortunately, the mechanism of the polymerization is not yet known.

Saponification of Poly(*o*-vinylphenol Benzoate). Poly(*o*-vinylphenol benzoate) was added to ca. 0.2*N* sodium ethylate solution and refluxed 24 hours. After refluxing, the solution was filtered, neutralized with hydrochloric acid, then poured into water to isolate the polymer. The polymer was filtered and washed with water.

This polymer was possibly identified to be poly-*o*-hydroxystyrene from its infrared absorption spectrum, shown in Figure 3.

Characteristics of Polymers

Viscosity Measurements. All viscosity measurements were carried out with an Ubbelohde-type viscometer in a thermostat bath kept at 30 ± 0.05°C. Tetrahydrofuran was used as solvent.

Molecular Weight Measurements. Molecular weight measurements were carried out with a Mechrolab vapor pressure osmometer. Tetrahydrofuran was used as solvent.

Measurements of Infrared Spectra. Infrared absorption spectra of polymers were taken by means of a spectrophotometer, EPI-S_2 (Hitachi, Ltd.). The KBr disk method was used.

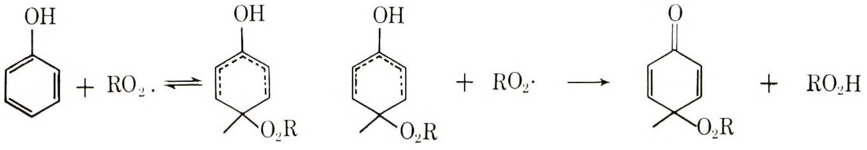
RESULTS AND DISCUSSION

Homopolymerization of *o*-Hydroxystyrene(OHS)

Polymerization conditions, conversions, and results of viscosity and molecular weight measurements for the homopolymerization of OHS are shown in Table I. It seems that OHS undergoes polymerization not only with free-radical initiators, but also with cationic ones, as indicated by other investigators.[2,3]

In the case of AIBN, conversions increased with increasing of temperature and conversely, the degree of polymerization decreased as seen in usual free-radical polymerizations.

In the case of BPO, BPO hardly appears to act as an initiator for OHS, since the rate of polymerization is much lower than that with AIBN. According to Hammond and others,[7] phenol reacts with the peroxide radical ($RO_2\cdot$) through the mechanism:



The first step of the reaction is the reversible formation of a loose molecular complex between phenol and $RO_2\cdot$. This complex is then destroyed by reacting with a second $RO_2\cdot$ radical.

A similar reaction seems to occur between BPO and OHS, thereby decreasing the catalytic action of BPO remarkably.

In the case of boron trifluoride as initiator, OHS was polymerized quickly, although this initiator is considered to interact with the hydroxyl group in OHS.

TABLE I
Homopolymerization of *o*-Hydroxystyrene

	Polymerization conditions							
Sample no.	Solvent	OHS concn., %	Initiator, %/OHS	Temp., °C.	Time, hr.	$[\eta]$	MW $(\bar{P})$	Conversion, %
A	None	100	AIBN, 0.5	75	20	0.10	—	35.7
B	None	100	None	75	20	—	—	0.9
C	None	100	AIBN, 0.5	50	20	0.13	9800 (82)	11.8
D	None	100	None	50	20	—	—	0.3
E	None	100	BPO, 0.5	75	20	0.06	—	6.1
F	Tetrahydrofuran	61.6	AIBN, 1.0	75	20	0.09	7410 (62)	77.5
G	Tetrahydrofuran	61.6	AIBN, 1.0	50	20	0.11	8850 (74)	27.2
H	CH_2Cl_2	33	$BF_3 \cdot O(C_2H_5)_2$, 8.5	−15	15	0.05	4950 (42)	92

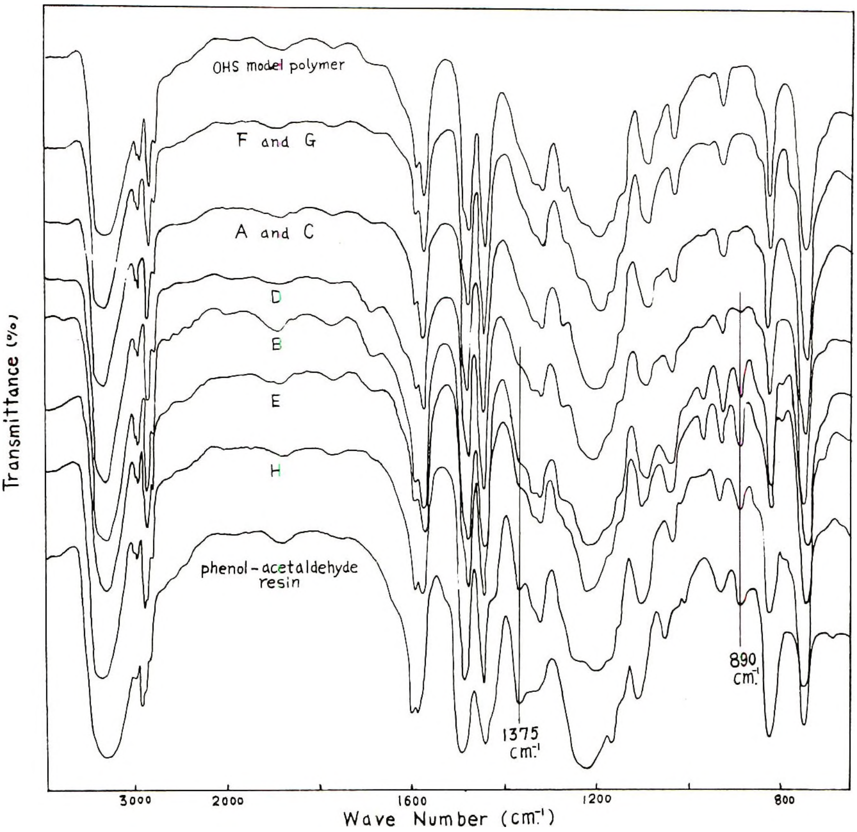


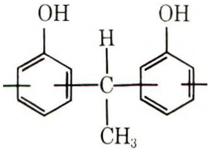
Fig. 4. Infrared spectra of various polymers of *o*-hydroxystyrene and a phenol–acetaldehyde resin.

Conversions in thermal polymerization were very low.

Color of the polymers obtained with AIBN was initially white but gradually turned to light brown on standing in air. This color change may be attributable to the air oxidation of the phenol group. Degrees of polymerization were low in all cases. This implies that considerable chain transfer to monomer takes place. These polymers were soluble in aqueous solution of sodium hydroxide, methanol, ethanol, acetone, and tetrahydrofuran, but insoluble in benzene, chloroform and carbon tetrachloride.

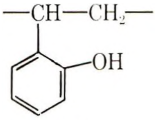
Infrared absorption spectra of these polymers were compared with that of the OHS model polymer in Figure 4. Furthermore, infrared spectrum of phenol–acetaldehyde resin prepared by a method similar to the one given by Marvel and others[8] is also shown. This resin was soluble in methanol and acetone. Each OHS polymer has strong bands at 3350 cm.$^{-1}$ due to the hydroxyl group and at 3000, 1600, 1582, and 1450 cm.,$^{-1}$ due to the aromatic ring. The absorption bands for the samples prepared by the polymerization with AIBN (A,C,F,G) are almost the same as for the model polymer. On the other hand, there are observed some changes in spectra at 1375 and 890 cm.$^{-1}$ for the samples obtained by the polymerization with boron trifluoride etherate (H), with BPO (E) and without initiator (B,D). The absorptions at 1375 cm.$^{-1}$ for samples B,D, and E are indicated as a shoulder, whereas that, for sample H is indicated as an obvious band. In the case of samples B and D, the intensity of the band at 890 cm.$^{-1}$ in the spectrum for B is considered to be higher than that for sample D.

It seems that there is a considerable correspondence between the infrared pattern of sample H and that of phenol–acetaldehyde resin. The latter also has absorption bands at 1375 and 890 cm.$^{-1}$. The phenol–acetaldehyde resin seems to be mainly composed of the structure:



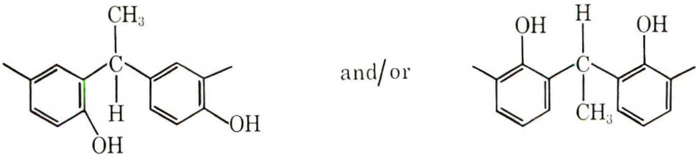
Absorptions at 1375 and 890 cm.$^{-1}$ might be tentatively assigned to the C—CH_3 deformation and the absorption characteristic of 1,2,4-trisubstituted aromatics,[9] respectively.

From these results, it can be seen that, although polymerization behavior of OHS is rather complicated, each polymer consists more or less of at least following two types of structure: the products of normal vinyl polymerizations (I)



I

and of polymerization through addition to benzene nuclei (II).



II

These appear to exist as homopolymers or copolymers in the products. Existence of structure II has also been recognized by other investigators.[2,3]

The composition of each polymer might be qualitatively summarized as follows.

(*1*) Polymerizations with AIBN (A,C,F,G): consist mainly of structure I in all cases.

(*2*) In polymerizations without initiator (B,D), some portion of structure II exist, but the content of the II in sample D is less than that in sample B. (The higher the temperature, the more structure II is produced.)

(*3*) Polymerization with BPO (E) is almost the same as for case *2*.

(*4*) In polymerization with boron trifluoride etherate (H), considerable portion of structure II exist.

Thus, in the free-radical polymerization with AIBN, polymerization seems to proceed almost exclusively through the normal free-radical mechanism, although considerable chain transfer takes place. This may be supported by the copolymerizing abilities of OHS described below.

Copolymerizations by Free-Radical Mechanism

The results of brief experiments on the copolymerization of OHS with MA, MMA and St using AIBN are as shown below.

Copolymer of OHS and MA. Conversion, 28.6%; [η], 0.23.

ANAL. Found: C, 67.65%; H, 6.73%; O (by difference), 25.62%.

The molar ratio of the OHS to MA unit in the polymer was calculated to be 1:1.06.

The infrared absorption spectrum of the polymer had strong bands at 3350 cm.$^{-1}$, and 1700 cm.$^{-1}$, due to the hydroxyl group in the OHS unit and the carbonyl group in the MA unit, respectively.

Copolymer of OHS and MMA. Conversion, 20.1%; [η], 0.26.

ANAL. Found: C, 67.73%; H, 7.23%; O (by difference), 25.04%.

The molar ratio of the OHS to MMA unit in the polymer was calculated to be 1:1.69.

The infrared spectrum of the polymer also indicated the presence of hydroxyl and carbonyl groups.

Copolymer of OHS and St. Conversion, 6.0%; [η], 0.16.

ANAL. Found: C, 83.00%; H, 7.02%; O (by difference), 9.98%.

The molar ratio of OHS to St units in the polymer was calculated to be 1:0.33.

The infrared spectrum of the polymer had a strong band at 695 cm.$^{-1}$ due to monosubstituted benzene and indicating the presence of styrene units, in addition to the band due to the hydroxyl group.

In order to obtain more detailed information on the mechanism for polymerization of OHS with AIBN, a kinetic study is now under investigation.

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Résumé

Les comportements à la polymérisation de l'*o*-hydroxystyrène avec des initiateurs radicalaires et cationiques et en l'absence d'un initiateur ont été examinés, et les structures des polymères ainsi obtenus ont été étudiées. Conformément à ces résultats il semble que bien que le comportement à la polymérisation de l'*o*-hydroxystyrène soit plutôt compliqué, chaque polymérisation puisse simultanément suivre les deux types de mécanismes suivant: 1° une polymérisation vinylique normale, 2° une polymérisation via l'addition au noyau benzènique. La proportion du type II de polymérisation a été considérée comme étant la plus élevée dans la polymérisation avec le $BF_3 \cdot O(Et)_2$ et la plus basse en présence de azobisisobutyronitrile. Les degrés de polymérisation de ces polymères sont bas dans tous les cas (42–82). Quelques expériences brèves concernant la copolymérisation de l'*o*-hydroxystyrène ont également été effectuées.

Zusammenfassung

Das Polymerisationsverhalten von *o*-Hydroxystyrol mit radikalischen und kationischen Startern sowie ohne Starter wurde untersucht, und die so erhaltenen Strukturen wurden bestimmt. Die Ergebnisse zeigen, dass, obgleich das Polymerisationsverhalten von *o*-Hydroxystyrol recht kompliziert war, eine jede Polymerisation mehr oder weniger folgenden zwei Mechanismustypen folgt: I. Normale Vinylpolymerisation, II. Polymerisation durch Addition an den Benzolkern. Der Anteil von Typ II scheint am höchsten bei der Polymerisation von $BF_3 \cdot O(Et)_2$ und am niedrigsten bei derjenigen mit Azobisisobutyronitril zu sein. Der Polymerisationsgrad dieser Polymeren war in allen Fällen niedrig (42–82). Einige orientierende Versuche über die Copolymerisation von *o*-Hydroxystyrol wurden ausgeführt.

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Donor–Acceptor Interactions in Cationic Polymerization. VII. Relationship between the Degree of Dissociation of Complex and the Molecular Weight of Polyisobutylene Formed in the Presence of Some Complexes of Aluminum Trichloride with Electron Donors

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Synopsis

The concentration dependence of the specific conductivity of the complexes of aluminum trichloride with dibutyl ether, anisole, phenol, and diphenyl ether at equimolar ratios of the two compounds has been measured. Conductivity measurements have been carried out in ethyl chloride at −78.5°C. Except for dibutyl ether, all the complexes studied are associated over the whole concentration range and their degree of dissociation and molar conductivity are independent of the concentration. In the case of the BuO-$Bu{\cdot}AlCl_3$ complex these quantities begin to be independent of the concentration only at concentrations higher than 20 mmoles/l. The degree of polymerization or the molecular weight of polyisobutylene formed by the polymerization in the presence of given complexes is inversely proportional to the concentration of the anions present. This is especially evident from the fact that the relation between $\varkappa$ and $1/\bar{M}$ is also linear in the case of the $BuOBu \cdot AlCl_3$ complex, whose degree of dissociation and therefore molar conductivity varies distinctly with the concentration of the complex. The comparison of the chain-breaking efficiency of the anions derived from phenol and diphenyl ether with those derived from phenetole and anisole shows that the mixed aryl alkyl ethers split after reacting with aluminum trichloride under these conditions, so that the phenyl group becomes a part of the cation and the alkyl group a part of the anion. On the basis of the different behaviors of the ions and the dipoles, the differences in the dependence of the degree of polymerization on the dielectric constant of the medium in the cationic polymerization have been explained.

Introduction

The object of this work is to confirm experimentally the assumption that the molecular weight of polyisobutylene depends primarily on the concentration of ions present and that it depends only slightly on the concentration of other chain breakers, especially if they influence the degree of dissociation of the aluminum trichloride complexes with electron donors.

In the last work of this series[1] we were unable to confirm this assumption definitely, because all of the studied complexes were associated in ethyl chloride at −78.5°C.

The dependence of the specific conductivity on complex concentration caused by dissociation of associates was linear in all cases and over the whole concentration range studied. Therefore the dependence of the reciprocal of the molecular weight of polymer on the molar concentration of the complex was also linear, and it was very difficult to prove that this linearity was the result of the independence of the degree of dissociation on the concentration and not simply the result of the validity of the Mayo equation in its generally acknowledged form.

In our subsequent work, described in this paper, a new donor—dibutyl ether—was found whose complex with aluminum trichloride gave a nonlinear dependence of the specific conductivity on the concentration. Thus the theory claiming the decisive influence of the ion concentration could be presented in a more convincing form.

An important difference in the chain-breaking efficiency of the anions of various composition allows us to formulate conclusions about the way in which the molecules of mixed alkyl phenyl ethers are split after having interacted with aluminum trichloride.

On the basis of additional experimental material showing the dominant role of the ions in the chain-breaking in cationic polymerization the Mayo equation can be made to account for the dependence of the molecular weight of polymer on the concentration of chain-breakers and thus can be made more generally valid. In this sense it is possible to complete and to correct somewhat Plesch's considerations[2,3] explaining the existence of maxima and other irregularities in the curves describing the dependence of the molecular weight of polymer on the concentration of some reaction ingredients.

Experimental

Di-*n*-butyl ether was prepared by heating *n*-butyl iodide and sodium *n*-butylate under the reflux condenser. The reaction mixture was washed with water; after removing the water layer di-*n*-butyl ether was refluxed with metallic sodium and distilled from metallic sodium.

Phenol (Lachema, chemically pure) was purified by distillation at normal pressure; a fraction boiling at 179.5–180.0°C. was taken.

Diphenyl ether (technically pure) was purified before use by double recrystallization from diethyl ether, and then it was dried at room temperature in the vacuum of a water jet pump over activated carbon.

Anisole and phenetole were purified by distillation and then dried by refluxing and distilling over metallic sodium.

Purification of other compounds, such as monomer,[4] solvent, and catalyst,[5] and experimental techniques of conductivity measurements[6] and polymerization experiments[4] were as described earlier.

Nitrogen used in all manipulations was dried by molecular sieves and was saturated by ethyl chloride vapors as described in the previous work.[1]

Results and Discussion

The dependence of the specific conductivity $\varkappa$ on the concentration of the $BuOBu \cdot AlCl_3$ complex is seen in Figure 1. The nonlinear course in

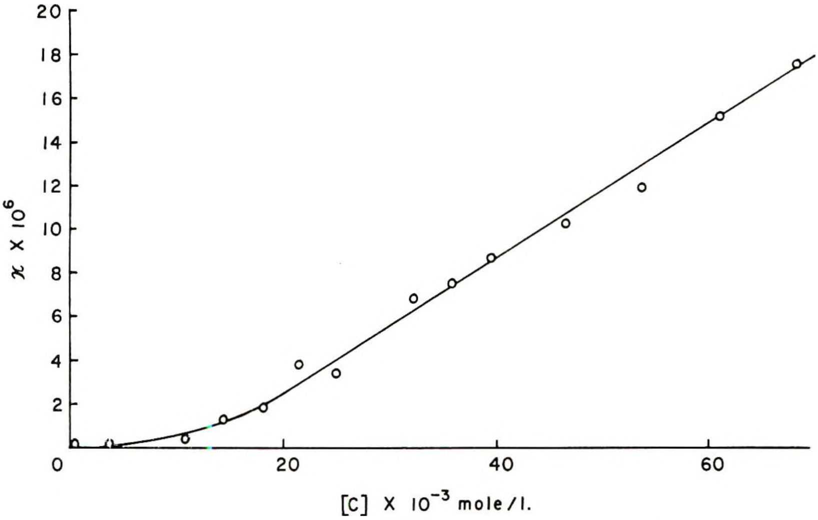

Fig. 1. Dependence of the specific conductivity on the concentration of the BuO-Bu·$AlCl_3$ complex in ethyl chloride at −78.5°C.

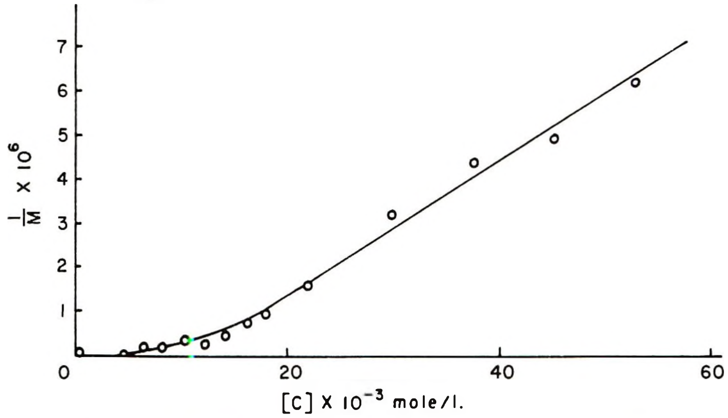

Fig. 2. Dependence of the reciprocal of the molecular weight of polyisobutylene on the concentration of BuOBu·$AlCl_3$ complex in ethyl chloride at −78.5°C.

the diluted range shows that the degree of dissociation γ is constant only at concentrations exceeding 20 mmole/l. Only above this concentration does the dependence take a linear form.

Figure 2 shows the course of the dependence of the reciprocal of the molecular weight of polyisobutylene on the molar concentration of the complex. The course of the dependence is quite analogous to that of Figure 1, viz., at low concentrations it is nonlinear and at higher concentrations linear. We have already emphasized[4-7] that under the given conditions, i.e., in conductive solutions, the molecular weight reached in cationic polymerization depends primarily on the quality and the concentration of the anions present. The un-ionized molecules play no or only subordinate roles in termination and transfer processes.

The Mayo relation holds in the form

$$1/\bar{M} = (k_4/k_2)\gamma[\mathrm{C}]/[\mathrm{M}] \tag{1}$$

where $\bar{M}$ is the molecular weight of the polymer; k_2, k_4 are rate constants of propagation and transfer, respectively, [M] is monomer concentration (in this work [M] = 3.68 mole/l. in all cases), γ is the degree of dissociation of the studied complex, and [C] is its concentration in moles/liter.

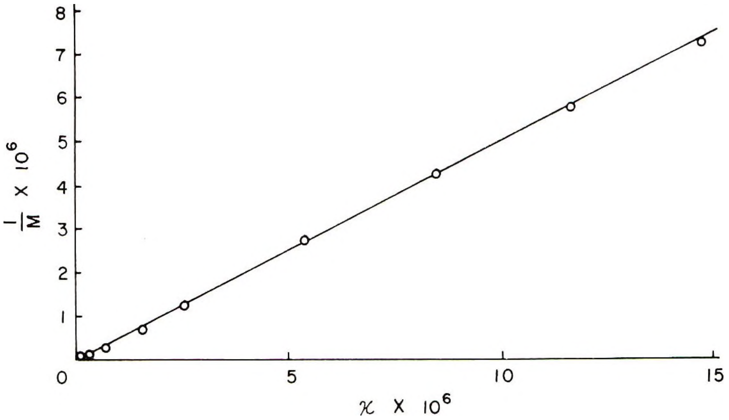

Fig. 3. Dependence of the reciprocal of the molecular weight of polyisobutylene on the specific conductivity $\varkappa$ of solutions of the BuOBu·AlCl$_3$ complex in ethyl chloride at −78.5°C. The $\varkappa$ and $1/M$ values were obtained from Figs. 1 and 2.

This relation is linear only when γ is constant. In contrast to complexes studied up to the present, γ is not constant in the case of dibutyl ether, but rather a function of [C]. Supposing no changes in the quality of the anions and no large changes in their mobility upon diluting the solutions of this complex, changes in the specific conductivity $\varkappa$ are caused by changes in the number of ions only, i.e., by the changes in γ; we can thus write the Mayo relation as

$$1/\bar{M} = (k_4/k_2[\mathrm{M}])[10^3\varkappa/F(v_\mathrm{A} + v_\mathrm{K})] \tag{2}$$

where F = 96,500 coul., v_A and v_K are mobilities of the anions and cations, respectively, and $\varkappa$ is the specific conductivity. Other symbols are as in eq. (1).

If the above assumption holds, the dependence of $1/\bar{M}$ on the specific conductivity $\varkappa$ should be linear over the whole range of concentrations, as shown in Figure 3.

Plesch[2,3] recently treated data of various authors—including ours—describing the irregularities in the dependences of the degree of polymerization on the concentration of reaction components in cationic polymerization. In this meritorious work Plesch tried to elaborate a general theory valid for all types of curves observed up to now. He inferred that all the described deviation from the Mayo equation can be explained in terms of a "neutralization and formation" of so called chain-breakers. This idea is very near our working hypothesis of donor-acceptor interactions. Plesch's algebraic formulation are more exact than those previously written by Veselý,[8] but they do not express—at least in our view—the whole substance of the problem.

The different chain-breaking activity of various complexes produced by the neutralization of donors with acceptors is given both by a change in their composition—which Plesch's theory brings out very well—and by a change in their degree of dissociation—which his formulation fails to express. Changes in ionization and accompanying changes in the molecular weight of the polymer cannot be rendered by the concept of the neutralization alone, i.e., with the help of chemical influences, because such changes can often be brought about by purely physical influences such as dilution, change of the dielectric constant, temperature etc.

Since the various chain-breaking mechanisms affect the cationic polymerization in a parallel way, we propose to rewrite the Mayo equation in a form satisfying all viewpoints

$$1/\bar{M} = \frac{k_3}{k_2[\mathrm{M}]} + \frac{\sum k_n[\mathrm{X}_n]^{x_n}}{k_2[\mathrm{M}]} + \frac{\sum k_m\gamma_m[\mathrm{Y}_m]^{y_m}}{k_2[\mathrm{M}]} \tag{3}$$

where k_3 is the rate constant of monomolecular termination, $k_n[\mathrm{X}_n]^{x_n}$ is the product of the rate constant and the concentration of the un-ionized component X_n reacting with the growing chain with the reaction order x_n; $k_m\gamma_m[Y_m]^{y_m}$ is the product of the rate constant and the concentration of the ionized compound Y_m with the degree of dissociation γ_m reacting with the growing chain with the reaction order y_m. Other symbols are as in eqs. (1) and (2).

The first term of eq. (3) answers the concept of firmly associated ion pairs on the growing end of the macroion. In accordance with this idea the termination is a spontaneous monomolecular reaction in which the cation is torn away from the growing chain. In systems where this termination mechanism predominates, the degree of polymerization is independent of the catalyst concentration. With increasing dielectric constant DC the distance between the associated ions in the pair increases and so does the molecular weight of the polymer.

The second term of eq. (3) includes all bimolecular mechanisms leading to an interruption of the growth except the reactions of the unpaired ions. This member is of importance only when the concentration of the un-ionized molecules is high compared to the concentration of the ions, because in our experience the rate constants k_n of the un-ionized molecules are of lower order than those k_m of the unpaired ions. In comparing $\bar{M}$ and $\varkappa$ we lump both constants of a given complex under the more significant k_m.

These un-ionized molecules and/or the more complicated structures are in many cases strong dipoles; these crowd together under the influence of the electrostatic field with decreasing DC of the medium; they also crowd around the growing end of macroions. The probability of an interruption of the propagation by a reaction with the dipole increases and the degree of polymerization decreases with decreasing DC. The decrease is considerably smaller than in spontaneous termination, where the DC influences the interaction of the ions, while in this case it influences the interaction of the dipoles.

Such a case is illustrated in Part IV of this series[7] by the small decrease of the molecular weight of polyisobutylene formed at high concentrations of the slightly ionized $EtOH \cdot AlCl_3$ complex, where the DC is lowered by gradually replacing the ethyl chloride by benzene or hexane.

The third term of eq. (3) expresses the contribution of the anions to the decrease of the degree of polymerization. In all cases studied by us this term was much more significant than the remaining terms. It also decides the linearity of eq. (3), because it contains the quantity γ_m—the degree of dissociation—which can be a function of the concentration $[Y_m]$, as in the case of dibutyl ether; eq. (3) is then nonlinear. The effect of the DC on this term is just the opposite of the effect on previous terms. The degree of dissociation and the concentration of the ions decrease with decreasing DC, and the degree of polymerization therefore increases as is also shown in Part IV of this series. We do not therefore exclude a situation in which the influences of DC on the first, second, and third terms of eq. (3) will compensate and the degree of polymerization will be independent of the dielectric constant of the medium.

Equation (3) does not contain algebraic formulations describing changes of the concentration and of the constitution of chain-breakers if the concentration of any reaction compounds changes. These formulations have no general validity and can be evolved from the concept of the donor–acceptor interactions as Plesch did in his work[2] referred to above.

In Part V of this series[5] we have pointed out the uncommonly high termination efficiency of the anions derived from the complexes of aluminum trichloride with phenol. Their assumed formula is shown in eq. (4):

$$AlCl_3 + C_6H_5OH \rightleftharpoons H^{\oplus}[AlCl_3OC_6H_5]^{\ominus} \rightleftharpoons [H]^{\oplus} + [AlCl_3OC_6H_5]^{\ominus} \quad (4)$$

TABLE I

Complex	Anion assumed	Λ	$\gamma\, k_4/k_2$	$(v_A + v_K)$ (k_2/k_4)	Molecular weight of complex
$BuOBu \cdot AlCl_3$	$AlCl_3OBu^{\ominus}$	0.265[a]	4.7×10^{-4a}	5.5×10^{-3}	526
$C_6H_5OEt \cdot AlCl_3$	$AlCl_3OEt^{\ominus}$	0.0194	1.2×10^{-4}	1.7×10^{-3}	511
$C_6H_5OMe \cdot AlCl_3$	$AlCl_3OMe^{\ominus}$	0.0314	1.5×10^{-4}	2.2×10^{-3}	482
$C_6H_5OH \cdot AlCl_3$	$AlCl_3OC_6H_5^{\ominus}$	0.00909	7.9×10^{-2}	1.2×10^{-6}	454
$C_6H_5OC_6H_5 \cdot AlCl_3$	$AlCl_3OC_6H_5^{\ominus}$	—	1.2×10^{-2}	—	606

[a] Data for dibutyl ether for the linear range, i.e., for concentrations higher than 20×10^{-3} mole/l.

Table I gives data on the chain-breaking activity and the conductivity of this complex and of the $AlCl_3$·diphenyl ether complex in which we assume an —OC_6H_5 group in the anion. These data are compared with data on the chain-breaking efficiency and the conductivity of mixed aryl alkyl ethers and the BuOBu·$AlCl_3$ complex.

The sixth column of Table I shows that the molecular weights of all the studied complexes differ only slightly so that it is quite impossible that the mobilities of their ions could differ appreciably. The differences in the values in the fifth column are due therefore primarily to the differences in the magnitude of the transfer constant k_4, which in the case of phenol, as Table I shows, is about three orders higher than in the case of the other donors shown.

The same picture is offered also in the fourth column of Table I, where the differences in the values of the transfer constants tend to be slightly obliterated by differences in the degree of dissociation. Also here the values of the product $\gamma - k_4/k_2$ for phenol and diphenyl ether are two orders higher than for the other donors. The conductivity data for the diphenyl ether·$AlCl_3$ complex are missing, as the conductivity of this solution in ethyl chloride changed too quickly with the time and therefore could not be measured reliably. Even so, a difference in the transfer efficiency of the complexes of phenol and diphenyl ether on the one hand and of the complexes of the other donors on the other hand is quite evident.

It follows from the above that this difference can be explained by the difference in the quality, i.e., in the structure of the anion. Since the chain-breaking efficiency of aryl alkyl ethers approaches that of dialkyl ethers, this means that also their anions must have a similar structure and different from the anions derived from the complexes of phenol or diphenyl ether. It follows from this that the mixed aryl alkyl ethers dissociate after reacting with aluminum trichloride in ethyl chloride at −78.5°C. according to eq. (5):

$$C_6H_5OR + AlCl_3 \rightleftharpoons C_6H_5^{\oplus}[AlCl_3OR]^{\ominus} \rightleftharpoons [C_6H_5]^{\oplus} + [AlCl_3OR]^{\ominus} \qquad (5)$$

So far this scheme was proved under the given conditions for anisole and phenetole. The possibility remains that the ionization scheme will alter if a rearrangement of the alkyl group, yielding a structure with a tertiary carbon atom, can take place.

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Résumé

La dépendance de la concentration de la conductivité spécifique des complexes de trichlorure d'aluminium avec l'éther dibutylique, l'anisol, le phénol et l'éther diphénylique à rapport équimolaire des deux composants a été mesurée. Des mesures de conductivité ont été effectuées dans le chlorure d'éthyle à −78.5°. Sauf pour l'éther dibutylique tous les complexes étudiés sont associés sur le domaine entier de concentration et leurs degrés de dissociation et de conductivité molaire sont indépendants de la concentration. Dans le cas du complexe dibutyléther–chlorure d'aluminium ces quantités commencent à être indépendantes de la concentration uniquement pour des concentrations plus élevées que 20 mmoles/l. Le degré de polymérisation ou le poids moléculaire du polyisobutylène formé par polymérisation en présence de complexes est inversément proportionnel à la concentration des anions présents. Ceci est particulièrement évident par suite du fait que la relation entre $\varkappa$ et $1/\bar{M}$ est linéaire dans le cas du complexe $BuOBu \cdot AlCl_3$ dont le degré de dissociation et donc la conductivité molaire varient de façon nette avec la concentration du complexe. La comparaison de l'efficacité de rupture de chaîne de ces anions dérivés du phénol et de l'éther diphénylique avec ceux dérivés du phénétol et de l'anisol montrent que les éthers aryl-alcoylés mixtes scindent après réaction avec le trichlorure d'aluminium dans ces conditions de telle sorte que le groupe phényle devient une partie du cation et le groupe alocyle une partie de l'anion. Sur la base de comportement différent d'ions, et des dipoles, les différences en ce qui concerne la dépendance du degré de polymérisation en fonction de la constante diélectrique du milieu en cours de polymérisation cationique ont été expliquées.

Zusammenfassung

Die Konzentrationsabhängigkeit der spezifischen Leitfähigkeit der Komplexe von Aluminiumtrichlorid mit Dibutyläther, Anisol, Phenol und Diphenyläther in äquimolarem Verhältnis der beiden Verbindungen wurde gemessen. Die Leitfähigkeitsmessungen wurden in Äthylchlorid bei −78,5°C ausgeführt. Mit Ausnahme von Dibutyläther sind alle untersuchten Komplexe im ganzen Konzentrationsbereich assoziiert, und ihr Dissoziationsgrad und ihre molare Leitfähigkeit sind von der Konzentration unabhängig. Im Fall des $BuOBu \cdot AlCl_3$-Komplexes beginnen diese Grössen erst bei Konzentrationen höher als 20 mMol/l unabhängig von der Konzentration zu werden. Der Polymerisationsgrad oder das Molekulargewicht des durch Polymerisation in Gegenwart eines gegebenen Komplexes gebildeten Polyisobutylens ist der Konzentration des anwesenden Anions umgekehrt proportional. Das wird besonders durch die Tatsache belegt, dass die Beziehung zwischen $\varkappa$ und $1/\bar{M}$ auch im Falle des $BuOBu \cdot AlCl_3$-Komplexes linear ist, dessen Dissoziationsgrad und daher auch molare Leitfähigkeit deutlich von der Konzentration des Komplexes abhängt. Ein Vergleich der Kettenabbruchswirksamkeit der vom Phenol und Diphenyläther abgeleiteten Anionen mit derjenigen der vom Phenetol und Anisol abgeleiteten zeigt, dass die gemischten Aryl-Alkyläther nach der Reaktion mit Aluminiumtrichlorid unter diesen Bedingungen gespalten werden, sodass die Phenylgruppe ein Teil des Kations und die Alkylgruppe ein Teil des Anions wird. Die Unterschiede in der Abhängigkeit des Polymerisationsgrades von der Dielektrizitätskonstanten des Mediums bei der kationischen Polymerisation wurden auf Grundlage des verschiedenen Verhaltens der Ionen und der Dipolmoleküle erklärt.

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Polymerization of Complex Systems. A Study of the System Methyl Methacrylate–Vinyl Isobutyl Ether–Maleic Anhydride by Means of an NMR Technique

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Synopsis

It has been shown that the rates of polymerization of individual monomers in a mixture of monomers can be followed by means of an NMR technique. The technique is rapid and simple and requires very little sample. The system MMA–MA–VIBE was investigated by the technique. From the data obtained it was concluded that the polymer formed in a mixture of the three monomers is a block copolymer made up of $(MMA)_m$ and $(MA–VIBE)_n$ units, the lengths of which depend on the monomer concentrations.

Introduction

A major difficulty in the study of polymerization kinetics of systems containing more than one monomer is the determination of the rates of disappearance of the individual monomers. In systems containing three or more monomers the commonly used analytical methods are often not applicable at all. This paper describes the use of an NMR technique for studying the polymerization of a three-component system: methyl methacrylate–vinyl isobutyl ether–maleic anhydride. The NMR procedure allows rapid analysis of the polymerizing system for each of the three monomers and thus furnishes data from which can be calculated the overall rate of polymerization, the rate of polymerization of each monomer separately, and the composition of the polymer formed at any time during the reaction.

The basis of the analytical technique is the fact that most vinyl monomers have vinyl hydrogen atoms which give well-resolved NMR signals. These signals disappear when the monomers polymerize. The vinyl hydrogen signals for many monomers are spaced such that mixtures of the monomers can be readily analyzed by observing the area under the NMR peaks for each monomer. As polymerization proceeds, the monomers disappear and the rates of disappearance can be followed by observing the change in area under the appropriate vinyl hydrogen peaks.

An attractive feature of the technique is that the reaction can be carried out in a sealed glass tube, and thus requires a single very small sample.

The polymerization can be followed as closely as desired, since only a few minutes are required for an analysis, and the reaction is not disturbed in the process.

In the methyl methacrylate (MMA)–vinyl isobutyl ether (VIBE)–maleic anhydride (MA) system, cleanly separated vinyl hydrogen peaks are observed for each monomer, and polymerization occurs readily to yield a polymer that is soluble in the reaction medium (ethyl acetate). The system is of interest because of the rather unusual interrelationships among the monomers. Neither vinyl isobutyl ether nor maleic anhydride homopolymerizes appreciably under radical conditions, but they copolymerize very readily to yield an alternating copolymer.[1] Methyl methacrylate undergoes homopolymerization and copolymerizes with maleic anhydride but copolymerizes to only a small extent with vinyl isobutyl ether.

The kinetics of copolymerization of the maleic anhydride–vinyl isobutyl ether system[1] have been studied, as well as other systems involving maleic anhydride.[2,3] Little has been reported on the kinetics of polymerization of systems containing more than two monomers. It is the purpose of this paper to present polymerization rate data for the three-monomer system described above and to draw qualitative conclusions concerning the structure of the polymer obtained.

Experimental

Methyl methacrylate, vinyl isobutyl ether, and ethyl acetate were obtained from commercial sources and distilled through a 40-plate column before use. Maleic anhydride was recrystallized from a 1:1 carbon tetrachloride–chloroform mixture.

Solutions of the concentrations shown in Figures 2–7 were prepared, degassed, and introduced into NMR tubes, which were then sealed under vacuum. The solutions each contained 50 vol.-% ethyl acetate, and 2.3×10^{-3} mole/l. AIBN in addition to the monomers.

The tubes were placed in a 60°C. bath, removed at intervals, chilled in an ice bath, and the NMR spectra obtained at ambient temperature. The process was repeated until polymerization was complete. At the end of the reaction the samples were quite viscous but still pourable. The final solutions were clear and colorless, except for the samples containing large amounts of maleic anhydride, which became light tan during polymerization.

Spectra were obtained on a Varian A-60 with integrating accessory. The portion of the spectrum of interest was between 5 and 8 δ, as shown in Figure 1. In the ethyl acetate solvent used in these studies, the vinyl protons of maleic anhydride appear at 7.2 δ, and those of methyl methacrylate at 5.5 and 6.0 δ. The —O—CH=C proton of vinyl isobutyl ether appears as four peaks at 6.3, 6.4, 6.5, and 6.6 δ.

In general, the spectra were recorded once at a sweep width of 250 cps. Then three recordings of the integral curves were made over the spectrum at instrument settings known to be safely below saturation.[4] In order to permit all curves to be referred to the same absolute basis, all integral spectra were recorded at a radiofrequency power level known not to saturate even the weak spectra of the final rather viscous solution. The three integral values were averaged and monomer content found by the relation: $c = f_0c_0$, where c is concentration, f_0 is fraction of the original area, and c_0 is known concentration of original solution. Equal areas were observed for equal proton concentrations for all three monomers. The usual standard deviation of the average of sets of three integrals was less than 2% over most of the concentration range covered; however, when greater than 80% of any one monomer had been consumed, the relative error increased rapidly due to the increasing relative importance of integration of random background noise.

Discussion

From the data presented in Figures 2–7, together with the facts that neither maleic anhydride nor vinyl isobutyl ether homopolymerizes under the conditions of the experiment,[1] certain statements can be made concerning the different monomer–radical reactions which occur in the system. The radical derived from each monomer (i.e., chain radicals in which the terminal unit is a given monomer) will be considered.

Methyl methacrylate radical adds to both methyl methacrylate monomer and maleic anhydride monomer, but not to vinyl isobutyl ether monomer. Further, the ratio of rates of reaction of the methyl methacrylate radical

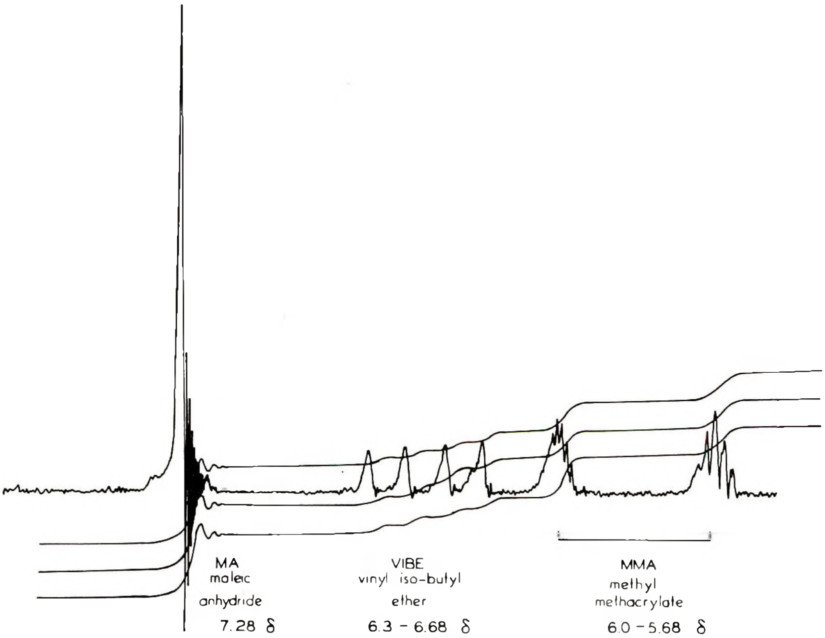

Fig. 1. NMR spectrum of monomer mixture in vinyl proton region.

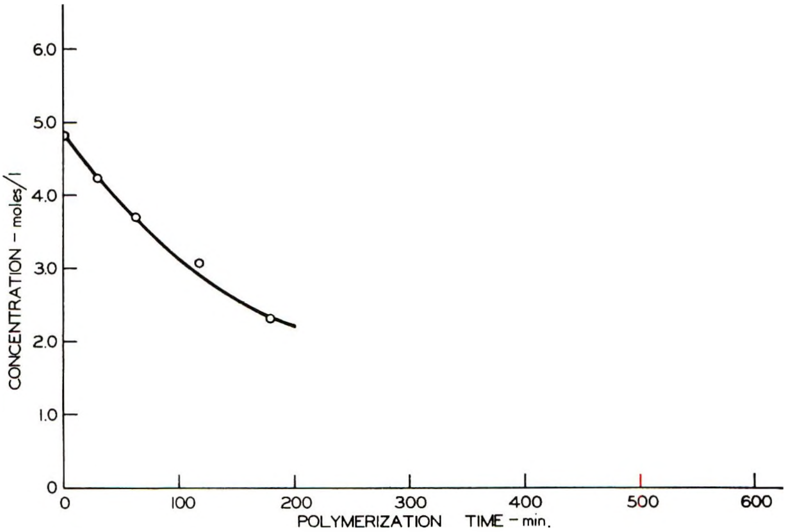

Fig. 2. Methyl methacrylate polymerization in ethyl acetate at 60°C.; [AIBN] = 2.3×10^{-3} mole/l.

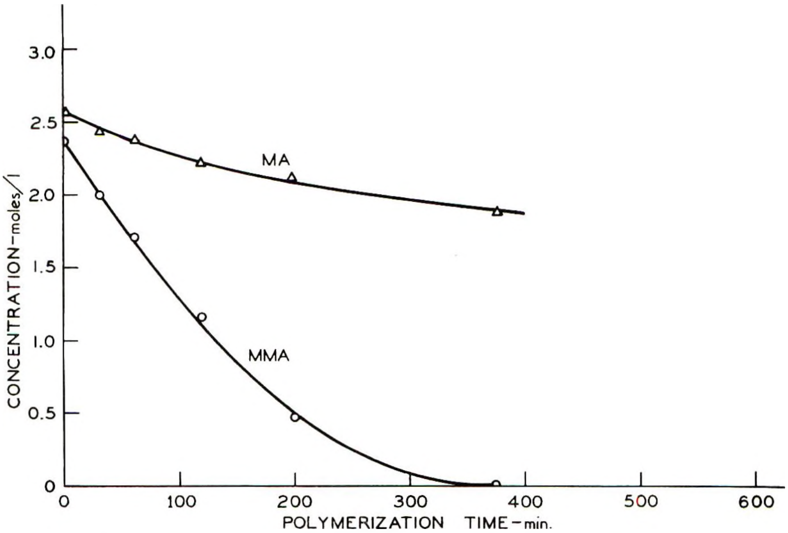

Fig. 3. Copolymerization of maleic anhydride and methyl methacrylate in ethyl acetate at 60°C.; [AIBN] = 2.3×10^{-3} mole/l.

with methyl methacrylate and with maleic anhydride is about 4 MMA/MA. This latter observation is taken from the initial polymerization rates of MMA and MA (Fig. 3).

Maleic anhydride radical adds to MMA monomer and adds readily to VIBE monomer, but does not add to MA monomer.[1]

Vinyl isobutyl ether radical adds to MA monomer (Fig. 4), but does not add to VIBE monomer. From energetic grounds it would be expected that

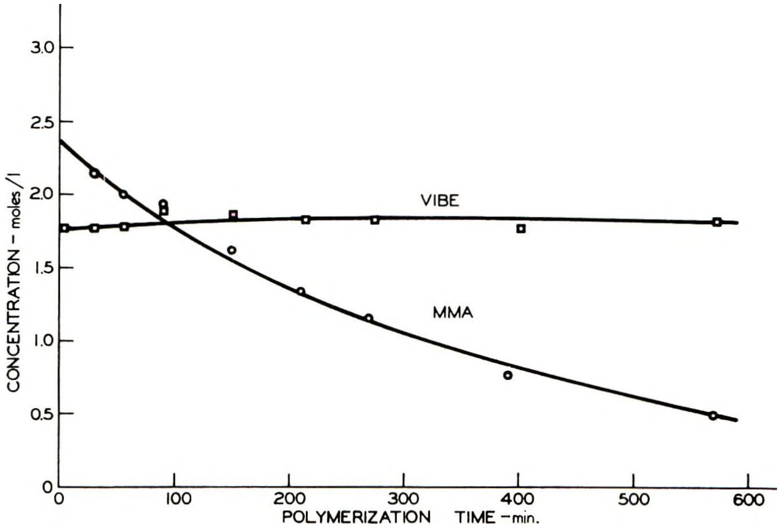

Fig. 4. Copolymerization of vinyl isobutyl ether and methyl methacrylate in ethyl acetate at 60°C.; [AIBN] = 2.3 × 10^{-3} mole/l.

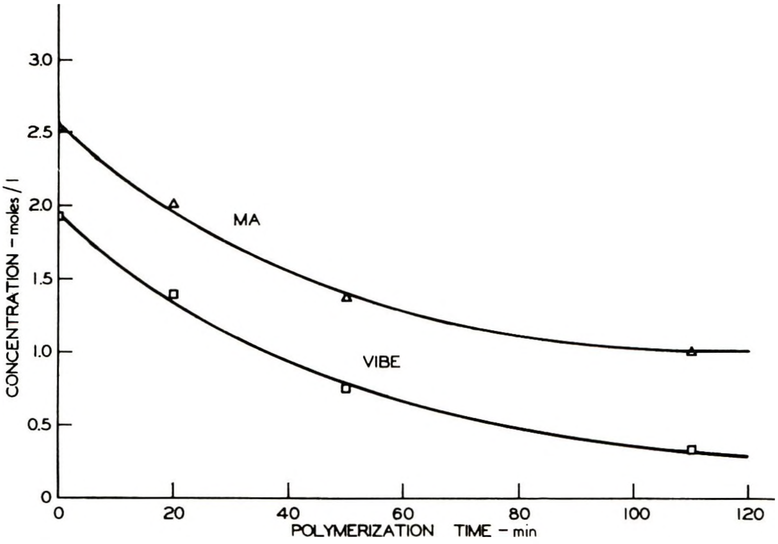

Fig. 5. Copolymerization of vinyl isobutyl ether and maleic anhydride in ethyl acetate at 60°C.; [AIBN] = 2.3 × 10^{-3} mole/l.

VIBE radical would add to MMA, which gives a relatively low energy, resonance stabilized radical, but the data presented here do not provide information on this subject.

These observations are sufficient to allow some explanation of the course of the reaction involving all three monomers. The assumption is made that in the three-component system the radical reactivities toward the three monomers are the same as in the various one- and two-component systems.

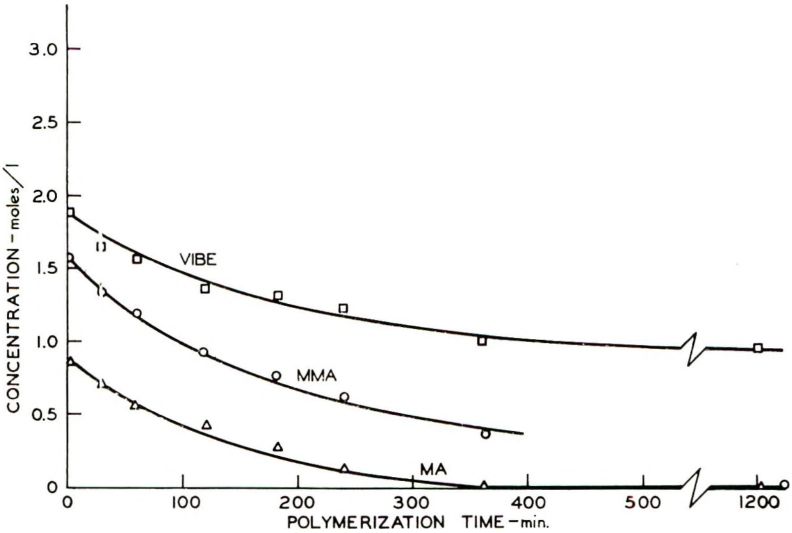

Fig. 6. Copolymerization of methyl methacrylate, vinyl isobutyl ether, and maleic anhydride in ethyl acetate at 60°C.; [AIBN] = 2.3 × 10^{-3} mole/l.

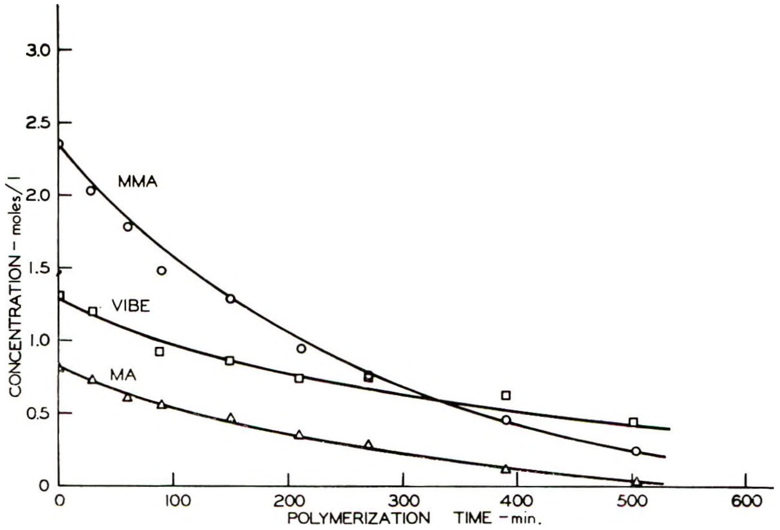

Fig. 7. Copolymerization of methyl methacrylate, vinyl isobutyl ether, and maleic anhydride in ethyl acetate at 60°C. [AIBN] = 2.3 × 10^{-3} mole/l.

An MMA· radical, for instance, adds successively to MMA monomer molecules until it adds to an MA molecule (approximately 4:1 for equal MMA and MA concentrations). The chain radical, which is then MA· reacts with either MMA or VIBE monomer, but from the rapidity of the VIBE–MA copolymerization, apparently reacts much more rapidly with VIBE. The VIBE· chain end likewise reacts with either MA or MMA. When the chain-end radical adds to MMA to form MMA·, the process is repeated.

It is observed from the above data that MMA polymerized at essentially the same rate in all experiments, regardless of the presence of the other monomers. This is reasonable if MMA is the most reactive monomer in the system, that is, if MMA reacts readily with any radical present in the system. In this case incorporation of MA and VIBE into the polymer (as alternating MA–VIBE regions) is stopped by reaction of either the MA· or VIBE· chain ends with MMA monomer. On the other hand, polymerization of MA–VIBE is much more rapid than MMA (Figs. 2 and 5), so that the MA–VIBE segments are of significant length.

Some statement about the relative lengths of the MMA and VIBE–MA segments can be made. Since to a first approximation only MMA monomer is incorporated into $(\mathrm{MMA})_m$ lengths and only VIBE and MA alternately in $[\mathrm{VIBE\text{-}MA}]_n$ lengths, the average lengths must be in proportion to the rates of monomer disappearance:

$$\frac{m}{n} = \frac{-d[\mathrm{MMA}]}{dt} \bigg/ -\frac{d[\mathrm{VIBE}]}{dt} = \frac{-d[\mathrm{MMA}]}{dt} \bigg/ -\frac{d[\mathrm{MA}]}{dt} \tag{1}$$

Approximate rates of monomer disappearance are easily obtained from the data in Figures 6 and 7. At 50 min. (Fig. 6) the rates of disappearance give an approximate m/n ratio of 3/2; at 50 min. with the monomer concentration of Figure 7, the m/n ratio is 3.

Estimates of absolute block length can also be made. Since VIBE does not end MMA blocks, only MA does (neglecting radical coupling). The rate of extension of an MMA section may be found from $k_{11}[\mathrm{MMA}]\cdot[\mathrm{MMA}]$; the rate of interruption approximately by $k_{13}[\mathrm{MMA}\cdot][\mathrm{MA}]$. The average number of MMA monomer units (including the first) reacting prior to interruption is:

$$\bar{n} - 1 \cong k_{11}[\mathrm{MMA}\cdot][\mathrm{MMA}]/k_{13}[\mathrm{MMA}\cdot][\mathrm{MA}] \tag{2}$$

that is, the rate of extension divided by the rate of interruption. The ratio k_{11}/k_{13} can be evaluated from a consideration of the system MMA–MA in Figure 3. Here the observed 4:1 ratio of MMA and MA initial disappearance rates is;

$$4 = \frac{d[\mathrm{MMA}]/dt}{d[\mathrm{MA}]/dt} = \frac{k_{11}[\mathrm{MMA}\cdot][\mathrm{MMA}] + k_{31}[\mathrm{MA}\cdot][\mathrm{MMA}]}{k_{13}[\mathrm{MMA}\cdot][\mathrm{MA}]} \tag{3}$$

since MA does not homopolymerize. Further, the rates of identity change of the chain radical must be equal (neglecting termination effects), i.e.;

$$-d[\mathrm{MMA}\cdot]/dt \cong k_{13}[\mathrm{MMA}\cdot][\mathrm{MA}] \cong -d[\mathrm{MA}\cdot]/dt \cong k_{31}[\mathrm{MA}\cdot][\mathrm{MMA}] \tag{4}$$

so that eq. (3) reduces in the case of equal monomer concentrations (Fig. 3) to:

$$4 \cong \frac{k_{11}[\mathrm{MMA}\cdot][\mathrm{MMA}]}{k_{13}[\mathrm{MMA}\cdot][\mathrm{MA}]} + 1 \tag{5}$$

or

$$k_{11}/k_{13} \simeq 3$$

Hence, combining eq. (5) with eq. (2) yields

$$n - 1 \approx 3[\mathrm{MMA}]/[\mathrm{MA}]$$

At 50 min. (Fig. 6), the average MMA length is thereby about 7 and the average VIBE–MA length is 4.7 pairs. At 50 min. (Fig. 7), the average MMA length is 10 and the average VIBE–MA length is 3.3 pairs.

The technical assistance of Mrs. A. G. Thomas and Mr. R. M. Redding is gratefully acknowledged. The work was performed under Army Ordnance Contract No. DA-01-021 ORD-11878 Modification No. 15.

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Résumé

On a montré que les vitesses de polymérisation de monomères individuels dans un mélange de monomères peuvent être suiview au moyen de la technique NMR. La technique est rapide et simple et requièré très peu d'échantillons. Les systèmes MMA, MA, VIBE ont été étudiés au moyen de cette technique. Au départ des résultats obtenus, on conclut que le polymère formé dans un mélange de trois monomères, est un copolymère à bloc formé de $(\mathrm{MMA})_m$ et $(\mathrm{MA\text{-}VIBE})_n$ unités, la longueur des séquences dépendant de la concentration en monomère.

Zusammenfassung

Es wurde gezeigt, dass die Polymerisationsgeschwindigkeit individueller Monomerer in einer Monomerenmischung mittels eines NMR-Verfahrens verfolgt werden kann. Das Verfahren arbeitet rasch und einfach und erfordert nur eine sehr geringe Probenmenge. Das System MMA, MA, VIBE wurde nach diesem Verfahren untersucht. Aus den erhaltenen Daten wurde geschlossen, dass das in einer Mischung von drei Monomeren gebildete Polymere ein aus $(\mathrm{MMA})_m$-und $(\mathrm{MA\text{-}VIBE})_n$-Einheiten aufgebautes Blockcopolymeres ist, wobei die Länge der Einheiten von der Monomerkonzentration abhängt.

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Polymerization of Styrene with Chromium Acetylacetonate and Triethylaluminum and Diethylaluminum Bromide*

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Synopsis

Kinetics of the polymerization of styrene in the presence of benzene at 30°C., with chromium acetylacetonate in combination with triethylaluminum and also in combination with diethylaluminum bromide as catalyst, have been studied. Chromium acetylacetonate forms a homogeneous system with triethylaluminum, and chromium acetylacetonate with diethylaluminum bromide behaves as a heterogeneous system. This homogeneous catalyst system, though reported inactive in the polymerization of α-olefins, has been found effective with styrene. Depending on the homogeneity and heterogeneity of the system, the rate of polymerization is proportional to half order and first order of catalyst concentration. A probable reason for the effect of homogeneity on the order of reaction has been discussed. A study of the effect of diethylzinc as a chain-transfer agent has helped to confirm the mechanism of polymerization.

INTRODUCTION

Homogeneous Ziegler catalyst systems have been reported[1] to polymerize only ethylene and diolefins but not α-olefins like styrene, propylene, and butene. On the other hand, it is well established that all types of heterogeneous Ziegler catalyst systems[2] polymerize most of the hydrocarbon monomers, particularly styrene. In recent communications, Overberger et al.[3] and Allen et al.[4] have reported that a soluble catalyst system consisting of dicyclopentadienyltitanium chloride and aluminum alkyl can polymerize styrene. Chromium acetylacetonate and triethylaluminum, a soluble catalyst system, was earlier used for a kinetic study of the polymerization of butadiene.[5,6] We have, however, found it to polymerize styrene, and it has been also observed by us that chromium acetyl acetonate and diethylaluminum bromide form a heterogeneous catalyst system. These two catalyst systems show different kinetic behavior with the same monomer, and detailed kinetic study of the polymerization of styrene with these catalyst systems is presented in this communication.

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* N. C. L. Communication No. 818.

EXPERIMENTAL

Preparation of Materials

Benzene was treated with concentrated sulfuric acid, washed many times with water, and stored over sodium after distillation. Immediately prior to use, it was refluxed overnight on sodium under a nitrogen atmosphere and redistilled over silica gel.

Styrene was purified by alkali washing followed by washing with distilled water and dried over sodium carbonate. Styrene was distilled under nitrogen prior to use, and traces of moisture were removed by adding activated silica gel. Triethylaluminum was prepared by the reaction of aluminum–magnesium alloy (Al_2Mg_3) with ethyl bromide as reported by Ziegler[7] and distilled under reduced pressure of (2 mm.) at 69°C.

Diethylaluminum bromide was prepared[8] by the reaction of magnalium (Al_2Mg) with ethyl bromide and distilled at 82°C./2 mm. Aluminum in aluminum alkyls was estimated by EDTA complexometric titration[9] against zinc sulfate.

Diethylzinc was prepared by the reaction of zinc–copper alloy (92% Zn and 8% Cu) with ethyl bromide and ethyl iodide and distilled under reduced pressure. It was redistilled at 110°C.

Chromium acetylacetonate was prepared[11] by reacting chromium chloride with acetylacetone under basic conditions. Brown-violet crystals that separated from the reaction mixture were dissolved in hot benzene and recrystallized with cold *n*-hexane under rapid cooling. These crystals were dried under vacuum at 62°C./2 mm. pressure for 4 hr.

Polymerization

All the experiments, preparing of catalyst, addition of monomer to the catalyst system, storing of the reagents etc., were carried out inside a glove box continuously flushed with oxygen-free nitrogen gas. This box was maintained dry with activated silica gel which was changed and activated daily. All the reagents were measured and mixed by means of all-glass hypodermic syringes with stainless steel needles.

A known quantity of benzene was placed in a 50-ml. Erlenmeyer flask with a well-greased B_{19} cone joint. A solution of chromium acetylacetonate in benzene was added, followed by triethylaluminum; the mixture turned brown-black in color. It was allowed to age for 10 min. and then the required amount of styrene was added. The flask was stoppered tightly with a B_{19} socket joint and removed to a thermostat, where it was maintained at 30°C. The reaction mixture was stirred vigorously with a specially fabricated magnetic stirrer[12] held inside the thermostat. Similarly, when the second catalyst system consisting of diethylaluminum bromide and chromium acetylacetonate was prepared, unlike the first system, a yellow solid separated and settled at the bottom of the brown-black solution.

After a specific reaction time, polymer was precipitated by adding the contents to a large volume of methanol containing 5% hydrochloric acid. On keeping overnight, the polymer slowly settled down as a fine precipitate. It was removed over a sintered disk of weighed crucible and washed several times with excess methanol before drying to constant weight.

Molecular weights were determined by viscosity method in benzene at 25°C. by using the relation:[13]

$$P_n = 1770\ [\eta]^{1.4}$$

RESULTS AND DISCUSSION

The catalyst complexes obtained by the reaction of chromium acetylacetonate and triethylaluminum or diethylaluminum bromide maintained their activity for about 8 hr., as shown by the plot of per cent conversion versus time (Fig. 1). To eliminate any polymerization of styrene by free radicals that are liberated during the formation of the catalyst complex shown below, styrene monomer was added after preparing the catalyst complex (c.f. polymerization of ethylene, butene-1, etc.[14,15]).

$$3\mathrm{Al(C_2H_5)_3} + \mathrm{Cr(AcAc)_3} \rightarrow 3(\mathrm{C_2H_5}) + \mathrm{X} \rightarrow 3(\mathrm{C_2H_4} + \mathrm{C_2H_6}) + \mathrm{X}$$

where X is the reaction product.

It has been well established by Natta[5] and others that aging of $\mathrm{AlEt_3}$–$\mathrm{Cr(AcAc)_3}$ catalyst for varying time intervals from 10 to 240 min. shows little difference in yield and structure of polymer. Under our experimental conditions an aging time of 10 min. was found sufficient to maintain constant catalytic activity for nearly 3 and 2 hr. in the case of the $\mathrm{AlEt_3}$ and $\mathrm{AlEt_3Br}$ systems, respectively (Fig. 1).

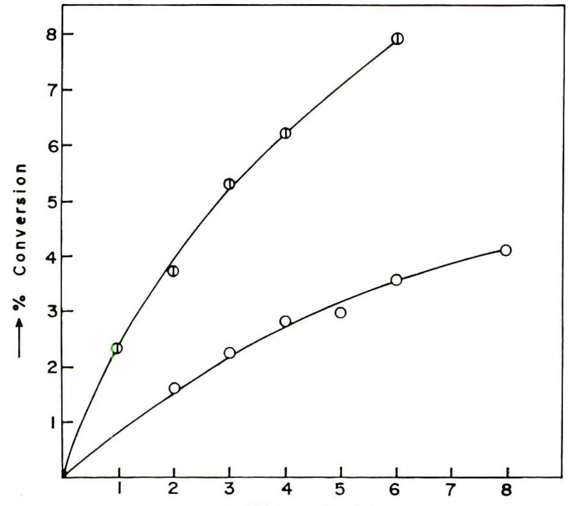


Fig. 1. Percentage conversion vs. time: (⦶) CrAcAc–$\mathrm{AlEt_2Br}$, molar ratio Al/Cr = 3.5, [$\mathrm{AlEt_2Br}$] = 5.5 × 10^{-2} mole/l.; (O) CrAcAc–$\mathrm{AlEt_3}$, molar ratio Al/Cr = 3, [$\mathrm{AlEt_3}$] = 5.25 × 10^{-2} mole/l.; [monomer] = 4.3 mole/l.

TABLE I[a]

Al/Cr ratio	$[Cr(AcAc)_3]$ × 10^2, mole/l.	$[AlEt_3]$ × 10^2, mole/l.	Yield, mg.	Molecular weight
1	1.0	1.0	78.12	54,610
3	1.0	3.0	168.9	27,970
6	1.0	6.0	185.3	36,180
9	1.0	9.0	190.0	23,510

[a] Conditions: benzene, 10 ml.; styrene, 10 ml. (4.325 mole/l.); reaction time, 3 hr.

TABLE II[a]

Al/Cr ratio	$[Cr(AcAc)_3]$ × 10^2, mole/l.	$AlEt_3$ × 10^2, mole/l.	R_p × 10^6, mole/l.-sec.	Molecular weight	Concentration of complex calculated at Al/Cr = 3, 10^2 mole/l.
1	3.5	3.5	7.742	56,080	1.167
2	2.35	4.65	9.752	33,360	1.55
3	1.75	5.25	9.752	33,350	1.75
3.5	1.5	5.5	7.491	45,160	1.5
4.4	1.3	5.7	8.247	41,840	1.3
6	1.0	6.0	5.577	39,650	1.0
9	0.7	6.3	5.395	48,060	0.7
13	0.5	6.5	4.709	30,470	0.5

[a] Conditions: styrene, 10 ml.; benzene, 10 ml. (4.325 mole/l.); reaction time, 3 hr.; total concentration of catalyst, 7.0 × 10^{-2} mole/l.

The $AlEt_3$–$Cr(AcAc)_3$ reaction product was brownish black in color and apparently quite homogeneous. Within 10 min. of reaction between $AlEt_2Br$ and $Cr(AcAc)_3$ green color instantaneously developed, which gradually changed to brownish black, and at the end a yellow product precipitated out. The initial appearanc of green color may be due to the formation of $C_2H_5AlCrBr$—AcAc residue, similar to $C_2H_5AlCoCl$ AcAc residue[16] detected as an intermediate green product between the reaction of cobalt acetylacetonate and diethylaluminum chloride in the polymerization of butadiene. The yellow product in our case might have been formed by further reduction of this intermediate product. Also the heterogeneous catalyst system is rather unstable and decomposes in about 2–3 hr., as indicated by the reappearance of greenish tinge.

In studies of different ratios of combination of the two components of the catalyst, $AlEt_3$ and $Cr(AcAc)_3$, polymerization was conducted under two different conditions. In the first case, concentration of $AlEt_3$ was varied and that of $Cr(AcAc)_3$ was maintained constant (Table I), whereas in the second case concentration of both $AlEt_3$ and $Cr(AcAc)_3$ were varied but at every ratio the total concentration of mixture was the same (Table II). The ratio of Al/Cr was varied up to 13, but a maximum rate of polymerization was observed at an Al/Cr ratio of 3, indicating the high activity of catalyst complex at this ratio. In the reaction of $AlEt_2Br$ with $Cr(AcAc)_3$ the Al/Cr ratio of maximum activity was, however, 3.5 (Fig. 2).

In a detailed study of the homogeneous catalyst system $AlEt_3$–$Cr(AcAc)_3$, it has been already pointed out by Sartori and Costa[17] that the active complex is formed at an Al/Cr ratio of 3. This result was further substantiated by plotting the rate of polymerization at Al/Cr ratios of 1–13 against the calculated concentration of catalyst complex by assuming a stoichiometry of reaction of 3 moles of $AlEt_3$ and 1 mole of $Cr(AcAc)_3$, at these ratios of Al/Cr in the second set of experiments above (Table II).

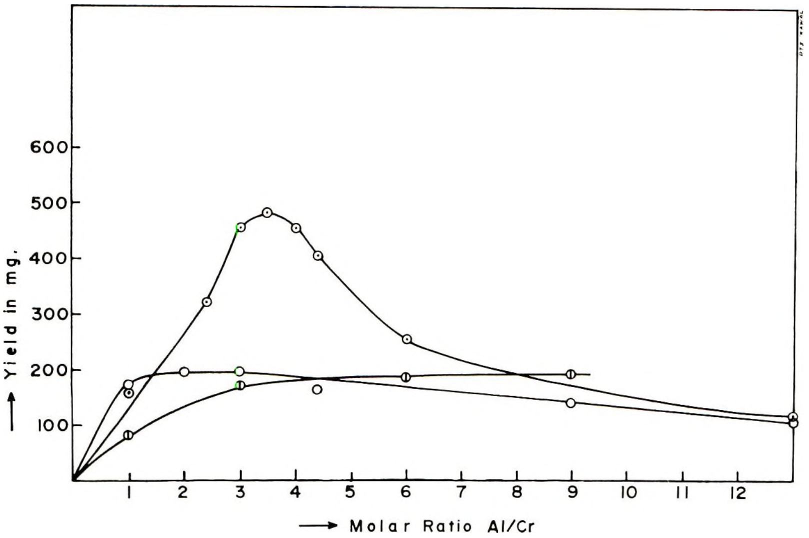
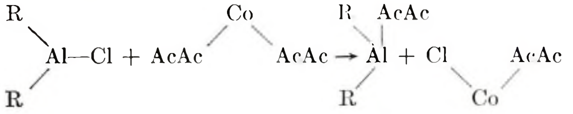


Fig. 2. Yield vs. molar ratio of Al/Cr: (⊙) [CrAcAc] + [$AlEt_2Br$] = 0.07 mole/l.; (O) [CrAcAc] + [$AlEt_3$] = 0.07 mole/l.; (⦶) [CrAcAc] = 0.01 mole/l., [$AlEt_3$] varying.

A linear plot so obtained shows maximum activity at ratio of Al/Cr of 3 (Fig. 3). It is thus clear from the present studies on the polymerization of styrene that the catalyst complex of maximum activity is formed by the reaction of 3 moles of $AlEt_3$ with 1 mole of $Cr(AcAc)_3$ and its structure is similar to that suggested by Sartori and Costa.[17] The second catalyst system is similar to the diethylaluminum chloride–cobalt acetylacetonate[16,18] and diethylaluminum chloride–vanadium acetylacetonate catalyst systems.[19] In the case of $AlEt_2Cl$–$Co(AcAc)_3$, it has been found[18] that in benzene at a molar Al/Co ratio of 2.5, the preliminary stage of this reaction consists of an exchange between the chlorine bonded to aluminum and acetyl acetonate groups bonded to cobalt, as shown in eq. (1).



$$R_2Al{-}Cl + AcAc{-}Co{-}AcAc \rightarrow R_2Al{-}AcAc + Cl{-}Co{-}AcAc \qquad (1)$$

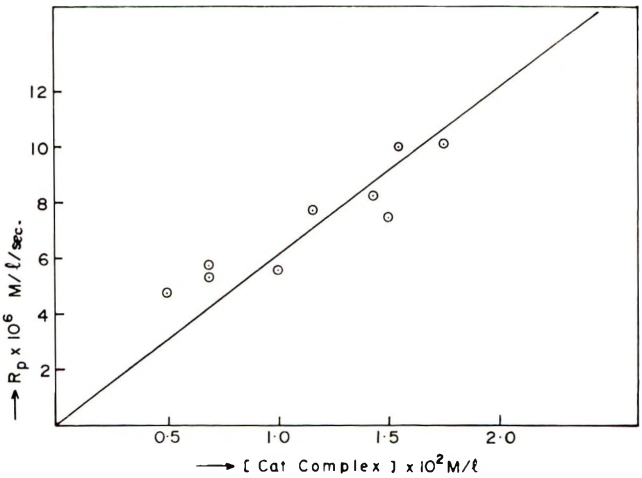


Fig. 3. Concentration of catalytic complex at Al/Cr molar ratio of 3 vs. rate of polymerization. See Table II.

Bawn[16] has also supported this idea of exchange mechanism. He suggested that by alkylation, chlorine-bonded cobalt compounds are converted into compounds like $(AcAc)_2CoEt$ or $(AcAc)CoEt_2$, and Co–Et bonds are further cleaved to form lower valency state cobalt alkyls. This exchange mechanism of AcAc for chloride has even been confirmed by proving the formation of $CoCl_2 \cdot THF$ complex in the reaction product between catalyst complex and tetrahydrofuran (THF). From these studies it has been suggested that the active catalyst intermediate was complexed cobalt alkyl.

During the polymerization of butadiene with the $AlEt_2Cl–V(AcAc)_3$ catalyst system in the presence of benzene in the wide range of molar Al/V ratio of 10–1000, the formation of $VCl_2(C_2H_5)$ in the catalyst complex and the growth of polymer chains at the V–C bond are postulated on the basis of the same argument, substitution of AcAc groups on vanadium by chloride of $AlEt_2Cl$ and alkylation of vanadium compounds.

Thus, on the same lines, $AlEt_2Br–Cr(AcAc)_3$ catalyst system is likely to be converted into the complex consisting of chromium alkyl which is possibly formed by the reduction of alkylated chromium bromide.

Kinetics of Polymerization

In the homogeneous $AlEt_3–Cr(AcAc)_3$ system the rate of polymerization is proportional to the square root of the concentration of $Cr(AcAc)_3$ and linear to concentration of monomer, while in the heterogeneous polymerization with the $AlEt_2Br–Cr(AcAc)_3$ system, the rate of polymerization varies in a linear fashion with the concentration of monomer and the concentration of $Cr(AcAc)_3$ (Figs. 4 and 5). Besides the rate constants (1.42×10^{-5} l./mole-sec.) with $AlEt_3Cr(AcAc)_3$ and (3.38×10^{-4} l./mole-

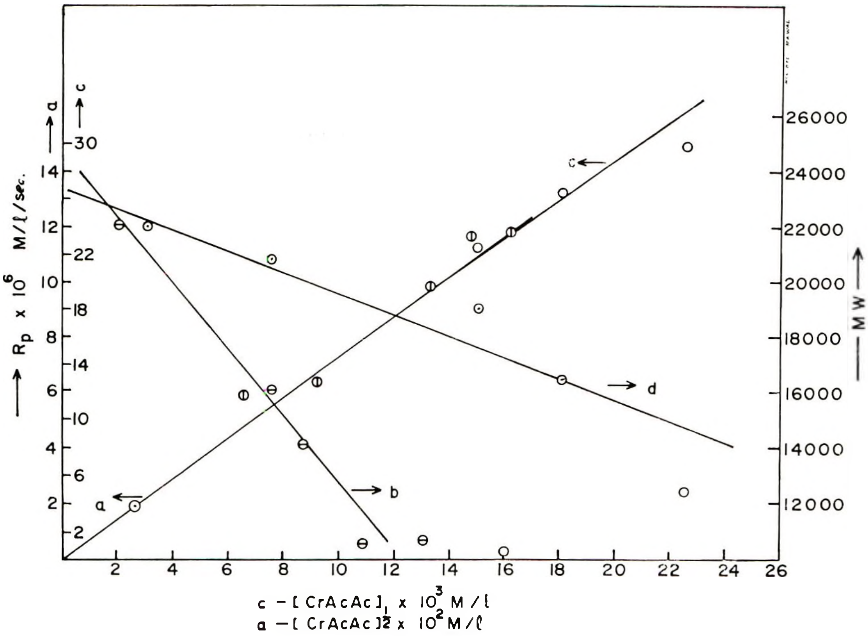


Fig. 4. Rate of polymerization and molecular weight vs. [CrAcAc]: (*a*) R_p vs. [CrAc Ac], CrAcAc–AlEt$_3$, Al/Cr = 3.0; (*b*) MW vs. CrAcAc, CrAcAc–AlEt$_3$; (*c*) R_p vs. [CrAcAc], CrAcAc–AlEt$_2$Br, Al/Cr = 3.5; (*d*) MW vs. [CrAcAc], CrAcAc–AlEt$_2$Br; [monomer] = 4.3 mole/l.

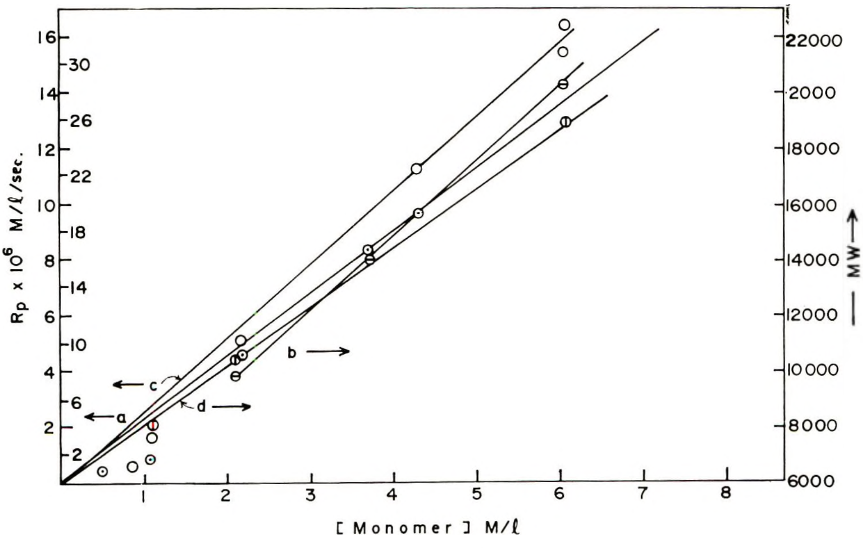


Fig. 5. Rate of polymerization and molecular weight vs. [monomer]: (*a*) R_p vs. monomer, CrAcAc–AlEt$_3$. AlEt$_3$ = 5.25 × 10^{-2} mole/l., Al/Cr = 3.0; (*b*) MW vs. [monomer], CrAcAc–AlEt$_3$, conditions as for (*a*); (*c*) R_p vs. [monomer], CrAcAc–AlEt$_2$Br, AlEt$_2$Br = 5.5 × 10^{-2} mole/l., Al/Cr = 3.5; (*d*) MW vs. monomer, CrAcAc–AlEt$_2$Br, conditions as for (c).

sec.) with $AlEt_2Br-(CrAcAc)_3$ suggest a very high rate of polymerization as compared with the rate constants reported[20] for polymerization of styrene with triethylaluminum, diethylaluminum chloride, and titanium trichloride catalyst systems, which suggests the formation of high-activity catalyst species in our systems.

The dependence of rate of polymerization on square root of concentration of $Cr(AcAc)_3$ in the case of homogeneous catalyst system in benzene may be attributed to a bimolecular termination, which is typical with a free-radical polymerization. Similarly, a bimolecular termination reaction has also been shown possible in the case of the homogeneous system of ethylene polymerization with the dicyclopentadienyltitanium dichloride–trimethylaluminum catalyst system.[21] By assuming bi-molecular termination, it is possible to deduce the rate law as given below.

Since the concentration of the growing catalyst species (C*) will be proportional to the catalyst concentration.

$$d[c^*]\,/\,dt = K[\mathrm{Cr(AcAc)_3}] \tag{2}$$

where K is the reaction constant. Due to bimolecular termination, two catalyst species deactivate and polymer product forms.

$$2\mathrm{C}^* \xrightarrow{K_t} \text{polymer product}$$

Then the rate of deactivation of catalyst species is proportional to the square of concentration of catalyst species, i.e.,

$$-d[\mathrm{C}^*]/dt = Kt[\mathrm{C}^*]^2 \tag{3}$$

where K_t is the termination constant.

It is debatable whether a steady state can be assumed, but it a steady state with reference to C* is obtained, eq. (2) becomes equal to eq. (4). Then

$$K_t[\mathrm{C}^*]^2 = K[\mathrm{Cr(AcAc)_3}] \tag{4}$$

$$[\mathrm{C}^*]^2 = (K/K_t)[\mathrm{Cr(AcAc)_3}]$$

and

$$[\mathrm{C}^*] = (K^{1/2}/K_t^{1/2}, [\mathrm{Cr(AcAc)_3}]^{1/2} \tag{5}$$

Since

$$R_p = K_p[\mathrm{C}^*][\mathrm{M}] \tag{6}$$

where K_p is the propagation constant, substituting eq. (5) for [C*] in eq. (6), we obtained

$$R_p = (K_pK^{1/2}/K_t^{1/2})\ [\mathrm{Cr(AcAc)_3}]^{1/2}\ [\mathrm{M}] \tag{7}$$

Hence

$$R_p \propto [\mathrm{Cr(AcAc)_3}]^{1/2} \tag{8}$$

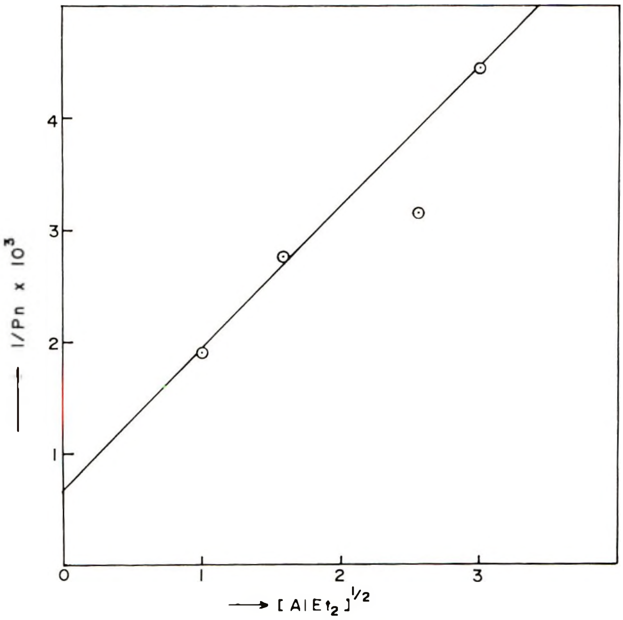


Fig. 6. Reciprocal degree of polymerization vs. $[AlEt_3]^{1/2}$ for Cr (AcAc)–$AlEt_3$, Al/Cr = 3.0, [CrAcAc] = 0.01 mole/l., [monomer] = 4.3 mole/l.

There is every possibility of termination through chain transfer with $AlEt_3$ since, as seen in Figure 6, degree of polymerization was observed to be inversely proportional to the square root of concentration of $AlEt_3$ at constant concentration of $Cr(AcAc)_3$ and the rate of polymerization was nearly constant regardless of increasing amount of $AlEt_3$. This relation between degree of polymerization with square root of $AlEt_3$ concentration can be explained in the following way.

Triethyl aluminum is normally dimeric in structure, and this dimeric form is in equilibrium with a monomeric structure as shown in eq. (9).

$$(AlEt_3)_2 \rightleftarrows 2(AlEt_3) \tag{9}$$

Then

$$AlEt_3 = [(AlEt_3)_2]^{1/2}$$

Monomeric $AlEt_3$ stops polymerization by a chain transfer reaction

$$AlEt_3 + Cat \text{----} P \rightarrow AlEt_2 \text{----} P + Cat\text{—}Et \tag{10}$$

Hence:

$$1/P_n \propto [(AlEt_3)_2]^{1/2}$$

In case of $AlEt_2Br$–$Cr(AcAc)_3$, a chain-transfer reaction is possible only with the soluble species of catalyst in a hydrocarbon because molecular weight decreases with increasing concentraion of CrAcAc (Fig. 4).

The activation energy of polymerization was calculated from the plot of logarithm of rate of polymerization versus reciprocal of absolute temperature (Fig. 7). It was found to be 10.5 kcal./mole of AlEt$_3$–Cr(AcAc)$_3$ and 11.0 kcal./mole for AlEt$_2$Br–Cr(AcAc)$_3$; these are in the range of values for

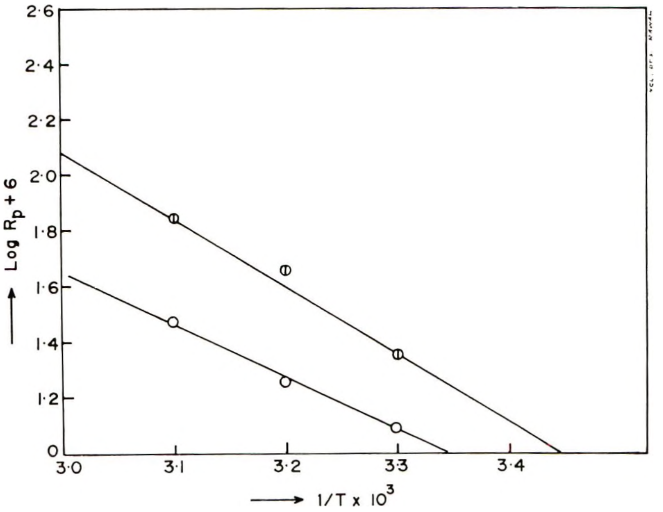


Fig. 7. Logarithm of rate of polymerization vs. reciprocal absolute temperature: (O) CrAcAc–AlEt$_3$; (⦶) CrAcAc–AlEt$_2$Br.

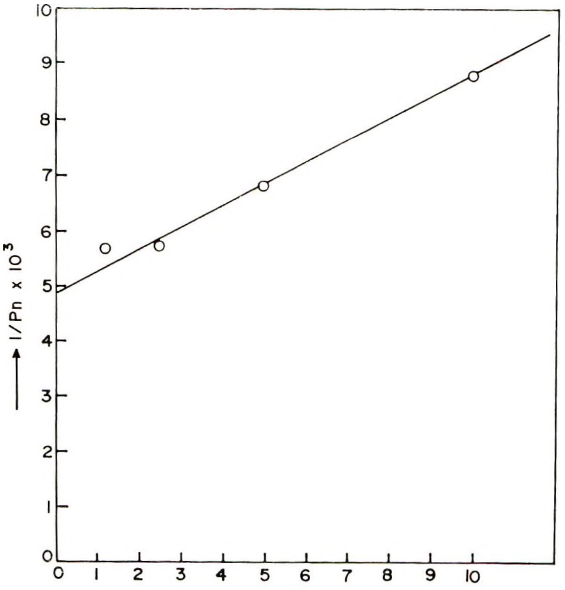


Fig. 8. Reciprocal degree of polymerization vs. [ZnEt$_2$]; [monomer] = 4.3 mole/l., [AlEt$_3$] = 0.01 mole/l., Al/Cr = 6.

TABLE III[a]

$[ZnEt_2]$, mole/l.	$R_p \times 10^6$, mole/l.-sec.	Molecular weight	$1/P_n$
0.1	3.921	13,570	0.74
0.05	6.474	15,190	0.66
0.025	8.149	18,310	0.5
0.0125	8.925	18,500	0.5
0.0	9.826	36,180	0.29

[a] Conditions: styrene, 10 ml. (4.325 mole/l.); benzene, 10 ml.; $[Cr(AcAc)_3]$, 1.0 × 10^{-2} mole/l.; [Al alkyl], 6.0 × 10^{-2} mole/l., Al/Cr molar ratio, reaction time, 2 hr.

a coordinate anionic polymerization. This thus rules out the possibility of a radical polymerization, as the activation energy for a radical polymerization of styrene is more than 22 kcal./mole, which is a very high value compared to the value obtained with these two systems. Further, diethylzinc acts in a manner similar to its action in anionic polymerization of propylene[22] with $TiCl_3$–$AlEt_3$ system in which degree of polymerization is inversely proportional to the concentration of diethylzinc added (Fig. 8, Table III). Thus, even though bimolecular termination reaction is working in this homogeneous catalyst system, the mechanism of polymerization can be an anionic one. A similar mechanism is reported in a case of ethylene[21] polymerization with dicyclopentadienyltitanium dichloride–trimethylaluminum, a homogeneous system.

On the basis of π-complex formation between the monomer and transition metal as suggested in the case of ethylene polymerization with the soluble catalyst system, dicyclopentadienyltitanium chloride–trimethylaluminum,[21] it may be assumed that π-complex formation is possible between styrene and chromium metal in catalyst complex. This is also supported by the reaction between nickel acetylacetonate and $P(C_6H_5)_3$ or $As(C_6H_5)_3$.[23] On reaction with triethylaluminum, chromium acetylacetonate is reduced to the zero valent state[14] and then forms the active catalyst complex. Similarly, nickel acetylacetonate is also present in a zero valent state in the catalyst complex, which then converts butadiene through the π-complex into vinylcyclohexene, cyclododecatriene, and cyclooctadiene. In addition to this, the carbon–chromium bond is likely to be involved in the polymerization reaction like the carbon–cobalt and carbon–vanadium bonds in the polymerization of butadiene with cobalt acetylacetonate and diethylaluminum chloride[16] or vanadium acetylacetonate and diethylaluminum chloride,[19] which are similar to chromium acetylacetonate and diethyl aluminum bromide. Hence it is possible to conclude that chromium acetylacetonate and aluminum alkyls form an active complex at the Al/Cr ratio of 3 and the propagation reaction may start at a carbon–chromium bond through π-complex formation between the monomer and the chromium metal in the catalyst complex. In spite of having bimolecular termination in the soluble catalyst system of polymerization, the mechanism is coordinate ionic.

Taken in part from the thesis submitted by one of the authors (A.B.D.) in fulfillment of the requirements for the Ph.D. degree, March 1964.

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Résumé

La cinétique de polymérisation du styrène en présence de benzène à une température de 30°C a été étudiée en présence d'un catalyseur à base de acétylacétonate de chrome combiné avec du triéthylaluminium et également avec une combinaison de bromure de diéthylaluminium. L'acétylacétonate de chrome forme avec le triéthylaluminium un système homogène et l'acétylacétonate de chrome avec le bromure de diéthylaluminium se comporte comme un système hétérogène. Le système catalytique homogène bien que signalé comme étant inactif pour la polymérisation des α-oléfines a été trouvé effectif pour le styrène. Suivant l'homogénéité ou l'hétérogénéité de ce système, la vitesse de polymérisation est proportionnelle à la puissance un demi ou première puissance de la concentration en catalyseur. La raison probable de cet effet de l'homogénéité sur l'ordre de la réaction est soumise à discussion. Une étude de l'effet du zincdiéthyl comme agent de transfert de chaîne a permis de confirmer le mécanisme de polymérisation.

Zusammenfassung

Die Kinetik der Polymerisation von Styrol in Gegenwart von Benzol und bei einer Temperatur von 30°C mit Chromacetylacetonat in Verbindung mit Aluminiumtriäthyl und auch in Verbindung mit Aluminiumdiäthylbromid als Katalysator wurde untersucht. Chromacetylacetonat bildet mit Aluminiumtriäthyl ein homogenes System und Chromacetylacetonat verhält sich mit Aluminiumdiäthylbromid als heterogenes Sys-

tem. Das homogene Katalysatorsystem welches als unwirksam bei der Polymerisation von α-Olefinen beschrieben wurde, zeigte sich gegen Styrol als wirksam. In Abhängigkeit von der Homogenität und Heterogenität des Systeme ist die Polymerisationsgeschwindigkeit in Bezug auf die Katalysatorkonzentration von der Ordnung $^1/_2$ oder 1. Eine wahrscheinliche Ursache für den Einfluss der Homogenität auf die Reaktionsordnung wurde diskutiert. Eine Untersuchung des Einflusses von Zinkdiäthyl als Kettenüberträger führte zu einer Bestätigung des Polymerisationmechanismus.

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Low-Temperature Polymerization of Isobutyl Vinyl Ether

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Synopsis

Isobutyl vinyl ether has been polymerized under conditions well known to yield isotactic polymer, viz., with boron trifluoride etherate at −78°C. in a nonpolar hydrocarbon diluent. A particular mixed solvent ratio and previous dissolution of catalyst enabled the polymerization to proceed homogeneously at the beginning. By following the temperature rise in an initially thermostatted system, we showed that the progress of the reaction eventually proceeded via a homogeneous phase to a gellike phase. Isotactic polymer is shown to be produced in both steps by a mechanism of slow chain propagation.

INTRODUCTION

It was first demonstrated by Schildknecht[1] that partially stereoregular vinyl ether polymers could be made by slow proliferous polymerization at −78°C. It was speculated at this stage that although the polymerization was clearly taking place at the surface of the boron trifluoride etherate catalyst droplet, the polymerization was itself taking place in a viscous homogeneous phase. Thus in contrast to Ziegler-Natta type polymerization, the heterogeneous surface appears not to be the stereoregulating influence.

To test this, Okamura devised a system in which the catalyst was soluble, thus removing the heterogeneous surface.[2] Polymers from isobutyl vinyl ether (IBVE) were still semicrystalline when produced in this homogeneous phase.

This observation has provoked much theoretical interest, and various mechanisms have been proposed for the homogeneous stereospecific polymerization.[3-5]

However, in view of the fact that this homogeneous stereospecific polymerization appears to be unique in a great field of heterogeneous stereospecific polymerizations, the authors feel it worthwhile to reinspect experimentally the details of the reaction.

EXPERIMENTAL

Purification of Reagents

Toluene was purified by shaking several times with concentrated sulfuric acid at room temperature and then with sodium hydroxide solution and water. It was distilled off calcium hydride and fractionated on an efficient column, the middle cut being taken.

n-Hexane was purified by shaking with acidified potassium permanganate solution, alkaline potassium permanganate solution, and water. It was distilled off calcium hydride as in the case of toluene.

Isobutyl vinyl ether (IBVE) was purified by shaking several times with dilute potassium hydroxide solution and then distilled off sodium in an efficient column. Generous end fractions were discarded.

Boron trifluoride diethyl etherate was distilled over calcium hydride, the middle cut being taken.

All reagents were distilled under vacuum before use after complete drying and degassing.

Polymerizations

All manipulations and metering was done under high-vacuum conditions, and the polymerization was carried out in a vessel similar to the Plesch calorimeter.[6] Solvents and catalyst were introduced, mixed, and thermostatted, and a bulb of monomer broken into the stirred catalyst solution. The course of the reaction was followed by a platinum resistance thermometer and a Wheatstone bridge. A pen recorder gave a plot of temperature versus time.

Reaction Vessel

The Plesch calorimeter consists of a double-walled glass vessel capable of evacuation between the walls so as to make a Dewar-type vessel. Reactions proceeding therein are adiabatic and temperature rises are experienced according to the enthalpy change of the reaction. At −78°C., even with an activation energy as low as 5 kcal./mole, a rise of 11°C. doubles the rate. Temperature rises in this order of magnitude are commonly encountered so that the reaction accelerates as it proceeds. This is clearly undesirable since: (*a*) single reaction curves cannot be analyzed; (*b*) the nature of the reaction and of the product may easily change over such a wide temperature range. To overcome this, a paradoxical technique has been devised where the reaction vessel is thermostatted but a temperature rise is recorded. A single-walled Pyrex flask comprises the reaction vessel which is immersed in a well-agitated carbon dioxide–acetone slurry. The temperature sensing element is at the center of the reaction vessel. Before a run, a cooling curve was plotted which could be added to the reaction curve for the true reaction rate. In this way the temperature rise during the homogeneous part of the reaction was about 2–3°C.

This treatment is only valid if the rate of cooling of the reaction mixture is always the same as that recorded before the run. To test this, the reaction was stopped with ethanol at various times and the cooling curve shown to be identical with the prerun curve. This is only true up to about 30% conversion with 0.285 mole/l. of monomer.

Viscosity Measurements

The limiting viscosity number for each polymer sample was determined with a Cannon-Fenske viscometer. Polymer solutions in toluene were filtered and run at 25°C. at 1% (w/w), 0.67%, 0.5%, and 0.33% concentration.

Yields

Polymers were dried and weighed to determine the percentage conversion. This was found to be a linear function of the corrected temperature rise accompanying the reaction,

$$\Delta T = 0.026n$$

where ΔT is the temperature rise and n the concentration of monomer converted.

Tacticity Measurements

Since it is not necessary to determine absolute per cent tacticity, a relative method was considered sufficient.

Solutions of polymer (0.5%) in methyl ethyl ketone were allowed to haze over a period of days and then warmed at a rate of 1°C./5 min. The temperature at which the haze disappeared (determined visually) was taken as a relative measure of the fraction of isotactic polymer in the sample. Clear points were reproducible to 2°C. and were independent of the rate of warming.[10] This method was considered an improvement on the precipitation temperature method of Okamura,[7] in which reproducibility depends on a constant and known rate of cooling.

RESULTS

Effect of Solvent Composition

With toluene and n-hexane in varying proportions, the results shown in Table I were obtained.

TABLE I

Polymerization of IBVE (0.285 mole/l.) with $BF_3 \cdot Et_2O$ (3.6×10^{-3} mole/l.) at −76°C. to High Yield

n-Hexane, vol.-%	Toluene, vol.-%	Initial rate × 10^4, mole/l. min.	Viscosity number	Clear point, °C.	Appearance of reaction mixture after reaction
50.0	50.0	78	1.07	37	Clear
41.5	58.5	75	1.21	37	Clear
33.0	67.0	71	0.83	29	Clear
25.0	75.0	64	1.07	—	Partly cloudy
16.5	83.5	66	0.65	29	Partly cloudy
0.0	100.0	38	0.82	—	Cloudy

It is evident that in the toluene-rich solvent the reaction mixture is hazy, tacticity is lower, viscosity is lower, and reaction rate is lower. It is known that the catalyst is not soluble in *n*-hexane, so as a compromise between high tacticity and high catalyst solubility, a solvent composition of 33% *n*-hexane and 67% toluene was chosen for future work.

Effect of Temperature on Reaction Rate

With all other variables fixed, the initial temperature of the polymerization was varied over the range −75°C. to −87°C.

The results are shown in Figure 1.

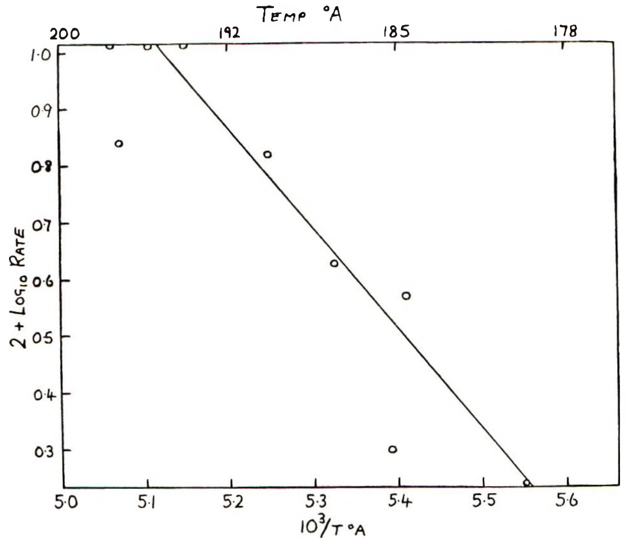

Fig. 1. Dependence of reaction rate on temperature for homogeneous reaction. [M] = 0.285 mole/l.; [C] = 3.6×10^{-3} mole/l.; toluene–*n*-hexane 40:20 (v/v).

The activation energy for the reaction of 7.0 kcal./mole differs insignificantly from that found in earlier work for a slightly different solvent composition.[8]

The Single Reaction Curve

The single reaction curve has a number of features which are exaggerated by the technique used. These are shown in curves *A*–*F* of Figure 2, and are as follows: (*A*) the normal cooling curve for the catalyst solution before the monomer was added; (*B*) the sudden temperature rise due to monomer bulb breakage and heat of solution of monomer; (*C*) homogeneous polymerization in a well-stirred medium; (*D*) as the concentration of polymer becomes high, the reaction mixture gels, and this region represents inefficient stirring of the gel solution mixture; (*E*) stirring is no longer possible, and the complete gellike system continues to polymerize adiabatically with

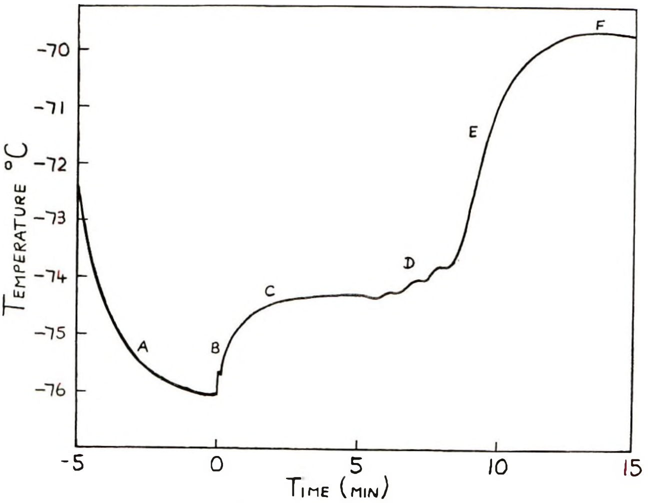

Fig. 2. Typical reaction curve.

accelerating reaction rate; and (*F*) the polymerization is complete, and the polymer gel cools under the influence of the thermostat bath. The cooling in this region is quite different from region *A*.

It is clear then, that the polymerization takes place in two distinct steps. In region *C* the polymerization is homogeneous, and in region *E* it occurs in a viscous gellike phase.

Comparison of the properties of the polymers produced in region *C* and in the whole reaction is shown in Table II.

TABLE II
Polymerization of IBVE (0.285 mole/l.) with $BF_3 \cdot Et_2O$ (3.6×10^{-3} mole/l.) in 20:40 *n*-Hexane–Toluene Solvent Initially at −76°C.

Conversion, %	Viscosity	Clear point, °C.	Final temperature, °C.
34.5	1.47	32	−73.6
34.8	1.08	27	−73.6
36.0	1.23	32	−73.5
89.0	1.32	31	−68.0
93.0	1.43	40	−65.0
98.0	1.13	34	−70.0

The tacticity is significantly higher for the polymerizations which went through the gellike phase, although the figures for the homogeneous polymerizations show that the polymer still contains a fair proportion of isotactic chains.

Homogeneous Reaction

Since the reaction up to 35% conversion proceeded in a fluid, well-stirred phase, stopping the reaction was possible by using a mixture of ethanol,

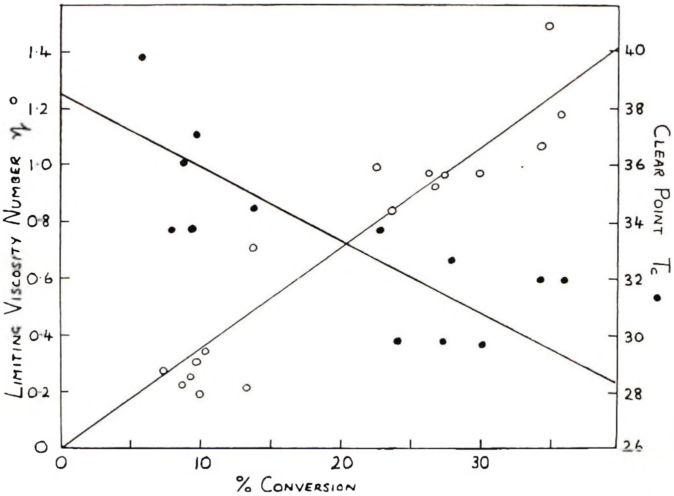

Fig. 3. Variation of molecular weight and tacticity with conversion in the definitely homogeneous region. [M] = 0.285 mole/l.; [C] 3.6 × 10^{-3} mole/l.; toluene–*n*-hexane 40:20 (v/v); $T = -76$°C.

ammonia, and a stabilizer. It was not possible to stop the heterogeneous reaction before complete conversion.

In order to observe the polymer properties at different stages of conversion, the reaction was stopped at different stages up to 35% conversion.

Figure 3 summarizes the progress of viscosity and tacticity.

It is clear that the molecular weight increases with conversion, indicating slow propagation during the homogeneous reaction. This is consistent with the concept of controlled propagation leading to stereoregulation of the incoming monomer unit and with a similar observation by Schildknecht for *n*-butyl vinyl ether polymerization.[9]

The tacticity is seen to fall very slightly as the reaction proceeds.

DISCUSSION

Previous work in this field has been clouded with doubt as to whether the polymerization truly does proceed to isotactic polymer in a homogeneous phase. The original discovery by Schildknecht[1] of this synthesis involved a nominally heterogeneous system where the polymer grew on the surface of catalyst droplets. In this system where no precautions were taken against atmospheric contamination, the boron trifluoride etherate (or hydrate) clearly formed a separate phase from the monomer–diluent mixture. The polymer, on forming, remained as a swollen solid phase, so in this system the polymerization was either truly heterogeneous with respect to the catalyst or else homogeneous within the swollen gel phase. The latter possibility was suggested at the time.

Okamura et al.,[2] by the use of mixed diluents, were able to modify the system so that both catalyst and polymer were soluble. From the conditions it was assumed that the polymerization had occurred in a homogeneous phase.

The present work shows that under high vacuum conditions where absence of moisture precludes any insoluble boron fluoride hydrates, the polymerization proceeds to completion with total optical clarity and that the initial reaction is indeed fluid and homogeneous. The latter part of the reaction may also be homogeneous, but it occurs in a gellike phase. It is the initial reaction in which we are interested because here we are sure of optical clarity, fluidity, and homogeneity.

The results show that in the homogeneous region the polymer produced is substantially isotactic, although not quite as much as in the later gel phase. The growth of chain length during the initial reaction indicates that the slow propagation is a kinetic effect and not due to diffusion through the gel phase. Indeed diffusion control probably is an important factor in enhancing slow isotactic growth; evidence for this comes from the higher tacticities of the samples produced by both steps, even though the gel-phase step occurred at approximately 5°C. higher than the homogeneous step. However, it is clear that diffusion control is not a prerequisite for isotactic growth.

It is not easy to understand why the highest isotacticity in the homogeneous step occurred at the beginning. In this region the polymerization rate is at a maximum with a high concentration of monomer and catalyst, conditions known to reduce isotacticity. However, tacticity is temperature-dependent, and a lower temperature is known to be a favorable condition for isotactic polymerization[8] as in the initial stages. Furthermore, the observation that isotacticity decreases as the gel phase is approached is complementary with Okamura's proof of lower tacticity in a heterogeneous system.

We believe that the evidence presented herein is sufficient proof of true homogeneous isotactic propagation and supports the work of Schildknecht[1] and Okamura[2] but contradicts Ketley.[11]

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Résumé

L'éther vinylisobutylique a été polymérisé dans des conditions bien déterminées de façon à former un polymere isotactique au moyen de l'éthérate de fluorure de bore à $-78°C$, dans un diluant hydrocarboné non polaire. Un rapport particulier de solvant mixte et une dissolution préalable du catalyseur permet d'obtenir une polymérisation homogène au début de la réaction. En suivant l'augmentation de température dans un système initialement thermotatisé on a montré que le progrès de la réaction s'accompagne du passage d'ue phase homogène à une phase gelifiée. Le polymère isotactique est produit en deux étapes par un mécanisme du propagation de chaîne lente.

Zusammenfassung

Iso-Butylvinyläther wurde unter Bedingungen, welche bekanntermassen isotaktisches Polymeres liefern, nämlich mit Borfluorid bei $-78°C$ in einem nicht polaren Kohlenwasserstoff-Verdünnungsmittel polymerisiert. Ein besonderes Mischungsverhältnis des Lösungsmittels sowie die vorhergehende Auflösung des Ktalysators ermöglichte einen homogenen Anfangsverlauf der Polymerisation. Durch Verfolgung des Temperaturanstiegs in einem anfänglich thermostatisierten System wurde gezeigt, dass die Reaktion tatsächlich über eine homogene Phase zu einer Gelphase verläuft. Es wird gezeigt, dass in den beiden Phasen isotaktisches Polymers durch einen Mechanismus mit langsamen Kettenwachstum erzeugt wird.

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Bulk Polymerization of α-Chloroacrylonitrile

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Synopsis

Poly-α-chloroacrylonitrile, which may be regarded as a hybrid of poly(vinyl chloride) and polyacrylonitrile, is, like these polymers, insoluble in its own monomer. Its bulk polymerization is thus heterogeneous, showing abnormal kinetic features by comparison with homogeneous polymerizations. The polymerization exhibits autocatalytic properties. The initiator exponents at 0 and 5% polymerization are 0.45 and 0.44, respectively, and the overall energy of activation is 23.0 ± 2 Kcal./mole. There is no significant change in molecular weight with catalyst concentration in the range 0.057–0.90% nor with conversion up to 12%, but the reaction is accelerated by addition of polymer. Bulk polymerization results in colored products, the color deepening with conversion. These results have been compared with those of Bamford and Jenkins for acrylonitrile and Bengough and Norrish for vinyl chloride and are found to be in closer accord with the latter. They can be accounted for satisfactorily by Bengough and Norrish's suggestion that transfer occurs between growing polymer radicals and dead polymer molecules, the radicals thus formed on the surface of the polymer being removed by transfer to monomer.

During the preparation of poly-α-chloroacrylonitrile for degradation studies[1] it became clear that certain features of the polymerization were of considerable interest, especially since the monomer may be regarded as a hybrid of acrylonitrile and vinyl chloride both of whose bulk polymerizations are rendered abnormal by the fact that they are heterogeneous, the polymer being precipitated as it is formed. The explanations which have been given of these abnormal behaviors are different for the two materials[2–4] and the aim of the present work was to establish how the polymerization of α-chloroacrylonitrile fits into the general picture.

EXPERIMENTAL

Preparation and Purification of Monomer

α-Chloroacrylonitrile was prepared by the method of Ivanov and Koton,[5] chlorine being absorbed in acrylonitrile to form the dichloro compound which was dehydrochlorinated by sodium acetate. After washing with water the monomer was distilled twice under atmospheric pressure (86°C.). It was stored at 0°C. without stabilizer. α-Chloroacrylonitrile is a colorless liquid with strong lachrimatory and vesicant properties.

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Initiator

The initiator was 2,2′-azoisobutyronitrile (Eastman Kodak Ltd.) purified by recrystallization from methanol.

Polymerization

Polymerizations were followed dilatometrically under vacuum, dilatometers being filled by the usual vacuum techniques, the monomer being degassed and twice distilled under vacuum. The volume contraction–conversion relationship for the polymerization of α-chloroacrylonitrile was determined from polymer recovery and volume contraction data. At 55°C. the contraction was found to be 34% for 100% polymerization.

Measurement of Intrinsic Viscosity

Intrinsic viscosities were measured in acetone solution at 25°C. in a suspended-level viscometer (P.C.L.).

RESULTS

When heterogeneous conditions arise due to precipitation of polymer, as in the bulk polymerization of acrylonitrile or vinyl chloride, the simple homogeneous reaction kinetics no longer apply. The fact that normal kinetic relationships are re-established when the reaction is carried out in a solvent for the polymer is sufficient proof that the abnormalities are a function of the heterogeneity of the system rather than of the properties of the monomer.[2–4]

α-Chloroacrylonitrile behaves similarly to vinyl chloride and acrylonitrile in that polymer is precipitated during bulk polymerization and that the reaction exhibits similar autocatalytic properties, as in Figure 1, which disappear when it is carried out in a solvent for the polymer such as methyl

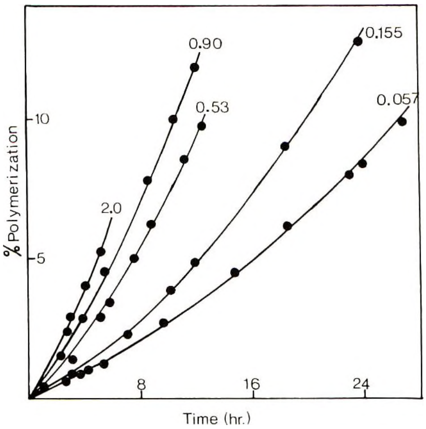


Fig. 1. Bulk polymerization of α-chloroacrylonitrile at 55°C. (Figures denote percentage azoisobutyronitrile initiator.)

ethyl ketone. It is thus of interest to study the principal kinetic features of the polymerization of α-chloroacrylonitrile in order to discover how far they can be accounted for in terms of the theories which have been evoked to explain the behaviors of the other two systems.

Influence of Initiator Concentration on Rate of Polymerization

The influence of initiator concentration on the polymerization of α-chloroacrylonitrile at 55°C. is illustrated in Figure 1. Since the rates accelerate continuously it is of interest to discover whether the catalyst exponent at various stages in the reaction reflects any change in mechanism as polymer accumulates in the system. The slopes of the curves in Figure 1 at 0 and 5% polymerization have been estimated and are represented in Figure 2. The slopes of the resulting linear plots are 0.45 and 0.44, respectively, indicating that within experimental error the rate of polymerization at least up to 5% conversion bears a constant relationship to the initiator concentration, and this is sufficiently close to 0.5 to assume an approximate square-root dependence.

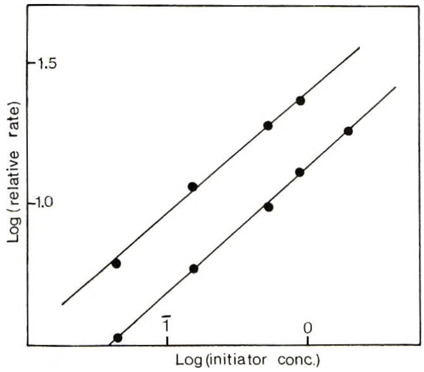


Fig. 2. Effect of initiator concentration on rate of polymerization of α-chloroacrylonitrile.

Influence of Temperature on Rate of Polymerization

The influence of temperature on the polymerization of α-chloroacrylonitrile is illustrated in Figure 3. By plotting the slopes of these curves against the reciprocal of the absolute temperature the overall energy of activation was found to be 23.0 ± 2 kcal./mole and to be independent of conversion at least up to 5%.

Influence of Initiator Concentration and Conversion on Molecular Weight

The intrinsic viscosities of polymers prepared at 55°C. are shown in Table I from which it is clear that within experimental error the molecular weight of the polymer formed is independent of both initiator concentration and conversion.

TABLE I

Initiator Concn., %	Conversion, %	$[\eta]$
0.90	5.48	1.085
0.90	11.82	1.055
0.155	12.68	1.10
0.10	8.30	1.01
0.057	4.57	0.962

Similar results obtained by Bengough and Norrish[3] for poly(vinyl chloride) illustrate that transfer to monomer is important.

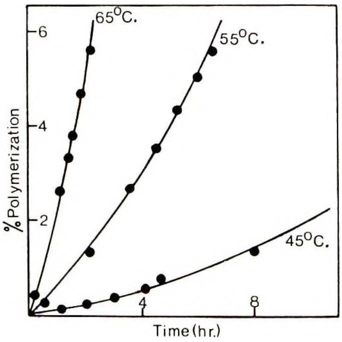


Fig. 3. Effect of temperature on polymerization of α-chloroacrylonitrile.

Effect of Addition of Polymer on Rate of Polymerization

That the acceleration in rate is associated directly with the accumulation of polymer in the system is illustrated by Figure 4 in which a typical polymerization curve for pure monomer is compared with a curve obtained under similar conditions but with the addition of approximately 2% of previously prepared polymer.

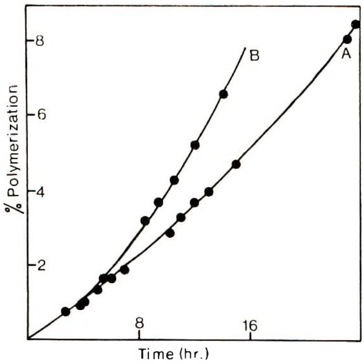


Fig. 4. Influence of polymer on the polymerization of α-chloroacrylonitrile: (*A*) pure monomer; (*B*) monomer + 2% added polymer.

Coloration

Polymers prepared by bulk polymerization of α-chloroacrylonitrile are always slightly colored, the color intensifying and moving progressively through the spectrum with increasing conversion and at a greater rate the higher the concentration of initiator. This coloration is presumably due to the development of conjugation in the polymer although the mechanism is obscure. It was possible to show, however, that polymer in solution in absence of monomer did not color at polymerization temperatures even in presence of initiator. This suggests that coloration is intimately linked with polymerization and like polymerization is probably a radical process.

DISCUSSION

In recent years the heterogeneous polymerizations of a number of monomers including vinyl chloride,[3] acrylonitrile,[2,6,7] vinylidene chloride,[8] and trifluorochloroethylene[9] have been studied. These systems have many features in common. Disagreement has arisen, however over the mechanism of the accelerative effects. Bamford and Jenkins[2,6,7] reported an initiator exponent of 0.9 and an overall energy of activation of 35.0 kcal./mole for the bulk polymerization of acrylonitrile. They proposed that active polymer radicals are trapped in the precipitated polymer. These occluded radicals can still participate in propagation and transfer reactions, although bimolecular termination reactions between polymer radicals are restricted. This reduction in the rate of termination would lead to the observed overall increase in the rate of polymerization.

Bengough and Norrish[3] found the initiator exponent to be 0.5 and the overall activation energy to be 22.0 kcal./mole in the bulk polymerization of vinyl chloride and they proposed an alternative explanation for the autocatalytic characteristics of the reaction. They suggested that transfer occurs between growing polymer radicals and dead polymer molecules resulting in immobile free radicals being formed on the surface of the polymer particles. These radicals can be removed by transfer to monomer. According to this theory the rate acceleration is proportional to the particle surface area.

Bamford and his colleagues have suggested that while the occlusion theory could apply to vinyl chloride, the surface transfer mechanism cannot describe the situation in polyacrylonitrile which does not readily undergo transfer reactions. More recently Mickley, Michaels, and Moore[10] have confirmed Bengough and Norrish's experimental results and have proposed a simplified moving boundary treatment of diffusion of radical activity in the polymer to explain the observed rate dependence on the polymer concentration.

It seems that transfer reactions involving poly-α-chloroacrylonitrile will occur even more readily than with poly(vinyl chloride) since the chlorine atom which must be involved will be rendered more reactive in the former case by the neighboring unsaturated nitrile group. Table I illustrates that this is certainly so as far as transfer to monomer is concerned, since the molecular weight proves to be independent of initiator concentration, which means that molecular chains are predominantly terminated by transfer. Similar initiator exponents and energies of activation further suggest that these two polymerizations proceed by the same mechanism.

As evidence for the occlusion theory, Bamford and Jenkins[2] subjected a mixture of acrylonitrile and initiator to irradiation at 25°C., at which temperature thermal polymerization is low. On subsequent heating to 60°C. an extremely rapid reaction occurs, "which may consume a further 10% of the monomer within two minutes." Thereafter the rate decreases to its normal value and proceeds in its normal accelerating fashion. Repeating these experiments with α-chloroacrylonitrile in the present work it was not found possible to reproduce a corresponding "fast" reaction.

On the other hand, according to the Bengough and Norrish theory which accounts for the bulk polymerization behavior of vinyl chloride, the rate of polymerization R_p is given by

$$R_p = -d[\mathrm{M}]/dt = K([\mathrm{M}] + K'[\mathrm{P}]^{2/3})([\mathrm{B}]/[\mathrm{M}])^{1/2} \tag{1}$$

in which [M] and [B] are the concentrations of monomer and initiator respectively, [P] is the amount of polymer in the system, and K and K' are constants. This would account for the square-root catalyst relationship found experimentally for the α-chloroacrylonitrile. In addition, for a given experiment in which [B] and [M] are constant, eq. (1) may be rewritten

$$R_p = K''[\mathrm{M}] + K'''\,[\mathrm{P}]^{2/3} \tag{2}$$

in which $K'' = K[\mathrm{B}]^{1/2}/[\mathrm{M}]^{1/2}$ and $K''' = KK'[\mathrm{B}]^{1/2}/[\mathrm{M}]^{1/2}$. Since $K''[\mathrm{M}]$ represents the rate of polymerization in absence of polymer, that is the initial rate, eq. (2) can be rewritten

$$\Delta R_p = K'''[\mathrm{P}]^{2/3} \tag{3}$$

Data obtained for a polymerization initiated by 0.9% initiator at 55°C. are recorded in Table II and illustrated in Figure 5.

TABLE II

R_p, % polym./hr.	ΔR_p	log ΔR_p	[P], g./l.	log [P]
0.595	0	—	0	—
0.743	0.148	−0.8297	10	1.0000
0.830	0.238	−0.6234	20	1.3010
0.910	0.325	−0.4881	30	1.4771
0.984	0.400	−0.3979	40	1.6021
1.025	0.445	−0.3516	50	1.6990
1.085	0.506	−0.2958	60	1.7782
1.121	0.546	−0.2628	70	1.8451
1.224	0.589	−0.2299	80	1.9031

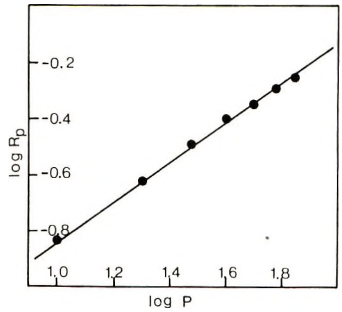
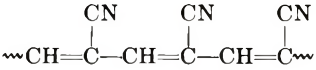


Fig. 5. Influence of polymer on rate of polymerization. [Table II and eq. (3).]

The gradient of the straight line is 0.70 which is in good agreement with the theoretically predicted value of 0.67.

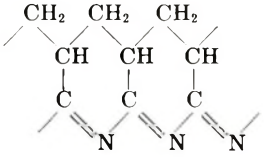
Thus the polymerization behavior of α-chloroacrylonitrile is closely similar to that of vinyl chloride rather than acrylonitrile. A subsequent paper will show that the same applies to the degradation behaviors of the corresponding polymers.

The colored structures which are formed during the polymerization of α-chloroacrylonitrile could be carbon–carbon conjugated sequences by analogy with the colored degradation product of poly(vinyl chloride):[11]



$$\sim CH{=}\overset{\overset{CN}{|}}{C}{-}CH{=}\overset{\overset{CN}{|}}{C}{-}CH{=}\overset{\overset{CN}{|}}{C}\sim$$

or carbon–nitrogen conjugated sequences by analogy with the colored degradation product of polyacrylonitrile:[12]



Both of these absorb characteristically in the 1650–1500 cm.$^{-1}$ region of the infrared spectrum and are thus rather difficult to distinguish. Even at advanced degrees of polymerization, however, the absolute concentration of colored structures in poly-α-chloroacrylonitrile is small and absorption in this region is not well enough defined to make the distinction. Since they are formed in a radical process, however, it may seem more likely that they will be of the poly(vinyl chloride) type which are probably formed during degradation in a radical process rather than of the acrylonitrile type which are formed in an ionic type mechanism. This would also be in line with the polymerization of α-chloroacrylonitrile and, as a subsequent paper will show, the degradation of its polymer, both of which properties prove it to be closely akin to vinyl chloride in its general behavior and quite unlike acrylonitrile.

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Résumé

Le poly-α-chloroacrylonitrile, qui peut être considéré comme un hybride du chlorure de polyvinyle et du polyacrylonitrile, est, de même que ces polymères, insoluble dans son monomère. Sa polymérisation en bloc, est par conséquent hétérogène manifestant des phénomènes cinétiques anormaux par comparaison avec des polymérisation homogènes. La polymérisation manifeste des propriétés autocatalytiques. L'exposant à l'initiateur à 0 et 5% de polymérisation est 0.45 et 0.44 respectivement et l'énergie globale d'activation est 23.0 ± 2 Kcal/mole. Il n'y a pas de modification significative de poids moléculaire avec la concentration en catalyseur dans le domaine 0.057–0.90% ni avec la conversion jusqu'à 12% mais la réaction est accélérée par addition de polymères. La polymérisation en bloc fournit des produits colorés, la couleur dépendant du degré de conversion. Ces résultats ont été comparés avec ceux de Bamford et Jenkins pour l'acrylonitrile en de Bengough et Norrish pour le chlorure de vinyle et sont trouvés en accord étroit avec les données de ces derniers. Ils peuvent être de façon satisfaissante expliqués par la suggestion de Bengough et Norrish suivant lesquels le transfert se passe entre les radicaux d'une chaîne en crossance et les molécules de polymères inactifs, les radicaux ainsi formés à la surface des polymères étant éliminées par transfert avec le monomère.

Zusammenfassung

Poly(α-chloracrylonitril), welches als ein Hybrid von Poly(vinylchlorid) und Polyacrylonitrile betrachtet werden kann, ist, wie diese Polymeren, in seinem eigenen Monomeren unlöslich. Seine Polymerisation in Substanz verläuft daher heterogen und zeigt in Vergleich zu homogenen Polymerisationen eine abnormale Kinetik. Die Polymerisation verläuft autokatalytisch. Der Starterexponent bei 0 und 5%. Polymerisation beträgt 0,45 bzw. 0,44 und die Bruttoaktivierungsenergie 23,0 ± 2 kcal/Mol. Es besteht keine merkliche Abhängigkeit des Molekulargewichts von der Katalysatorkonzentration im Bereich von 0,057–0,90% und auch nicht vom Umsatz bis zu 12%; die Reaktion wird durch Zusatz von Polymerem beschleunigt. Die Polymerisation in Substanz führt zu gefärbten Produkten, wobei sich die Farbe mit steigendem Umsatz vertieft. Die Ergebnisse wurden mit denjenigen von Bamford und Jenkins für Acrylonitril und *W*on Bengough und Norrish für Vinylchlorid verglichenu nd stehen in enerer Beziehung zu letzteren. Sie können befriedigend durch die Annahme von Bengough und Norrish erklärt werden, dass eine Übertragung zwischen wachsenden Polymerradikalen und toten Polymermolekülen auftritt und die so in der Oberfläche des Polymeren gebildeten Radikale durch Übertragung zum Monomeren abreagieren.

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Macromolecular Models for Branched PVC. I. Copolymer of Vinyl Chloride with Isopropenyl Chloride

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Synopsis

A new type of model for study of polymer anomalies by copolymerization is proposed. For branched PVC, the vinyl chloride–isopropenyl chloride copolymer was used as the macromolecular model. A regulatory and inhibitory action of isopropenyl chloride during the polymerization was demonstrated. To determine the composition of the copolymer, methods based on elemental analysis and NMR and infrared spectra were utilized. It was found that the copolymer composition is very close to that of the polymerization mixture. The structure of the copolymer was studied from infrared spectra. It was found that both forms T_{CHH} and T_{HHH} are present, the former being present in a larger quantity. The possibility of the utilization of spectral methods on macromolecular systems to determine the structure and content of a chlorine atom bound to a tertiary carbon atom (Cl_T) in the presence of an excess of chlorine bound to a secondary carbon was verified.

The possibility of accurate determination both by infrared spectra and chemical methods of content of chlorine bound to the tertiary carbon atom (Cl_T), on the low molecular weight model compounds was previously shown.[1,2] However, the results cannot be applied directly to the determination of Cl_T in PVC because the influence of the chlorine atoms on the spectral and chemical properties is not known. Moreover, little is known about the macromolecular structure which is responsible for the disappearance of free rotation around the C—C bond and the creation of steric hindrance.

To obtain an appropriate macromolecular model, a copolymerization method was used. Suitable vinyl groups are introduced during the polymerization of the basic monomer (vinyl chloride), so that the desired tertiary systems appear in the macromolecular chain. By choosing a suitable monomer ratio one can obtain the structural unit in the macromolecular chain in the required concentration.

In this connection, we first studied the copolymerization of vinyl chloride with isopropenyl chloride. Thus the simplest macromolecular model for the branched PVC with tertiary chlorine is obtained (see following page):

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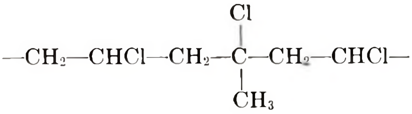


$$\text{—CH}_2\text{—CHCl—CH}_2\text{—}\overset{\text{Cl}}{\underset{\text{CH}_3}{\text{C}}}\text{—CH}_2\text{—CHCl—}$$

The present paper deals with: (*1*) synthesis and composition determination of the copolymer and (*2*) infrared spectra of the copolymer in the region of the C—Cl stretching vibration.

SYNTHESIS OF THE COPOLYMER AND COMPOSITION DETERMINATION

Data for the vinyl chloride–isopropenyl chloride copolymer are to be found only in a patent[3] which mentions the block emulsion and suspension polymerization at 35–100°C. with a variety of initiators. The content of isopropenyl chloride in the monomer mixture was 2–5 wt.-%. However, only emulsion polymerization at 50°C. initiated by lauryl peroxide was used in all the six experiments described.

We were unable to make use of this method on account of the possibility of undesired branching which might lead to errors in calculation of the branched chains. Also, it is impossible to work in polar media because of the possibility of $Cl_{T'}$ reactions (e.g., hydrolysis).

TABLE I

Results of Copolymerization of Vinyl Chloride with Isopropenyl Chloride

Sample	Isopropenyl chloride in the polymerization mixture, mole-%	Total weight of polymerization mixture, g.	Weight of obtained polymer, g.	Total yield, %	Molecular weight (osmometry)[a]
1	0	53.2	29.66	55.7	225,000
2	5	52.7	4.23	8.0	120,000
3	10	52.8	1.76	3.3	53,000
4	25	52.6	0.56	1.1	24,500
5	50	51.4	0	—	—
6	100	51.5	0	—	—

[a] The average molecular weight was calculated by a static method from osmometry measurements. The instrument used was a Hellfritz osmometer, the solvent being THF except for sample 1, for which the solvent was cyclohexanone.

To avoid the branching of PVC block polymerization at −40°C. with triisobutylboron initiator was used.

Materials. Commercial, fractionated vinyl chloride was redistilled before polymerization directly into the reaction vessel. Isopropenyl chloride was prepared from acetone and PCl_5 and purified by fractional distillation through a column with the head cooled at −35°C. The reflux ratio was 20:1. The fraction boiling at 21.7°C. was used for the polymerization. Its purity was confirmed by gas chromatography.

Triisobutylboron was prepared from isobutyl bromide and BF_3 by a Grignard synthesis and redistilled before use.

Polymerization. Glass ampules were cooled at Dry Ice–acetone temperature and swept with argon. A calculated quantity of freshly distilled isopropenyl chloride was added with a pipet with the temperature controlled at 0°C.; then vinyl chloride was distilled in, and finally the initiator (1.5 g./100 g. monomer mixtures in all cases) was charged into the reaction flasks. To accelerate the reaction, small quantities of air (the same for all the experiments) were introduced in the ampules, polymerization rates being too low under pure argon. The ampules were sealed and allowed to stand at −40°C. for 10 days. Then the ampules were cooled to −79°C. and opened. The copolymer was separated from the reaction mixture by filtering at −60 to −80°C. To remove the traces of the initiator the samples were washed several times with cooled petroleum ether. The results are summarized in Table I.

Samples 5 and 6 did not polymerize, not even after several months at room temperature. Moreover, sample 6 was heated at 105°C. for 7 days with twice the quantity of catalyst without polymerizing. There is only a browning of the product owing to a certain degree of decomposition (when opened HCl gas was identified).

Purification of the Copolymer. Solutions of copolymer in as little as possible polar solvents were prepared under continuous stirring and at as low as possible a temperature. Conditions for the solutions of the copolymers are given in Table II.

The working temperatures were low enough except for sample 1 which is a crystalline low-temperature PVC. The polymer was then precipitated by dropping in a tenfold quantity of petroleum ether and dried for 2 weeks in vacuum at normal temperature.

In the infrared spectra of samples 1, 2, and 3, traces of cyclohexanone were noted. This was removed by swelling the polymer in dichloroethane, reprecipitation with petroleum ether, and drying in vacuum.

NMR Spectra. Recording of NMR spectra was very difficult on account of poor solubility of the copolymers. It is well known that NMR measure-

TABLE II
Solution Conditions for the Copolymer

Sample	Solvent	Temperature, °C.	Concentration, %	Solution time, hr.
1	Cyclohexanone	130	1	3
2	Cyclohexanone	45	1.4	2
3	Cyclohexanone	20	2	1
4	Dichloroethane	20	2.8	Several minutes

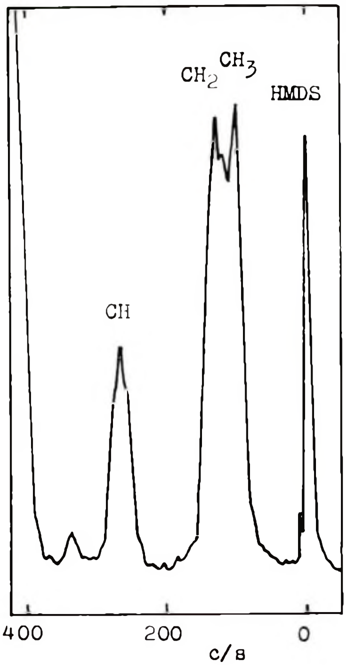


Fig. 1. NMR spectra of copolymer 4.

ments require high concentrations of polymers (about 25%). At such a concentration the samples 1, 2, and 3 are gelled. For this reason it was possible to measure only the spectrum of sample 4 dissolved in chlorobenzene ($c = 25\%$) at 65°C. on a JNM-3-60 spectrometer. NMR spectra are given in Figure 1.

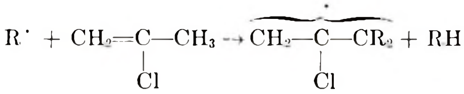
Analyses. Results of elemental analysis in duplicate of these copolymers are given in Table III.

TABLE III
Elemental Analysis of the Copolymers

Sample	C, %	H, %	Cl, %
1	38.84, 39.11	5.00, 5.11	55.09, 55.33
2	39.08, 39.17	5.19, 5.04	54.95, 54.96
3	40.12, 39.92	5.37, 5.25	53.66, 53.41
4	42.43, 42.14	5.68, 5.64	52.38, 52.41

Results and Discussion

Inspection of Table I shows that increasing the concentration of isopropenyl chloride brings rapid decreases in the yield of the copolymer and decreased molecular weight of the resulting product. Therefore isopropenyl chloride acts as an inhibitor and as a growth regulator. Aelterman and Smets[8] reported on the polymerization of isopropenyl chloride. They supposed the occurrence of a radical transfer during the process by abstraction of a hydrogen atom from the CH_3 group. Thus a more stable allyl radical appears, as:



$$R^{\cdot} + CH_2{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH_3 \rightarrow \overset{\cdot}{\overbrace{CH_2{-}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CR_2}} + RH$$

This transfer may account for this inhibitory and regulatory action of the isopropenyl chloride during the copolymerization. Allyl radical has too small an energy to initiate the polymerization reaction but it can either combine with itself or with a macromolecular radical, thus governing growth of the copolymer.

Similarly, the radical can also react with the initiator acting as an inhibitor.

As the experimental part describes, there was no copolymerization in case of samples 5 and 6 (pure isopropenyl chloride) when triisobutylboron was used. The radical transfer reaction may account for this behavior. In this connection it would be interesting to determine whether the product obtained by Aelterman and Smets[8] and described as poly(isopropenyl chloride) actually has this structure.

Structure of the Copolymer. Several methods were used to determine the structure of the copolymer. The difference between the elemental composition of the monomers and the elemental analyses of the resulting polymer was the basis of the first method.

The molar percentage of isopropenyl chloride in the copolymer (N_1) was calculated from eq. (1)

$$N_1 = 100/\{1.225[(E_1 - E_2)/(E - E_2)] - 0.225\} \tag{1}$$

Here E_1 and E_2 are gravimetric percentages of one of the elements of the monomers 1 and 2, respectively, and E is the gravimetric percentage of the same element in the resulting copolymer. This calculation fits for any element (C, H, or Cl) in both monomers. The values E_1 and E_2 for vinyl chloride and isopropenyl chloride are given in Table IV.

The difference between C, H, and Cl contents of both monomers is quite small, the highest are for Cl and C. On the other hand, the results are much influenced by the experimental errors in the determination of elemental analysis. These errors are particularly marked in the case of the copolymer with a low isopropenyl chloride content, where the difference from vinyl chloride is about the same as the experimental error.

Even when one component is polymerized (vinyl chloride) there are always differences between the calculated values and those found from elemental analysis. One may always observe a small decrease of chlorine content when the carbon content increases slightly.[9,10] To reduce this

TABLE IV
Theoretical Elemental Composition of the Monomers

	E_1 (isopropenyl chloride)	E_2 (vinyl chloride)
C, %	47.1	38.4
H, %	6.54	4.8
Cl, %	46.4	56.8

systematic source of errors, we utilized the experimental values found for PVC (Table III, sample 1) instead of theoretical values from eq. (1). This correction is justifiable only on supposing that the causes for the deviations from theoretical values are the same for the copolymers and PVC. E_1 values were not corrected since it was not possible to obtain poly(isopropenyl chloride) as reference substance. Equation (1) then becomes:

$$N_1 = 100/\{1.225[(E_1 - E_2')/(E - E_2')] - 0.225\} \qquad (2)$$

where E_2' is the analytical content of the element as found for sample 1.

The composition of the copolymers 3 and 4 calculated from elemental analysis is given in Table V.

TABLE V
Composition of Copolymers 3 and 4

	Isopropenyl chloride in copolymer (N_1), mole-%	
Sample	Calculated from % Cl	Calculated from % C
3	14.3	11
4	27.8	33.4

This method could not be used for sample 2 because its precision is lower for small values of N_1.

Data of NMR spectra provided the second method for the determination of copolymer composition. As the experimental part describes, the NMR spectra could be obtained only for copolymer 4. NMR spectra of the copolymer are reproduced in Figure 1. Maxima corresponding to CH_2 and CH_3 protons are partially overlapping. However, as the peak of CH group is isolated in spectrum, one may find precisely enough the CH and $CH_2 + CH_3$ intensities ratio, as:

$$R = I_{CH}/I_{CH_2} + I_{CH_3} \qquad (3)$$

The signal intensity given by a group is proportional to proton concentration, and therefore I_{CH} is proportional to the molar fraction of vinyl chloride (N_2), I_{CH_3} is proportional to the threefold molar concentration of isopropenyl chloride ($3N_1$); the molar concentration of the CH_2 group is always equal to 100, and I_{CH_2} is proportional to 2 × 100. From eq. (3) is obtained

$$R = N_2/200 + 3N_1 \tag{4}$$

Since $N_2 = 100 - N_1$, the resulting equation is:

$$N_1 = (1 - 2R/1 + 3R)100 \tag{5}$$

To calculate the composition of the copolymer the R value is needed. This value was calculated from the integral intensities of the CH and CH_2 + CH_3 NMR lines. The molar content of isopropenyl chloride bound in copolymer 4 accordingly calculated was 28%. This value agrees quite well with that calculated on the basis of elemental analysis (Table V). We consider this method of determination of the composition to be more exact because the results are less dispersed than in the case of elemental analysis.

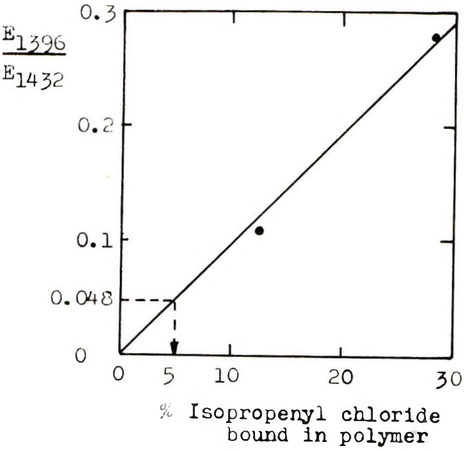


Fig. 2. Graphic determination of the composition of copolymer 2 from infrared spectra.

It was possible to use these methods only for samples 3 and 4. For sample 2, with a very low content of isopropenyl chloride, data from infrared analysis were used to determine the composition. We used the 1390 cm.$^{-1}$ (sym. CH_3 deformation) and 1432 cm.$^{-1}$ (CH_2 scissor) peaks. From the intensity ratio for samples 3 and 4 (with a known composition) sample 2 it was possible to find by interpolation the molar content of isopropenyl chloride in sample 2 to be about 5% (Fig. 2).

The content of isopropenyl chloride in all the above copolymers are as follows: 5% in copolymer 2, 12% in copolymer 3, and 28% in copolymer 4.

The molar content of isopropenyl chloride in the copolymer (N_1) is numerically equal to the percentage of Cl_T related to the total chlorine content in the copolymer molecule.

INFRARED SPECTRA OF THE COPOLYMER IN THE C—Cl STRETCHING VIBRATION REGION

Previously,[1,2] infrared absorption bands for the C—Cl stretching vibrations have been assigned for all rotation isomers of the secondary and tertiary chlorides. The values found are given in Table VI.

TABLE VI
Frequencies of C–Cl Stretching Vibrations of Secondary and Tertiary Chlorides

Secondary chloride		Tertiary chloride	
Rotational isomer	Frequency, cm.$^{-1}$	Rotational isomer	Frequency, cm.$^{-1}$
S_{HH}	608	T_{CHH} (T'_{CHH})	595–632
S'_{HH}	628	T_{HHH}	560–581
S_{CH}	657	T'_{HHH}	538–544
S'_{CH}	668		

An increase in the isopropenyl chloride content causes the appearance of a large band at 500–600 cm.$^{-1}$. Its intensity visibly changes with the content of Cl_T (Fig. 3).

For the isopropenyl chloride–vinyl chloride copolymer T_{CHH} and T_{HHH} conformations have been found. However they are not separated and appear as a large band at 500–600 cm.$^{-1}$ with a maximum at 580 cm.$^{-1}$.

As for 3-chloro-3-ethylpentane, one may conclude from the aspect of this band that T_{CHH} is prevailing.

Inspection of the infrared spectra shows that the C—Cl stretching vibrations for the tertiary chlorides are about the same for the polymers as for

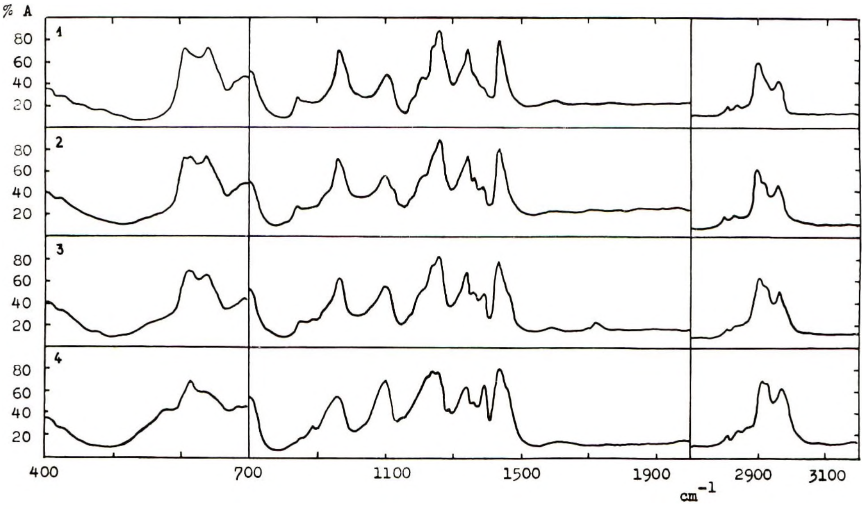


Fig. 3. Infrared spectra of the copolymers: (*1*) sample 1; (*2*) sample 2; (*3*) sample 3; (*4*) sample 4.

the model compounds, as in the case of secondary chlorides.[11] Therefore, the presence and conformation of Cl_T in the polymers may be conveniently determined by infrared analysis.

To determine quantitatively the content of Cl_T, a comparison between the molecular extinction coefficients of both secondary and tertiary chlorides was required. The integral molecular extinction coefficient was measured for 3-chloro-3-ethylpentane at 520–660 cm.$^{-1}$ and for 3-chloropentane at 560–700 cm.$^{-1}$. The obtained values were very close. Consequently Cl_T may be quantitatively determined in the presence of secondary chloride by comparing the infrared intensities of C—Cl stretching vibrations.

The integral intensity of absorption band at 580 cm.$^{-1}$ has been compared with the integral intensity of all C—Cl stretching vibrations in the range 500–740 cm.$^{-1}$. The content of Cl_T related to the entire quantity of chlorine (which is the same as the molecular content of isopropenyl chloride in copolymer) was about 20% for copolymer 4. This value agrees sufficiently with that found previously.

One may conclude from our results that the infrared analysis method can be applied to macromolecular systems too, and may be used to determine the presence and content of Cl_T in PVC.

The author wishes to express his gratitude to the leadership of UMCH Prague, where this work was carried out and particularly to thank the analytical laboratory for chemical analyses, Mr. Solc for determining the molecular weights, Mr. M. Bednarek who prepared the triisobutylboron, Mr. Sykora for the NMR spectra, and Mr. Schneider for many inspiring discussions concerning this work.

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Résumé

On propose un nouveau type de modèles pour étudier les anomalies de structure des polymères au moyen de la copolymérisation. On a obtenu le modèle macromoléculaire à base de chlorure de vinyle–chlorure d'isopropényle en vue d'étudier le chlorure de polyvinyle ramifié. Durant la polymérisation on a constaté l'action régulatrice et inhibitrice du chlorure d'isopropényle. Pour établir la composition du copolymère on a utilisé des méthodes basées sur l'analyse élémentaire, les spectres RMN et les spectres IR. On a constaté que la composition du copolymère est très proche de celle du mélange soumis à la polymérisation. On a étudié la structure du copolymère à l'aide des spectres infrarouges et on a pu constater que dans le copolymère les deux formes T_{CHH} et T_{HHH} sont présentes, la première s'y trouvant en plus grande quantité. On a vérifié la possibilité d'utiliser les méthodes spectrales dans le cas d'un système macromoléculaire afin de déterminer sa structure de même que le contenu du Cl_T en présence d'un excès de chlore lié à un atome de carbone secondaire.

Zusammenfassung

Ein neuer Typ von Modellen zur Untersuchung der Polymeranomalien durch den Kopolymerisationsprozess wird vorgeschlagen. Als makromolekulare Modelle für verzweigtes PVC werden Kopolymere aus Vinylchlorid und Isopropenylchlorid dargestellt. Bei der Polymerisatinsreaktion kann ein regulierender und inhibierender Einfluss des Isopropenylchlorids festgestellt werden. Die Zusammensetzung des Kopolymeren wird mittels Elementaranalyse sowie IR- und NMR-Spektroskopie bestimmt. Die Zusammensetzung der Kopolymeren kommt derjenigen des Polymerisationsansatzes sehr nahe. Die Struktur der Kopolymeren wird infrarotspektroskopisch untersucht. Es wurde festgestellt, dass in den Kopolymeren beide Formen, T_{CHH} und T_{HHH}, vorhanden sind, und zwar die erstere in grösserer Menge. Die Möglichkeit, die spektroskopischen Methoden zur Erforschung der Struktur und zur Bestimmung von Cl_T in Gegenwart eines Überschusses von an sekundären Kohlenstoff gebundenem Chlor heranzuziehen, wird überprüft.

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Macromolecular Models for Branched PVC. II. Reactivity of Chlorine Bound to a Tertiary Carbon Atom in the Copolymer Vinyl Chloride–Isopropenyl Chloride

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Synopsis

The selectivity of the phenolysis reaction of a chlorine atom bound to a tertiary carbon Cl_T on a macromolecular model, i.e., the copolymer of vinyl chloride–isopropenyl chloride, was verified. The phenolysis reaction can be used as a chemical method to determine Cl_T in the copolymers. Phenolic polyelectrolytes are obtained as products. The increase of the Cl_T content leads to an appreciable decrease of the thermal stability of the polymer. The thermal decomposition by dehydrochlorination is a chain reaction. The γ and ultraviolet radiolysis processes did not reveal a remarkable influence of Cl_T; the samples with an increased Cl_T content showed a decreased stability towards sunlight. One concludes that when Cl_T is present in PVC it can initiate the decomposition reaction at lower temperatures than would be expected.

In the previous paper[1] some aspects of the specific reactivity of chlorine atom bound to a tertiary carbon atom (Cl_T) on model compounds with small molecules were reported.

The obtained conclusions were verified for a copolymer of vinyl chloride and isopropenyl chloride,[2] and the results are described in this paper.

Also, we wanted to establish the role of the Cl_T in the destruction process of the polymer in order to elucidate the role of Cl_T in the aging process of PVC.

SELECTIVE PHENOLYSIS

The specific phenolysis reaction of Cl_T on model compounds has been described.[1] The work reported here deals with the application of this selective reaction on macromolecular systems (copolymer of vinyl chloride with isopropenyl chloride).

Experimental

The synthesis and determination of composition of the polymer samples was described previously.[2] The content of Cl_T relative to the total chlorine

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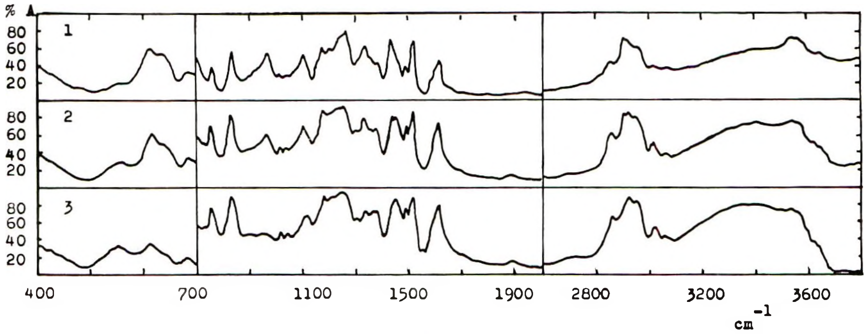


Fig. 1. Infrared spectra of products of 98 hr. phenolysis: (*1*) copolymer 2; (*2*) copolymer 3; (*3*) copolymer 4.

quantity was 0% for sample 1, 5% for sample 2, 12% for sample 3, and 28% for sample 4.

A mixture of 0.05 g. polymer and 5 ml. G.R. phenol was heated at 60°C. in a glass ampule. The heating time varied with every series of samples (Fig. 1). After the reaction, the excess phenol was removed with petroleum ether. The precipitated polymer was decanted and washed once more with 50 ml. petroleum ether; the decanted product was dried, suspended in 5 ml. dichloroethane, and stirred for 15 min. at 50°C. The resulting suspension was added to 50 ml. petroleum ether, decanted, and the polymer washed again with 50 ml. petroleum ether. The purification method was repeated and the polymer kept overnight in 75 ml. petroleum ether, then decanted, and dried. The infrared spectra of the resulting products are given in Figure 1.

Table I shows the results of elemental analysis for the polymers obtained after 98 hr. phenolysis.

TABLE I
Elemental Analysis of the Polymers Obtained by Phenolysis Reaction

Sample	C, %	H, %	Cl, %
2	46.34,	5.48,	44.71,
	46.18	5.45	44.57
3	55.41,	6.15,	32.71
	55.67	6.10	32.56
4	67.15,	6.79	17.27,
	67.32	6.93	17.49

In other experiments, phenol saturated with HCl was used instead of pure phenol. The processing of the products was the same.

Results and Discussion

The kinetics of the phenolysis reaction was followed by the infrared spectra, the aromatic band at 1518 cm.$^{-1}$ being used. The peak at 1432

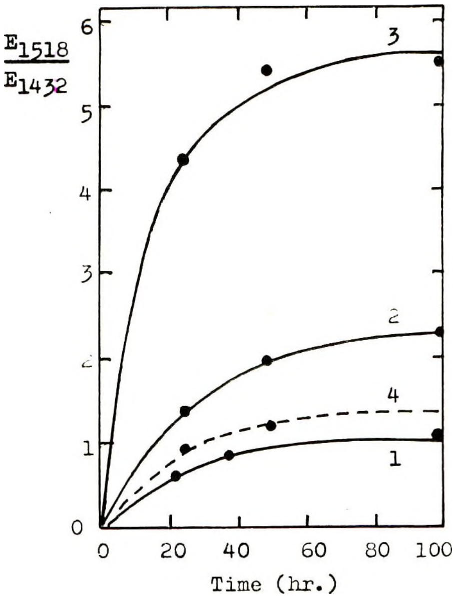


Fig. 2. Course of the phenolysis reaction in pure phenol: (*1*) copolymer 2; (*2*) copolymer 3, (*3*) copolymer 4; (*4*) copolymer 2 in phenol saturated with HCl.

cm.$^{-1}$ (CH_2 deformation) served as internal standard. Figure 2 shows the variation of intensity ratio with the time. As may be seen, the phenolysis proceeds rapidly at the beginning, but, after a certain degree of conversion, it becomes slow. For the samples for which the phenolysis lasted 98 hr., the dependence of intensity ratio of absorption bands A_{1538}/E_{1432} on the content of Cl_T was followed. A linear dependence was found (Fig. 3).

From Figure 2 one can see that with phenol saturated with HCl, the reaction proceeded more quickly (curves *2* and *4*). This fact confirms the catalytic action of HCl during the phenolysis of Cl_T in the polymer, as well as for the model compounds with small molecules.

Degree of Phenolic Substitution for Cl in Copolymer. The degree of substitution of chlorine was determined from results of elemental analysis before and after phenolysis. The percentage of substituted chlorine (Cl_{Subst}) relative to the total chlorine was calculated from the equation

$$\mathrm{Cl}_{\mathrm{Subst}} = \{(\mathrm{Cl} - \mathrm{Cl}_f)/[\mathrm{Cl}(100 + 1.65\mathrm{Cl}_f)]\} \times 10^4$$

TABLE II

Degree of Substitution of Chlorine in Copolymer Calculated on the Basis of Cl Content

Sample	Cl, %	Cl_f, %	Cl_{Subst}, %
2	54.95	44.64	10.8
3	53.53	32.63	25.4
4	52.39	17.38	52.0

where Cl is percentage of chlorine in the initial copolymer and Cl_f is the percentage of chlorine in the final products. The results are shown in Table II.

Similarly, $\mathrm{Cl}_{\mathrm{Subst}}$ was calculated on the basis of carbon content, from the equation:

$$\mathrm{Cl}_{\mathrm{Subst}} = \{(\mathrm{C}_f - \mathrm{C})/[\mathrm{Cl}(203 - 1.65\,C_f)]\} \times 10^4$$

where C denotes carbon content of the copolymer and C_f is carbon content after phenolysis. The results are given in Table III.

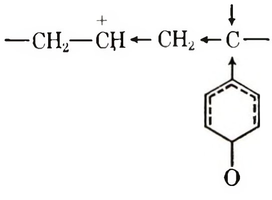
TABLE III
Degree of Substitution of Chlorine in Copolymer Calculated on the Basis of C Content

Sample	C, %	C_f, %	$\mathrm{Cl}_{\mathrm{Subst}}$, %
2	39.12	46.26	10.2
3	40.02	55.54	26
4	42.29	67.23	51.8

The results obtained on the basis of chlorine and carbon content agree very well.

When the phenolysis lasted 98 hr., the absolute value of the substituted chlorine is larger than Cl_T (Tables II and III), although the degree of substitution is proportional to the quantity of Cl_T (Fig. 2). This is the same as for the phenolysis of 2,4-dichloro-2-methylpentane when the activating action of the CH_3 group accounts for the enhanced reactivity of the secondary chlorine. As for the copolymer this explanation is not more valid; the only possible explanation is the labilizing effect of the secondary chlorine after replacement of Cl_T with the phenol group.

The phenoxide ion produces a strong conjugative effect which results in increasing electron density in the *para* position of the phenol ring. There is an inductive displacement of the electrons in the aliphatic chain, which enhances the capacity of forming the carbocation, the secondary chlorine being split off. The CH_3 group has a concordant action. However one cannot understand how this effect is transmitted through three simply bonded carbon atoms:



The kinetic curves for the phenolysis (Fig. 2) show that the rapid substitution of Cl_T proceeds in the first stage. The substitution of the other chlorine atoms is much slower. From the kinetic results, the moment of Cl_T substitution can be found.

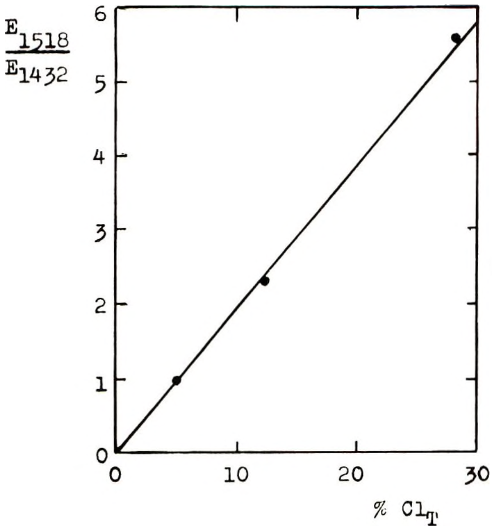
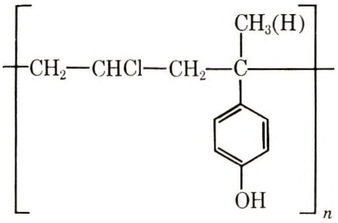


Fig. 3. Dependence of degree of substitution on the content of Cl_T in the phenolysis reaction.

As may be seen from Figure 3, the replacement of chlorine by phenol is directly proportional to the Cl_T content. This is essential for our purpose.

One can conclude that the phenolysis reaction applied to macromolecular compounds is a very selective one and consequently may be used for the Cl_T determination in PVC. The Cl_T concentration in the copolymer may be determined to about 0.5%, if the reaction is followed by infrared analysis (15 mg. product in a 1-g. KBr disk). The sensitivity can be further enhanced either by increasing the concentration of compound in the KBr disk or by subsequent ultraviolet spectroscopy.

Phenolysis Products. It is interesting to study the phenolysis also for the products which resulted. As may be seen from Tables II and III, in the case of copolymer 4 the attained degree of substitution of chlorine is 52%. Hence, the reaction product would have the structure:



$$\left[-CH_2-CHCl-CH_2-\underset{\underset{OH}{C_6H_4}}{\overset{CH_3(H)}{C}}-\right]_n$$

with the formula $(C_{11}H_{13}OCl)_n$. The elemental analysis of the obtained products agree quite well with the calculated values.

ANAL. Calculated for $C_{11}H_{13}OCl)_n$: C, 67.2%; H, 6.6%; Cl, 18.1%. Found: C, 67.23%; H, 6.8%; Cl, 17.38%.

Therefore during the phenolysis of the copolymers, polyphenols are obtained.

The substitution in the aromatic ring occurs only in the *para* position, as may be seen by comparing the infrared spectra of 3-chloro-3-phenoxypentane in the overtone region between 1600 and 1900 cm.$^{-1}$ characteristic for *para* substitution.

It is a very difficult problem to obtain high molecular polyphenols. They cannot be prepared by direct polymerization owing to the inhibitory effect of the phenol group. Except the novolacs, which are low molecular polyphenols (maximum molecular weight $\simeq$ 2000) obtained by polycondensation, there are only indirect and difficult methods to obtain them. These methods involve either blocking of the phenol groups of vinylphenols, polymerization, and then unblocking the phenol groups[3,4] or on the diazotization of the diamines and coupling with phenols.[5]

In case of the sample 3 the obtained polyphenol has polyelectrolyte properties, being soluble in aqueous NaOH. These solutions can form complexes, e.g., the precipitation of ferric ions from solutions. All the analogous series of polymers obtained in the copolymer phenolysis were coupled with the diazotized sulfanilic acid. The resulting products are red and behave as pH indicators.

The main prospect of this phenolysis reaction is its possible utilization for PVC stabilization, owing to the antioxidizing property of the phenol group. The stability of PVC should be realized either through directly bonding the phenolic nucleus to the PVC molecule or by synthesis of some polyphenols of this type and subsequent mixture with PVC. These are only some possible uses of the phenolysis reaction.

THERMAL AND IRRADIATION STABILITY OF THE VINYL CHLORIDE–ISOPROPENYL CHLORIDE COPOLYMER

The existence of Cl_T in PVC and its importance for the aging process of PVC is generally supposed by many authors.[6–10] However, there are some literature data which run counter to this supposition. Condo[11] reported that in the copolymerization of isopropenyl chloride with vinyl chloride (where Cl_T was formed), polymers with enhanced thermal and irradiation stability were obtained. Baum and Wartman[8] considered the sites for initiation of thermal decomposition of PVC to be unsaturated chain ends at about 150°C. and Cl_T at 190°C. They considered that the double bond at the chain end is responsible for PVC instability although its concentration is less than that supposed for Cl_T.[8]

These results do not agree with the great instability of the tertiary chlorides, which partially decompose even at room temperature (*tert*-butyl chloride and 3-chloro-3-ethylpentane rapidly show acid reaction).

To elucidate the role the Cl_T plays in PVC stability, the thermal and irradiation stability of the obtained copolymer were studied.

Thermal Stability

Thermal stability was followed on polymer films about 20 μ thick, pressed in KBr. Films of copolymers 3 and 4 were obtained by evaporating solutions in dichloroethane; films of copolymers 1 and 2 were obtained from cyclohexanone solutions. The traces of cyclohexanone in the latter films were removed by swelling the films in dichloroethane and drying *in vacuo*. The films were washed several times with dichloroethane until no more cyclohexanone was on the basis of infrared spectra.

To determine the thermal stability, the samples were heated at 65, 105, 141, 181, or 220°C., for 2 hr., respectively. The infrared spectra of the samples, when cool, were measured after every heating period (Figs. 4–7). The changes in appearance of the samples are summarized in Table IV.

TABLE IV
Change in Appearance of Polymers on Heating

Sample	65°C.	105°C.	141°C.	181°C.	220°C.
1	Unchanged	Unchanged	Unchanged	Slight yellowing	Black
2	Unchanged	Unchanged	Blackened	Black	Black
3	Unchanged	Unchanged	Blackened	Black	Black
4	Unchanged	Blackened	Black	—	—

As may be seen from Table IV and Figures 4–7, there is a strong dependence of copolymer stability on the Cl_T content, in contrast to the above mentioned observations.[8,11] As the changes in the intensity of the C—Cl_T stretching vibration relative to the intensity of C—Cl_S stretching vibrations show, the content of both types of chlorine atom decreases simultaneously, which confirms the idea that the destruction mechanism is a chain reaction. Moreover, the fact that the blackening of the sample begins at the same time as its decomposition indicates the appearance of double-bond systems. The infrared spectra confirm the appearance of a polyene polymer structure during the thermal decomposition. The spectra are similar to the spectra of the products obtained by Tsuchida and co-workers[12] by dehydrochlorina-

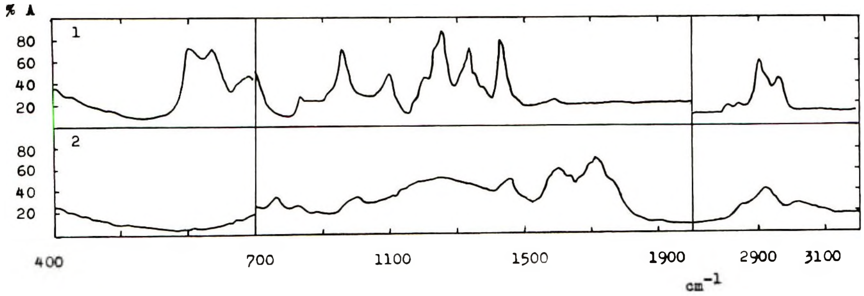


Fig. 4. Thermal stability of PVC sample 1: (*1*) initial; (*2*) after heating at 220°C. (After heating the initial sample at 65, 105, 141, and 181°C. the spectra were not changed.)

tion of PVC (solution of $NaNH_2$ in NH_3). The infrared spectra show the absorption bands $\nu_{C=C}$ (1600 cm.$^{-1}$), $\delta_{=C-H\ trans}$ (990 cm.$^{-1}$), and $\nu_{=C-H}$ (3030 cm.$^{-1}$). Although the samples were pressed in KBr, oxygen takes part in the decomposition reaction, as indicated by the C=O vibration at 1700 cm.$^{-1}$. The diffusion rate of oxygen in the KBr disk influences the

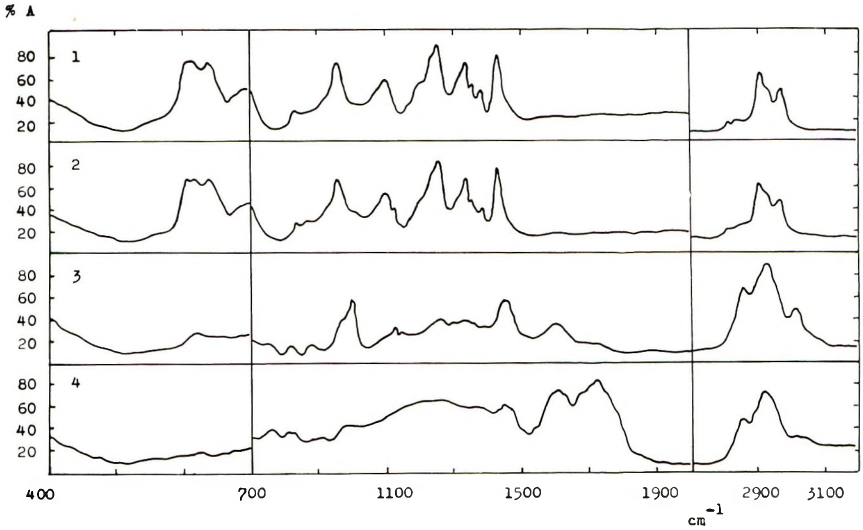


Fig. 5. Thermal stability of copolymer 2 (Cl_T 5% of the total chlorine). (*1*) initial (same as after heating at 65 and 105°C.); (*2*) after heating at 141°C.; (*3*) after heating at 181°C.; (*4*) after heating at 220°C.

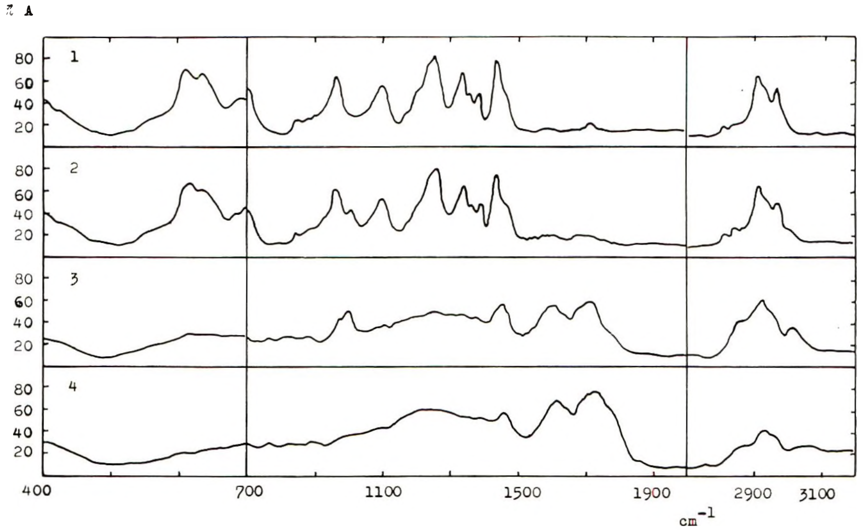


Fig. 6. Thermal stability of copolymer 3 (Cl_T 12% of the total chlorine): (*1*) initial (same as after heating at 65 and 105°C.); (*2*) after heating at 141°C.; (*3*) after heating at 181°C.; (*4*) after heating at 220°C.

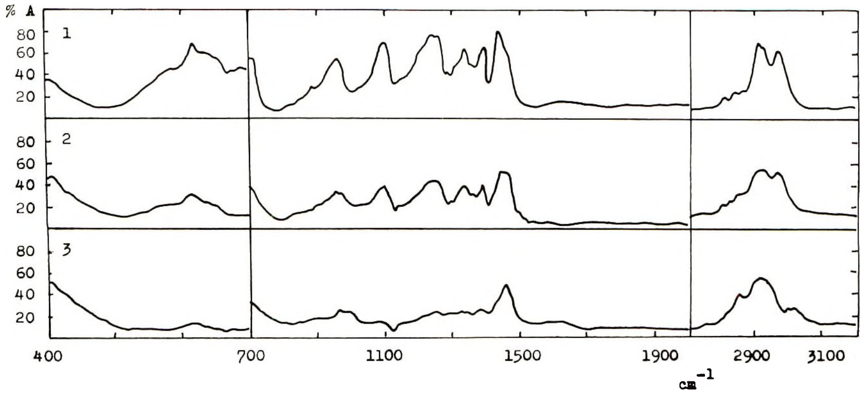


Fig. 7. Thermal stability of copolymer 4 (Cl_T 28% of the total chlorine): (*1*) initial (same as after heating at 65°C.); (*2*) after heating at 105°C.; (*3*) after heating at 141°C.

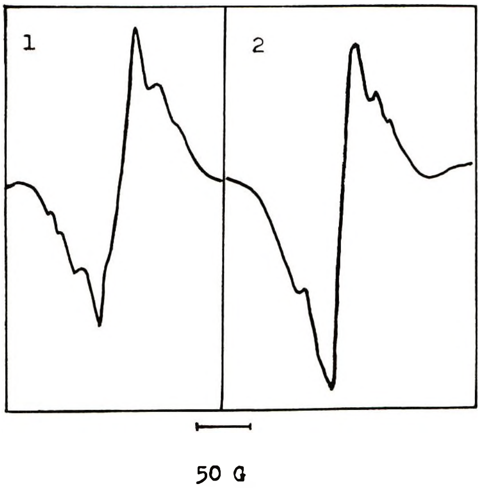


Fig. 8. EPR spectra of ^{60}Co γ-ray-irradiated polymers: (*1*) copolymer 4; (*2*) PVC sample 1.

oxidation rate. Yet it seems that when the reaction begins at lower temperature (140°C.) the oxidation is less.

γ-Irradiation. Equal quantities of PVC (sample 1) and copolymer (sample 4) (0.040 g.) were sealed separately *in vacuo* in quartz ampules. The samples were irradiated with γ-rays from a ^{60}Co source at −196°C. Irradiation was carried out with a dose rate of 600 r/min. The EPR spectra of the irradiated samples were measured on a JEOL 3B spectrometer with 100 Khz. modulation at −196°C. The EPR spectra are given in Figure 8.

Ultraviolet Irradiation. Samples of PVC and copolymer as above cooled with liquid nitrogen were irradiated with ultraviolet rays from 200-w. hydrogen source. The distance from the ultraviolet source was 3 cm. The EPR spectra are given in Figure 9.

As one may see from Figures 8 and 9, the γ-ray and ultraviolet-irradiated samples show similar stability. This is accounted for by the fact that the energy of the utilized radiation was far greater than that required for breaking of the C–Cl bond. For this reason the cleavage of the chlorine atom proceeds unselectively. The EPR spectra of the resulting radicals are similar for both the samples, excepting that there is better resolution for sample 4.

When identical samples of PVC and copolymer 4 were subjected to solar irradiation (of a smaller energy) an enchanced instability of the copolymer as compared to the PVC was observed. Copolymer samples turned yellow in a few days.

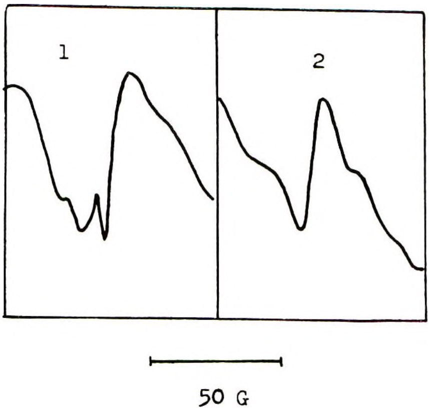


Fig. 9. EPR spectra of ultraviolet-irradiated polymers: (*1*) copolymer 4; (*2*) PVC sample 1.

From our results it appears reasonable to conclude that the Cl_T content has a marked influence on PVC stability. When Cl_T is present in PVC it can initiate the decomposition reaction at lower temperatures than was supposed.[8]

A low content of Cl_T in the polymers may account for the different results obtained by Condo[11] and Baum and Wartman.[8] It is very likely that the structure of Condo's copolymers changed during polymerization, because the polymers were prepared in a very polar medium (water) and at relatively high temperatures. The loss of most of the Cl_T is possible under such conditions. One may suppose the same for work of Baum and Wartman, the quantity of Cl_T probably being much smaller than expected from theory.

The author wishes to express his gratitude to the leadership of UMCH Prague, where this work was carried out, and particularly, to thank the analytical laboratory for chemical analysis, Mr. K. Ulbert for EPR spectra, and Mr. Vack for ^{60}Co irradiation tests.

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Résumé

On a vérifié la sélectivité de la réaction de phénolyse du Cl_T sur un modèle macromoléculaire, à savoir le copolymère: chlorure de vinylechlorure d'isopropényle. La réaction de phénolyse peut être utilisée comme méthode chimique pour le dosage du Cl_T dans les polymères. Par cette réaction, on obtient des polyélectrolytes phénoliques. L'augmentation du contenu en Cl_T a comme résultat une diminution considérable de la stabilité thermique des polymères. Le procèssus de décomposition thermique par déhydrochloration est une réaction en chaîne. Le Cl_T n'a pas d'influence notable sur les processus de radiolyse par radiations γ et UV; quant à la lumière solaire, les échantillons ayant une teneur plus élevée en Cl_T montrent une stabilité moindre. On conclut que par suite de la présence de Cl_T dans la molécule de PVC, la réaction de décomposition peut être initiée à des températures plus basses qu'on ne supposait précédemment.

Zusammenfassung

Es wird die Selektivität der Phenolysereaktion des Cl_T an einem makromolekularen Modellmolekül und zwar am Vinylchlorid-Isopropenylchloridkopolymeren überprüft. Die Phenolysereaktion kann zur quantitativen Bestimmung des Cl_T-Gehaltes im Polymeren herangezogen werden. Als Endprodukte der Reaktion erhält man phenolische Polyelektrolyte. Ein Anwachsen der Konzentration von Cl_T im Polymeren führt zu einem erheblichen Absinken der thermischen Stabilität desselben. Die thermische Zersetzung durch Abspaltung von HCl ist eine Kettenreaktion, die zu Polyenen führt. Bei den Radiolyseprozessen mit γ- und UV-Strahlen kann kein besonderer Einfluss des Cl_T beobachtet werden. Gegen Sonnenlicht zeigen die Proben mit grösserem Cl_T-Gehalt eine geringere Stabilität. Man kommt zu dem Schluss, dass die Gegenwart von CL_T im PVC zu einer Zersetzung desselben bei niedrigerer Temperatur als, erwartet, führen kann.

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Preparation and Properties of Poly(methylene terephthalates)

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Synopsis

A systematic study of poly(methylene terephthalates) has been made. Melting points, second-order transition temperatures, and solubility temperatures are presented for the homologous series of terephthalate polyesters of ethylene glycol through 1,10-dodecanediol, and for terephthalate copolyesters of: (*1*) ethylene glycol/1,3-propanediol and (*2*) ethylene glycol/1,4-butanediol. Fiber properties of the terephthalate polyesters and the 70/30 ethylene glycol/1,3-propanediol copolyterephthalate ester are presented. Only the first three members of the poly(methylene terephthalate) series show promise for use in textile fibers.

INTRODUCTION

When the large amount of literature dealing with poly(ethylene terephthalate) is considered, the paucity of information available on the higher homologues of this polyester is indeed surprising. Melting points for most of the lower members of the poly(methylene terephthalates) are available.[1–3] Aside from these, however, very little else has been published.

During the course of our study of polyesters, we have accumulated data on polyesters and copolyesters of the poly(methylene terephthalate) series. These data deal with melting points, second-order transition temperatures, solubility temperatures, and fiber properties. This paper presents our findings.

RESULTS AND DISCUSSION

Preparation

The polyesters were prepared by melt-phase polymerization under reduced pressure. A typical preparative procedure is described in the experimental section. The temperatures used were selected so that the evolved diol would be highly volatile and distil from the reaction flask as rapidly as possible. Table I shows the polyesters prepared, the polymerization temperatures selected, and the inherent viscosities obtained. No attempt was made to find the optimum preparative conditions.

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TABLE I
Poly(methylene terephthalates) Prepared and the Polymerization Conditions[a]

Diol	Polymerization Temp., °C.	Polymerization Time, hr.	[η] of polymer[b]
Ethylene glycol	270	1	0.56
	280	1	0.85
1,3-Propanediol	280	1	0.83, 0.86
1,4-Butanediol	250	1	1.12, 1.04
	260	1	1.20
	270	1	0.84
	280	1	1.05, 1.06, 0.93, 0.79, 0.56
1,5-Pentanediol	280	1	1.09, 1.04, 0.98
	280	1.5	0.94
1,6-Hexanediol	280	1	0.77, 0.76
1,7-Heptanediol	270	1	1.01
	280	1	0.79
1,8-Octanediol	290	1	0.87, 0.83, 0.73, 0.65
1,9-Nonanediol	290	1	0.90
1,10-Decanediol	280	1	0.85

[a] Prepared from diols and dimethyl terephthalate.

[b] Multiple values represent the viscosities obtained in duplicate runs.

With one exception, tetraisopropyl titanate[4] (at a concentration of 150 ppm titanium metal) was the catalyst used for the polymerizations. In general, this is an excellent general-purpose alcoholysis catalyst. The single exception was in the preparation of poly(ethylene terephthalate), where a zinc acetate–antimony trioxide catalyst system (65 ppm zinc and 230 ppm antimony) was used.[5] Although tetraisopropyl titanate is an effective catalyst for the preparation of highly polymeric poly(ethylene terephthalate), the polymers produced are highly colored.

The polymerization temperature was found to be an important factor in the preparation of poly(tetramethylene terephthalate). At temperatures in excess of 260°C., the viscosity of the final polymer was reduced and varied greatly from run to run. Such a temperature sensitivity for this polymer has been reported previously.[6]

Melting Points

The melting points were determined on a Fisher-Johns melting point apparatus. The sample was placed on the hot stage at approximately 20°C. below the melting temperature and observed while the temperature rose. A gentle pressure was applied to the sample from a pencil point. The melting point was taken as that temperature at which the sample flowed freely under pressure.

Differential thermal analysis (DTA) was also used to determine melting points and, in addition, second-order transition temperatures. These data have been presented[7] elsewhere but are included here for comparison.

TABLE II
Physical Properties of Poly(methylene terephthalates)

Diol	Melting point, °C. Fisher-Johns	Melting point, °C. DTA	DTA second-order transition temp., °C.	Solubility temp., °C.
Ethylene glycol	258–262	256	69	170–160
1,3-Propanediol	225	227	35	164–160
1,4-Butanediol	225	221	22	150–147
1,5-Pentanediol	136–140	134	10	53–45
1,6-Hexanediol	157	148	−9	65–60
1,7-Heptanediol	97–104	98	3	<25[a]
1,8-Octanediol	137–140	132	—	64–54
1,9-Nonanediol	92–95	90	−3	27
1,10-Decanediol	123–126	131	−5	56–50

[a] Solution set to a clear gel after 1 hr. at room temperature.

TABLE III
Physical Properties of Copolyesters of Poly(ethylene terephthalate)

Diol	Poly(ethylene terephthalate), mole-%	Melting point, °C. Fisher-Johns	Melting point, °C. DTA	DTA second-order transition temp., °C.	Solubilty temp., °C.	$[\eta]$
1,3-Propanediol	100	258–262	256	69	164–160	0.66
	88	220–225	223	67	150–140	0.82
	63	170–175	—	63	120–110	0.86
	49	160–170	—	56	102–96	0.97
	42	175–179	181	50	110–103	0.70
	34	185–190	191	41	122–115	0.96
	12	210–215	214	40	150–145	0.90
	0	225	227	35	164–160	0.90
1,4-Butanediol	100	258–262	256	69	164–160	0.66
	87	235–240	230	67	143–137	0.74
	74	210–215	209	56	122–116	0.57
	54	180–185	181	51	100–96	0.62
	42	175–180	183	34	102–98	0.81
	32	185–190	188	29	110–107	0.49
	14	205–210	203	28	130–125	0.61
	0	225	221	22	150–147	0.80

Table II contains a summary of the melting point data, second-order transition temperatures, and solubility temperatures for the poly(methylene terephthalates). Table III contains similar data for the two copolyester systems studied. Graphical presentations of the same data are shown in Figures 1–3.

No DTA melting points are recorded for the 1,3-propanediol copolyesters containing 40–50 mole-% of this diol. These samples did not crystallize under the conditions employed in the measuring technique.

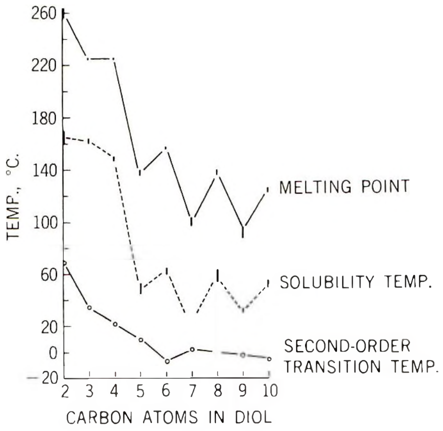

Fig. 1. Melting points, solubility temperatures, and second-order transition temperatures of poly(methylene terephthalates).

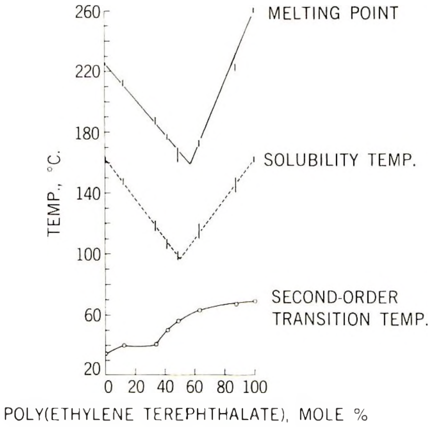

Fig. 2. Melting points, solubility temperatures, and second-order transition temperatures of copolyesters of ethylene glycol and 1,3-propanediol.

Solubility

An estimation of the comparative solubility characteristics of the polyesters was made. The polyester (1 g.) was dissolved in hot diphenyl ether (25 ml.) and the solution allowed to cool with stirring. The temperature was noted when the first haze developed and again when a dense precipitation occurred. These temperatures were reproducible within 2–3°C., and the range of temperatures between the first appearance of precipitate and dense precipitation was usually of the order of 5°C. This procedure for determining solubility temperatures has been reported[8] in the literature as a means of comparing the relatively efficacy of solvents.

The data on solubility characteristics are presented in Table II for the poly(methylene terephthalates) and in Table III for the two copolyester

TABLE IV
Fiber Properties of Poly(methylene terephthalates)

Diol	Spinning temp., °C.	Draft		Heat-setting conditions	Tenacity, g./den.	Elongation, %	Initial modulus, g./den.	Flow point, °C.[a]
		Ratio	Temp., °C.					
Ethylene glycol	270	4.8	120 steam	15 min., 170°C.[b]	2.8	5	76	219
1,3-Propanediol	270	4.2	150 air	15 min., 170°C.[b]	2.5	21	21	196
1,4-Butanediol	250	4.4	120 steam	15 min., 140°C.[b]	3.4	26	20	214
1,5-Pentanediol	250	—	—	—	—	—	—	—
1,6-Hexanediol	205	4.6	110 steam	15 min., 105°C.[b]	3.0	9	43	134
1,7-Heptanediol	250	—	—	—	—	—	—	—
1,8-Octanediol	160	4.0	80 air	15 min., 90°C.[b]	2.3	15	27	122
Copolyester (70/30 ethylene glycol/ 1,3-propanediol)	250	5.8	110 steam	15 min., 120°C.[b]	2.7	29	36	156

[a] Temperature at which a fiber flows under a loading of 0.2 g./den.

[b] At constant length.

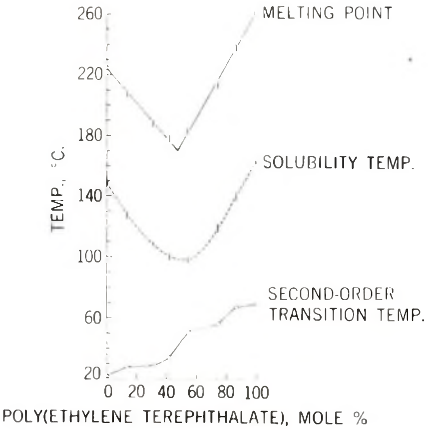

Fig. 3. Melting points, solubility temperatures, and second-order transition temperatures of copolyesters of ethylene glycol and 1,4-butanediol.

systems studied. These solubility temperatures are also plotted in Figures 1–3 for comparison with the melting point data.

Fiber Properties

Fibers were prepared by melt-spinning the polyesters. The fibers were drawn and heat-set, and fiber properties determined on an Instron tester. The conditions for preparing the fibers and the fiber properties are summarized in Table IV. The filaments of the polyesters from 1,5-pentanediol and 1,7-heptanediol plastered on the package after spinning indicating a very low flow point. Consequently, data on the properties of fibers from these diols are not available.

A single copolyester system (70/30 ethylene glycol/1,3-propanediol) was spun into fibers. The fiber properties of this material are also shown in Table IV.

Analysis of Copolyesters

In the case of copolyesters of ethylene glycol with either 1,3-propanediol or 1,4-butanediol, the two diols are evolved at different rates during melt-phase polymerization. An analysis of each copolyester was obtained through the examination of the nuclear magnetic resonance (NMR) spectrum of a solution of the copolyester dissolved in trifluoroacetic acid. Methylene groups adjacent to an oxygen atom absorb at a different field strength than those further from the oxygen atom. Since the area of an NMR peak is directly proportional to the number of hydrogen atoms producing that peak, the ratio of the areas of these two absorption peaks permits one to determine the mole ratio of the two diols present in the copolyester. The standard deviation of a single measurement is about 2 mole-% absolute.

EXPERIMENTAL

Materials

Dimethyl terephthalate, ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, and 1,10-decanediol were obtained from commercial sources.

1,6-Hexanediol, 1,7-heptanediol, 1,8-octanediol, and 1,9-nonanediol were synthesized by the catalytic reduction over copper chromite of dimethyl adipate, dimethyl pimelate, dimethyl suberate, and dimethyl azelate, respectively.

Viscosities

The viscosities reported are inherent viscosities measured on 0.25% solutions of the polyester dissolved in a mixture of 60 parts of phenol and 40 parts of tetrachloroethane. The polyester samples were dissolved by heating 1 hr. at 100°C., and the flow times of the solutions were measured after cooling to 20°C.

Typical Preparation

Poly(tetramethylene terephthalate). A 500-ml. flask was charged with 77.6 g. (0.4 mole) of dimethyl terephthalate, 54 g. (0.6 mole, 50% excess) of 1,4-butanediol, and 0.08 g. of tetraisopropyl titanate as a 10% solution in butanol. The flask was equipped with a head having a nitrogen inlet, a take-off to remove volatile materials, and a socket joint to accommodate a stirrer. The stirrer shaft ran through the socket joint and had a ball joint attached by pressure tubing to the shaft to seal the socket joint.

The flask was swept with a slow stream of nitrogen, stirred, and immersed in a Wood's metal bath preheated to 200°C. Alcoholysis began as soon as the contents of the flask were molten. The methanol evolved was swept by the nitrogen stream into a condensing system where it could be measured. Heating and stirring at 200°C. were continued for 90 min., and then the temperature of the bath was increased to 270°C. This heating period required 50 min. At 270°C. the nitrogen inlet was closed and a vacuum pump was applied. Within 5 min., a pressure of less than 0.5 mm. of mercury was attained. Stirring and heating under reduced pressure were continued for 60 min. At the end of this time, the flask was removed from the bath and cooled under reduced pressure. The polymer was recovered by breaking the flask. Inherent viscosity of the polymer was 0.84.

CONCLUSIONS

There is a surprising difference between the melting points and solubility temperatures of the first three members of the poly(methylene terephthalate) series and those of the remaining members. The polyesters of ethylene glycol, 1,3-propanediol, and 1,4-butanediol all melt above 220°C. and have solubility temperatures of approximately 150°C. The higher homologs have much lower melting points (160°C. or less) and are much more soluble (solubility temperatures of 60°C. or less). Because of these characteristics, the only polyesters which show promise for use in textile fibers are the first three members of the series.

Insofar as copolyesters are concerned, it was expected and found that a eutectic composition existed having a minimum melting point and a maximum solubility. It is interesting to note that the DTA melting points indicate that 1,3-propanediol with its odd number of carbon atoms is much more effective in eliminating crystallinity in the copolyester than 1,4-butanediol with its even number of carbon atoms.

The authors express their appreciation to Dr. Wilson Goodlett for the nuclear magnetic resonance analyses of the copolyesters, to Dr. E. V. Martin and Mr. L. E. Wooten who melt-spun the polyester samples, and to Mr. W. A. Arnold who aided in the preparation of the polyesters.

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Résumé

Une étude systématique de téréphthalates de polyméthylène a été effectuée. Les points de fusion, les températures de transition de second ordre et les températures de solubilité sont présentées pour les séries homologues de polyesters téréphthaliques d'éthylène glycol jusqu'au dodécanediol, 1–10 et pour les copolyesters téréphthaliques de (*1*) l'éthylène-glycol/1,3-propanediol et (*2*) l'éthylène-glycol/1,4-butanediol. Les propriétés fibrogènes de ces polyesters téréphthaliques et des copolytéréphthalates 70/30 éthylène glycol 1,3-propanediol sont présentées. Uniquement les trois premiers membres des séries tétéphthaliques polyméthylèniques sont intéressantes pour l'usage comme fibres textiles.

Zusammenfassung

Eine systematische Untersuchung von Poly(methylenterephthalaten) wurde durchgeführt. Schmelzpunkte, Umwandlungstemperaturen 2. Ordnung und Löslichkeitstemperaturen werden für die homologe Reihe der Terephthalatpolyester von Äthylenglycol bis zum 1,10-Dodekandiol und für Terephthalatcopolyester von: (*1*) Äthylenglycol/1,3-Propandiol und (*2*) Äthylenglycol/1,4-Butandiol angegeben. Die Faser-

eigenschaften der Terephthalatpolyester und der 70/30-Äthylenglycol/1,3-Propandiol-Copolyterephthalatester werden beschrieben. Nur die ersten drei Glieder der Poly(methylenterephthalat)-Reihe scheinen für die Verwendung als Textilfasern geeignet zu sein.

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Preparation and Characterization of Syndiotactic Polypropylene

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Synopsis

The preparation and characterization of syndiotactic polypropylene are reported. The influence of polymerization variables on the syndiotactic regulating capacity of the VCl_4–$AlEt_2Cl$ catalyst were investigated. Vanadates could be substituted for VCl_4, and $Al(C_6H_5)_2Cl$ or $AlEt_2Br$ for $AlEt_2Cl$ under suitable conditions. Hydrogen functioned as a chain transfer agent for the $AlEt_2Cl$–VCl_4 catalyst, and polymerizations which were terminated with tritiated alcohols yielded polymers containing bound tritium. The syndio-regulating capacity of the $AlEt_2Cl$–VCl_4 catalyst was increased under specific conditions when cyclohexene, oxygen, or *tert*-butyl perbenzoate was incorporated. A polymerization mechanism is proposed. According to this mechanism, preference for a monomer complexing mode which minimizes steric repulsions between methyl groups of the new and last added monomer unit is responsible for syndiotactic propagation. Characterization included determination of infrared syndiotactic indices, melting points (65–131°C.), glass transition temperature, densities (0.859 to 0.885 g./cc.), nuclear magnetic resonance spectra, birefringence, differential thermal analysis spectrograms, solubility, and heat of fusion (~450 cal./mole).

Introduction

Considerable interest in syndiotactic polypropylene centers on its properties and on the synthetic methods by which it can be prepared in very high steric purity. This interest was heightened some years ago by the suggestion of Natta and co-workers that syndiotactic polypropylene should have a melting point very close to or perhaps higher than that of isotactic polypropylene.[1] In support of their conclusion they reported melting points ranging up to 165°C. for partially syndiotactic crystalline samples. These samples were chromatographically isolated from predominantly isotactic polymer prepared with moderately specific conventional Ziegler catalysts.

It is the intent of this paper to show that syndiotactic polypropylene samples melt significantly below their isotactic counterparts of comparable steric regularity. Some features of the synthetic methods used and some of the other properties which characterize this polymer are also discussed.

The disclosure by Natta, Pasquon, and Zambelli[2] that VCl_4 combined with $AlEt_2Cl$ and anisole polymerizes propylene at -78°C. to a syndiotactic polymer which is free of the isotactic form constituted a major break-through in the preparation of this new polymer. In later papers,[3,4] these authors discussed this work in some detail. We feel that our own studies, made in the interim, complement and supplement their work and thus contribute toward a better understanding of their unique syndiotactic-regulating catalyst system.

In the course of this investigation a family of polymers having moderate to very high syndiotactic regularity was prepared. These polymers were characterized by several physical methods. Portions of the characterization data were presented in a preliminary communication.[5]

SALIENT FEATURES OF THE SYNDIOTACTIC-REGULATING CATALYST

In keeping with our intent of complementing and supplementing the disclosures made by Natta, Zambelli, and Pasquon,[2,3] we would like to briefly summarize their findings before presenting our own.

The Natta, Zambelli, and Pasquon system consists of AlR_2Cl, VCl_4, or vanadium(III) acetylacetonate, plus a donor (anisole). This syndiotactic-regulating system, according to these authors, is characterized by the following features:

(*1*) It is apparently homogeneous and stable at about −40°C. and below.

(*2*) Ethylene and propylene are homopolymerized and copolymerized, but 1-butene is not homopolymerized.

(*3*) The formed syndiotactic polypropylene is free of isotactic crystalline polymer; the chains have practically homogeneous steric composition, each polymer chain, considering the weak crystallinity, is a stereoblock, that is to say it contains syndiotactic sequences alternating with sequences having a different steric configuration. It was not possible to isolate from the whole sample by solvent extraction methods or by chromatography fractions richer in the syndiotactic structure.

(*4*) The stereoregulating capacity of the AlR_2X–VCl_4–donor catalyst is influenced by (*a*) dimensions of R (the bulkier the R-substituent the greater is the syndiospecificity); (*b*) nature of X (only when X = Cl, but not Br, F, or I, is syndiotactic polypropylene formed); (*c*) temperature and time of polymerization (lower temperatures, i.e., below −40°C. and shorter times favor syndiotactic propagation); (*d*) donor type (anisole was found to be best); (*e*) ratio of AlR_2Cl/V (about 5 optimum) and ratio of donor/V (about 1 optimum); (*f*) order of addition of catalyst components (anisole mixed with VCl_4 before AlR_2Cl added at −78°C. was best).

(*5*) The mechanism is of the anionic-coordination type, the R in AlR_2X is finally present in the formed polymer. The active site involves an alkylated trivalent vanadium associated with $AlRCl_2$.

Only a reading of the original papers[1–4] can do full justice to the work of these authors; we have attempted to highlight the more significant results here. We now wish to provide a framework for our results which are summarized in the following.

TABLE I
Effect of Anisole[a]

Expt. no.	Solvent	Anisole, mmole	Propylene, g.	Polymerization time, hr.	Polymer formed, g.	IR syndio index
1	Heptane	0	25	1.5	0.3	1.35
2	"	1.0	"	1.5	0.2	2.33
3	"	1.0	"	4.5	0.5	2.30
4	"	0	"	20	2.3	0.90
5	"	1.0	"	20	10	0.84
6	Toluene	0	53	3.0	13.2	0.64
7	"	1.0	"	3.0	5.1	1.10
8	"	0	10	"	2.8	0.38
9	"	1.0	"	"	2.9	1.10

[a] Conditions: 100 ml. solvent, 1.0 mmole VCl_4, and anisole, if used, mixed at room temperature; after cooling to −78°C., 5.0 mmole $AlEt_2Cl$ and precondensed propylene were added; polymerizations were carried out at −78°C.; all materials were transferred under nitrogen.

A small syndiotactic polypropylene fraction can be extracted from the polypropylene produced by many, but not all, heterogeneous catalysts which yield a significant amorphous fraction. Similar results have been reported by Natta and co-workers.[1] Addition of electron donors, e.g., Et_3N to the $AlEt_2F$–γ-$TiCl_3$ catalyst, eliminated all but the more highly isotactic polymer fractions. These results suggest that syndiotactic polypropylene is produced at the more exposed sites.*

In our hands, the syndiotactic-regulating ability of the $AlEt_2Cl$–VCl_4 catalyst[2,3] was greater in heptane than in toluene solvent. Natta, Zambelli, and Pasquon prepared a polymer having an infrared ratio (index of syndiotactic regularity), $A_{11.53\mu}/{}^1/_2(A_{2.32\mu} + A_{2.35\mu})$† of about 0.4 with $Al(i\text{-}Bu)_2Cl$–VCl_4 in toluene. In heptane solvent with $AlEt_2Cl$–VCl_4 catalyst we have prepared a polymer having an IR syndio index of 1 ± 0.3. This difference must be attributed to the solvent or impurities present in the solvent since Natta and co-workers have found that with VCl_4, $AlEt_2Cl$ has a lowering stereoregulating capacity than $Al(i\text{-}Bu)_2Cl$.

Anisole increases the syndiotactic-regulating ability of the $AlEt_2Cl$–VCl_4 catalyst in heptane only if the conversions are kept low (Table I). The IR syndio index was increased from 1.35 to 2.33 by anisole in a 1.5-hr. run, but the index was unchanged if the polymerization time was increased to 20 hours. Anisole was effective in toluene at short (Table I) and long polymerization times.[2,3]

The specificity of the catalyst depended upon the conditions of prepara-

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* That the stereoregulating ability of the site depends on the chlorine environment of the exposed titanium site has been proposed.[6]

† We shall refer to this ratio as the IR syndio index. The 11.53 μ band is due to a mixture of CH_2 rocking, C–C stretching, and a small amount of C–H bending in the syndiotactic helices; hence, the intensity of this band is a relative measure of syndiotactic regularity.[7]

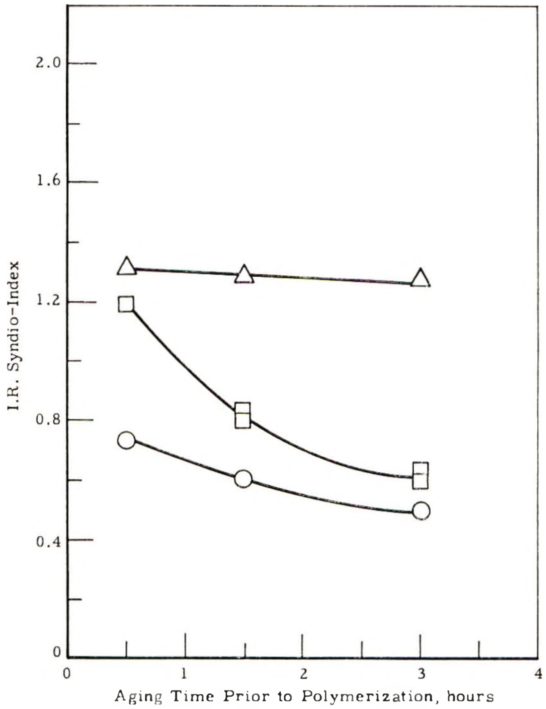


Fig. 1. Effect of aging of catalyst: (△) catalyst components aged t_x hours at −78°C., then polymerized t_x hours at −78°C.; (□) catalyst components aged t_x hours at −45°C., then polymerized t_x hours at −78°C., (○) catalyst components aged t_x hours at −78°C., then polymerized t_x hours at −45°C. (t_x of catalyst aging = t_x of propylene polymerization.) Polymerizations carried out in glass tube reactor (method 2 as described in Experimental Section).

tion and polymerization (Fig. 1). Mixing and aging the catalyst components, $AlEt_2Cl$ plus VCl_4, at −78°C. for various periods of time prior to propylene addition had little effect on catalyst stereospecificity (△, Fig. 1) while aging at −45°C. greatly reduced the IR syndio indices of the polymers obtained (□, Fig. 1). Taking into consideration that the change at −78°C. is small, the bottom curve (○, Fig. 1) demonstrates clearly that the syndiotactic-regulating ability of the catalyst changed with time in the course of polymerization itself when the polymerization was carried out at −45°C. That similar changes take place slowly even at −78°C. is shown in Figure 2, which gives changes in polymerization rate and polymer molecular weight as well as changes in syndiotactic index as a function of polymerization time. Obviously, any attempt to assess the influence of temperature on syndiotactic propagation specificity must take into account the simultaneous changes in the catalyst nature.

Lower polymerization temperatures favor syndiotactic propagation (Fig. 3). In these experiments an attempt was made to separate the effect of temperature on catalyst structure (the aging effect) from its effect on the

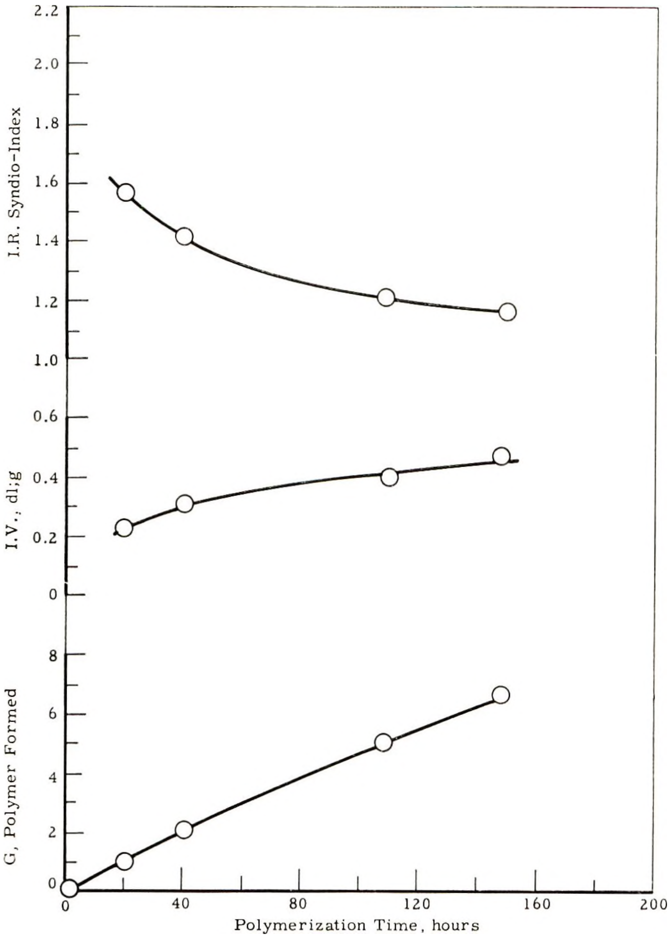


Fig. 2. Dependence on polymerization time of IR syndio index, intrinsic viscosity, and polymer formed. Propane (150 cc.), VCl_4 (1 mmole), $AlEt_2Cl$ (5 mmole), 5 g. propylene mixed in order at −78°C.; polymerization at −78°C. Average propylene concentration maintained reasonably constant by addition of 2 g. monomer at 20, 40, and 108 hr. Polymerizations carried out in glass tube reactor (method 2 described in the Experimental Section).

propagation step itself. To this end, the catalyst for the −78°C. and −95°C. polymerizations was aged at −45°C., while the catalyst for polymerization at −45°C. was aged at −78°C. Thus, all of the polymerization catalysts received a similar average thermal treatment during the combined aging and polymerization steps.

The apparently greater temperature dependence of propagation specificity found by Zambelli et al.[3] is readily explained. It is undoubtedly due to extensive aging effects, like those of Figure 1, which would occur during the long polymerization times (24 hr.). These effects would be most pronounced at the higher polymerization temperatures.

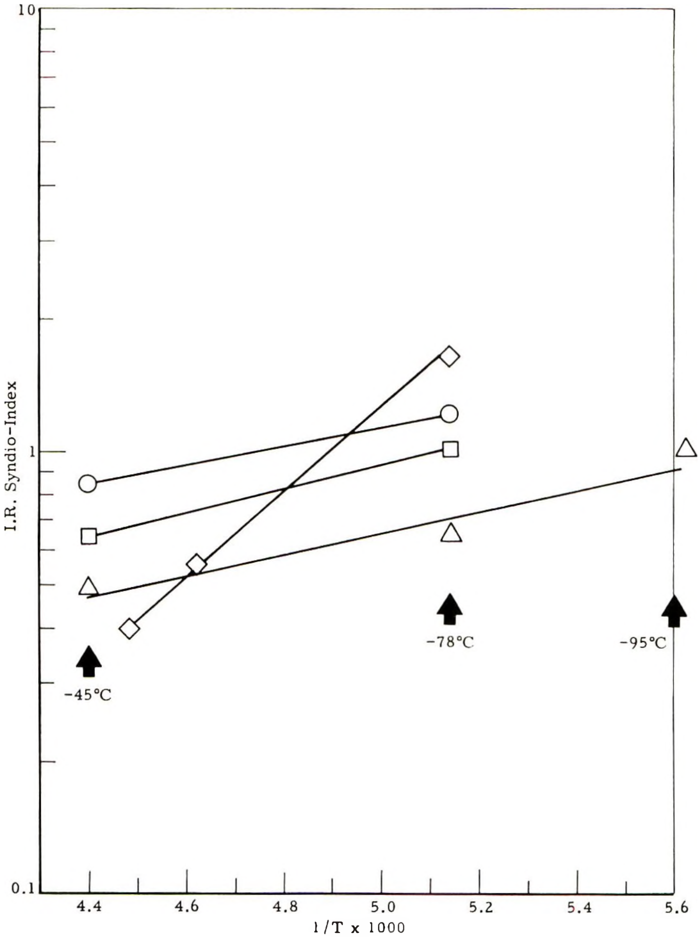


Fig. 3. Dependence of IR syndio index on polymerization temperature: (◇) Al-(*i*-Bu)$_2$Cl + VCl$_4$ + anisole + propylene (data of Zambelli et al.[3]). (○,□,△) AlEt$_2$Cl + VCl$_4$, catalyst aging time = polymerization time = t_x. (○) t_x = 0.5 hr.; (□) t_x = 1.5 hr.; (△) t_x = 3 hr. For the −78 and −94°C. polymerizations aging was at −45°C.; for the 45°C. polymerizations aging was at −78°C. Polymerization method 2 in Experimental Section.

Polymerizations terminated with tritiated alcohols yielded polymers containing only small amounts of bound tritium. About one out of 100–150 polymer chains was calculated to be alive when the alcohol was added; short-lived metal–carbon growth sites are indicated by this result. This has been observed previously with vanadium-based heterogeneous catalysts which polymerize propylene to isotactic polymer[8] and copolymerize propylene and ethylene.[9] These findings support the conclusions of Zambelli, Natta, and Pasquon[3] that the mechanism is of the coordinated-anionic type. These authors showed by means of labeling with ^{14}C that the alkyl component of AlEt$_2$Cl became attached to the polymer.

TABLE II
Vanadates as Cocatalysts[a]

Vanadate, (~2 mmole)	$AlEt_2Cl$, mmole	Aging		Propylene, g.	Polymer, g.	IR syndio index[b]	$\frac{A_{10.02\mu}}{A_{10.25\mu}}$[c]
		Temp., °C.	Time, hr.				
1 $VO(EtO)Cl_2$	10	−45	2	50	0.9	0.60	−
2 $VO(EtO)_3$	10	−45	2	50	0.2	0.74	−
3 $VO(i\text{-}PrO)Cl_2$	10	−45	2	50	0.8	0.80	+
4 $VO(i\text{-}PrO)_3$	10	−45	2	50	0.3	0.84	−
5 $VO(t\text{-}BuO)_3$	10	−45	2	50	0.05	Not done	Not done
6 $VO(i\text{-}PrO)Cl_2$	10	−45	4	50	1.9	0.40	−
7 $VO(i\text{-}PrO)Cl_2$	20	−45	4	50	1.0	0.46	−
8 $VO(i\text{-}PrO)Cl_2$	(10 + 5 mmole $AlEtCl_2$)	−45	2	50	0.9	1.0	−

[a] Procedure: To 100 ml. heptane was added the vanadate. This was cooled to −78°C., and $AlEt_2Cl$ was added. The mixture was warmed to −45°C. and kept at this temperature for 2–4 hr. The aged catalyst was cooled to −78°C. and propylene was added. The polymerizations were carried out in 8-oz. bottles (method 1) at −78°C. for 20 hr.

[b] IR syndio index = $A_{11.53\mu}/{}^1/_2(A_{2.32\mu} + A_{2.35\mu})$

[c] Taken as an index of isotacticity. Here plus (+) denotes that some isotactic polymer was formed while minus (−) denotes that none of the isotactic form was observed.

Hydrogen was found to be an effective chain-transfer agent with the apparently homogeneous catalyst, $AlEt_2Cl-VCl_4$. For example, 100 cc. of hydrogen at 1 atm. and −78°C. over 150 cc. heptane, 25 g. propylene, and $AlEt_2Cl$ (5 mm.) and VCl_4 (1.0 mm.) mixed and aged at −45°C. for 3 hr. reduced the intrinsic viscosity of the syndiotactic polypropylene formed from 1.3 to 0.5 dl./g. in a 3-hr. polymerization. Similar results were obtained with catalysts aged at −78°C. These results provide further evidence for a metal–carbon growth site. Hydrogen has been shown by Vandenberg to be an effective transfer agent for heterogeneous catalysts.[10]

A number of vanadates when combined with $AlEt_2Cl$ produced syndiotactic polypropylene at −78°C., provided the catalyst components were first aged at −45°C. for 2 hr. or more; if aged with $AlEt_2Cl$ at −78°C., the vanadates were inactive. The stereoregulating ability ofthe various vanadates under these conditions (Table II) was about the same as that of the VCl_4-AlEt_2Cl combination. Natta, Zambelli, and Pasquon[2,3] have reported that V(III) acetylacetonate is also an effective catalyst component.

The metal alkyls, $Al(C_6H_5)_2Cl$ and $AlEt_2Br$, form syndiotactic-regulating catalysts when combined with VCl_4. The whole polymer formed with the $AlEt_2Br-VCl_4$ catalyst has both long syndiotactic sequences (IR syndio index = 1.0) and long isotactic sequences; polymer from $Al(C_6H_5)_2Cl-VCl_4$ contained long syndiotactic, but no long isotactic sequences. Zambelli et al. reported[3] that no syndio polymer was formed when $AlEt_2Br$ was used with VCl_4. They related this finding to the structure of the site which they envisaged and postulated that only when X = Cl in the AlR_2X-VCl_4 catalyst did syndiotactic propagation take place. The present finding that $AlEt_2Br$ is effective requires a modification of their view.

Under comparable preparative conditions we have found $AlMe_2Cl-VCl_4$, $AlEt_2Cl-VCl_4$ and $Al(C_6H_5)_3-VCl_4$ catalysts to be similarly specific, i.e., IR syndio indices of about 1 were found for the formed polymers.

The branched α-olefins, 3-methyl-1-butene and 3,3-dimethyl-1-butene were polymerized with the $AlMe_2Cl-VCl_4$ catalyst in the temperature range −50 to −78°C. Infrared spectra and pyrolysis gas-liquid chromatography patterns of the obtained polymeric products were very similar to those of polymers produced by $AlCl_3$ catalysis. This suggested that both 1,2- and 1,3-type addition polymerization had taken place. Cationic polymerizations of this type have been reported recently for a number of higher α-olefins.[11,12] These findings suggest that the above catalyst must have had some cationic character for this type of addition to occur, since the coordinated-anionic type polymerization is presumed to take place by a 1,2 addition only.

As noted by Natta, Zambelli, and Pasquon,[2,3] the syndio-regulating ability of the $AlR_2Cl-VCl_4$ catalyst is increased by certain Lewis bases, notably anisole. We have found other additives to be similarly effective under certain conditions; all polymerizations were carried out at −78°C. (Table III).

TABLE III
Effect of Additives other than Anisole[a]

Additive	Amount additive, ml.	Polymerization time, hr.	Polymer		Catalyst preparation[b]
			Yield, g.	IR syndio index	
Cyclohexene	0	5.0	5.0–13.1	0.86–1.0	A
"	2	"	8.2	0.86	B
"	5	"	2.7	1.1	B
"	10	"	0.8, 2.0	1.5, 1.3	B
"	20	"	0.4	1.7	B
"	0	1.5	0.15	1.2, 1.3, 1.4, 1.4 (4 experiments)	C
"	10	"	0.15	1.2, 1.4 (2 experiments)	D
Oxygen	0	5.0	0.5	1.2	E
"	45	"	0.1	1.4	F
"	75	"	0.1	1.8	F
"	75	"	0.1	1.4	G
"	100	"	0.1	1.8	G
tert-Butyl perbenzoate	0	1.5	0.15	1.2, 1.3 (2 experiments)	H
"	0.25	"	0.15	2.3, 2.5 (2 experiments)	I

[a] Procedure: All polymerizations were carried out in 8-oz. bottles (method 1). The catalyst components consisted of 5.0 mmole $AlEt_2Cl$ (1.5M), 1.0 mmole VCl_4 (0.65M), and additive when used. For all polymerizations 100 ml. heptane and 25 g. propylene (added in condensed form) were used. Polymerization was at −78°C. for the indicated times.

[b] Description of catalyst preparation as designated by letters A to I: (A) $AlEt_2Cl$ was added to precooled (−78°C.) heptane solution of VCl_4, the mixture was warmed to and aged at −45°C. for $^1/_2$ hr., cooled to −78°C., and used as catalyst; (B) same as A except that precooled (−78°C.) cyclohexene was also added to the prepared catalyst; (C) same as A, except that the catalyst was aged at −78°C. for $^1/_2$ hr.; (D) same as C except that cyclohexene was also added; (E) a solution of VCl_4 in heptane was cooled to −78°C. and then $AlEt_2Cl$ was added; (F) same as E except oxygen was first added to the heptane solution of VCl_4 at 25°C. before it was cooled to −78°C.; (G) oxygen was added to $AlEt_2Cl$ at 25°C., the mixture was then cooled to −78°C. and VCl_4 was then added; the mixture was aged at −45°C. for $^1/_2$ hr. and then cooled to −78°C.; (H) VCl_4 was added to a precooled (−78°C.) solution of $AlEt_2Cl$ in heptane; (I) same as H except that *tert*-butyl perbenzoate was first added at 25°C. to the $AlEt_2Cl$–heptane solution and the mixture was maintained at 25°C. for 5 min. before it was cooled to −78°C., and the VCl_4 was then added.

Cyclohexene (2–20 ml.) was found effective if it was added to the catalyst which was previously aged at −45°C. for $^1/_2$ hr. It increased the IR syndio index from 0.8 to 1.7. The cyclohexene influence was absent if the catalyst components were mixed and aged at −78°C.

Oxygen was found effective if it was added at ambient temperatures to VCl_4 and then the mixture was cooled to −78°C. before $AlEt_2Cl$ was added. The IR syndio index was increased from 1.1 to 1.8 by addition of 75 ml. pure oxygen to a heptane solution of 1.0 mmole VCl_4.

tert-Butyl perbenzoate was found effective if it was added to $AlEt_2Cl$ at ambient temperature, and the mixture was cooled within 5 min. to −78°C. and VCl_4 was then added. In this way the IR syndio index was increased from 1.1 to 2.5.

Only minute traces of polymer were obtained from butene-1 after many hours under polymerization conditions which were satisfactory for propylene (expt. 4, Table I). However, rapid copolymerization immediately took place at −78°C. when ethylene was slowly bubbled into a mixture rich in butene-1 (40 g. butene-1, 25 cc. heptane). The copolymer obtained was elastomeric and absorbed strongly at 13.2 μ in the infrared, showing the presence of butene-1 units; the doublet at 13.7 and 13.9 μ characteristic of long methylene sequences was absent.

MECHANISM OF SYNDIOTACTIC PROPAGATION

The syndiotactic-regulating capacity of the apparently homogeneous catalysts derived from a variety of vanadium compound–metal alkyl combinations is influenced strongly by polymerization temperature and by a variety of additives such as anisole, oxygen, peroxides, etc. We join Zambelli et al. in their view that the polymerizations are of the coordinated anionic type and that an alkylated vanadium species is an essential part of the active site.[3]

The rapid copolymerization of ethylene and butene-1, even though butene-1 homopolymerizes very slowly, suggested that steric interactions between substituents of the last added and the new monomer units dominate the transition state for propagation. This prompts us to suggest that the same factor is mainly responsible for the syndiotactic preference in propylene polymerization. The nature of other groups attached to vanadium appears to be a less important factor in determining syndiotactic

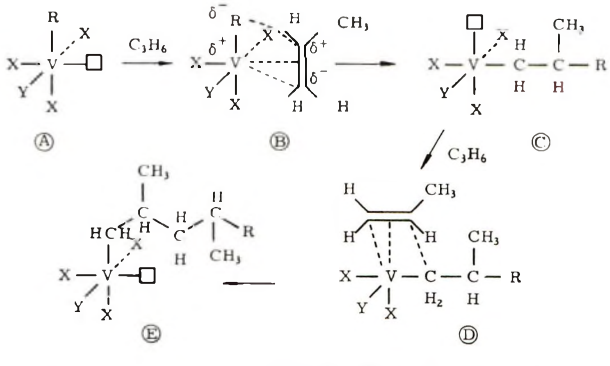


Fig. 4. Suggested model for syndiotactic propagation.

specificity, since differently structured vanadium compounds, combined with $AlEt_2Cl$, have similar stereoregulating abilities. Based on these ideas we would like to suggest a useful working model which, we believe, can qualitatively accommodate the experimental results. We visualize an octahedral vanadium complex containing an R group (the growing chain after addition of monomer to an alkyl group derived from the organoaluminum compound) as one of the ligands and an open position or vacancy (structure A, Fig. 4).

Essential features of the mechanism are as follows.

(*1*) Propylene is so complexed that its CH_2 and CH groups can develop bonds with vanadium and the R group, respectively (the V—R bond being polarized as shown in Fig. 4) in a concerted four-center reaction. As the reaction proceeds, partial ionic character, $^{\delta\ominus}\mathrm{CH_2}{=\!=\!=}\mathrm{CH}^{\delta\oplus}\text{—}\mathrm{CH_3}$, develops, and *cis*-opening of the double bond and head-to-tail enchainment result. The opposite complexing mode will seldom be fruitful because a less stable polarization of the double bond is required, $^{\delta\oplus}\mathrm{CH_2}{=\!=\!=}\mathrm{CH}^{\delta\ominus}\text{—}\mathrm{CH_3}$. No steric objections to the latter complexing mode exist.

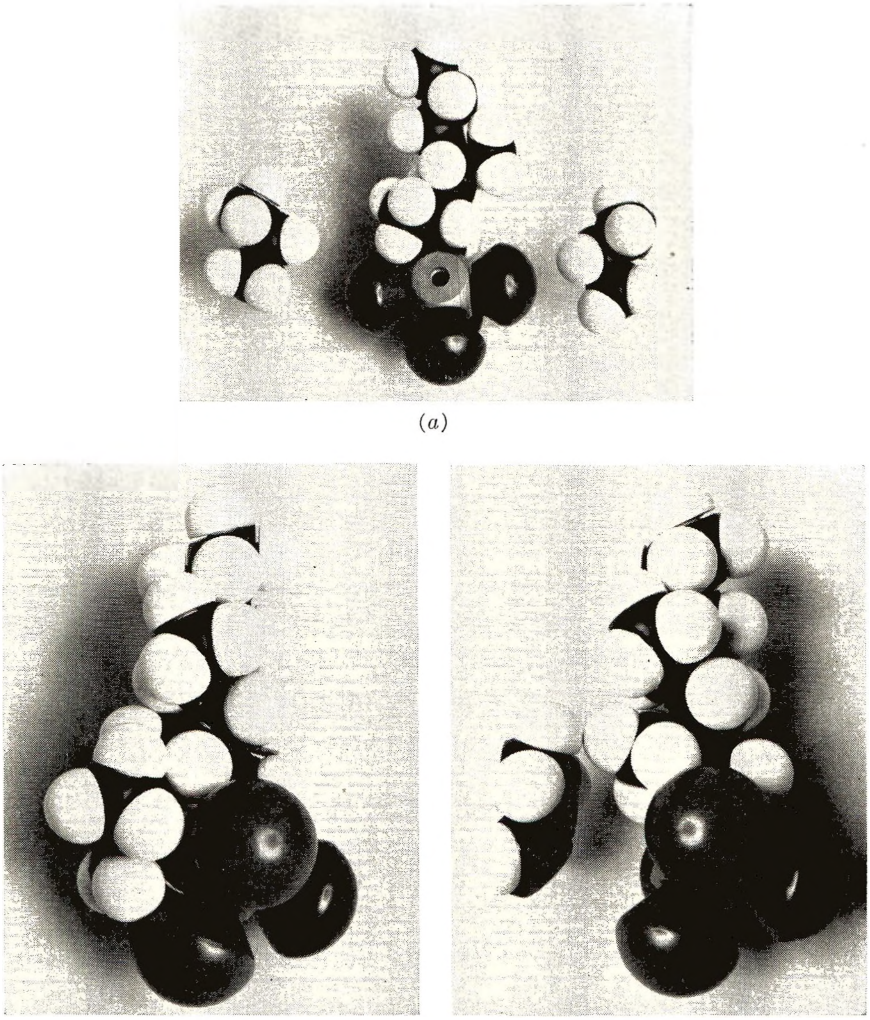
(*2*) The R group and vacancy exchange ligand positions with each growth step (Fig. 4, structure C). Alternatively, the new monomer might be inserted directly into the V—R bond without exchange of ligand positions. As far as the proposed mechanism is concerned, the end results are equivalent.

(*3*) Rotation about the R—V bond is not completely free. Specifically, it is difficult for the CH_3 group of the last added monomer unit to pass over the adjacent chlorine (or other) ligand, as can be seen clearly in models. Carbon–carbon bonds along the chain rotate freely to expose the vacant ligand position for another complexing step (Fig. 5*a*).

(*4*) Keeping feature (*1*) in mind, there are still two orientations of monomer possible (Fig. 5*a*). One of these, with its methyl group directed away from the methyl group of the last added unit, permits a close approach to vanadium (Fig. 5*b*) and leads to syndiotactic placement. In the other, methyl–methyl repulsion makes close approach to vanadium difficult (Fig. 5*c*); if approach to bonding distance is achieved, isotactic placement results.

(*5*) Isotactic and syndiotactic placements are equally probable if the rotational barrier discussed in (*3*) is surmounted, e.g., at higher temperatures or with smaller ligands. In this event, methylene hydrogens attached to the carbon atom directly bound to vanadium, rather than the methyl group and hydrogen atom attached to the second carbon atom in the chain, face the vacancy and both monomer orientations are equally probable.

Various catalyst combinations will have different stereoregulating capacities because the detailed structure of the complex will be different. Specifically, the magnitude of the rotational barrier, hence the stereospecificity, depends on the size of the central atom and the nature of the ligands adjacent to the vacancy. Zambelli et al.[3] have suggested that a complex of $RVCl_2$ with an aluminum alkyl halide might be the active site. This would



(a)

(b) (c)

Fig. 5. Model of complex: (a) front view of octahedral complex and two possible orientations of propylene molecules (the latter are shown after double-bond opening; (b) side view showing monomer orientation to minimize methyl–methyl repulsion and allow close approach to vanadium; (c) side view showing monomer orientation with high methyl–methyl repulsion preventing close approach to vanadium.

represent a specific example of our general model if ligand Y (Fig. 4) were considered a halogen bridge to the aluminum alkyl.

The differences and similarities between our model and Cossee's isotactic model[13] in its present form[14] are instructive. In both mechanisms, the center is considered to be an octahedral complex of a transition-metal atom having an alkyl ligand and a vacant ligand position for complexing the monomer. In the homogeneous case the monomer complexing mode leading to head-to-tail enchainment is energetically favored, while in the heterogeneous case it is the only orientation permitted by the crystal geometry. In homogeneous catalysis, the monomer is oriented such as to minimize repulsions between the methyl groups of the new and last added monomer units; in heteroogeneous catalysis, a particular, invarient orientation of the monomer methyl group is forced by the crystal structure. Both mechanisms employ a four-centered growth step during which the R group and vacancy may exchange ligand positions. In Cossee's proposal the R group returns to its original position between growth steps. The driving force for this rearrangement is a large difference in crowding about the two octahedral positions. Thus, growth always occurs in one stereochemical sense, e.g., clock-wise. This feature, combined with fixed orientation of the monomer methyl group, produces isotactic enchainment; a syndiotactic placement results whenever one propagation step follows another without an intervening rearrangement of R and vacancy, according to Cossee. With homogeneous catalysts, rearrangement or lack of rearrangement of R and vacancy is of no consequence.

On the basis of the above ideas and our present knowledge of Ziegler catalysis, we conclude that (*a*) highly isotactic polymerization of α-olefins is extremely difficult except with heterogeneous catalysts, (*b*) homogeneous catalysts will produce atactic* to syndiotactic structures, with lower temperatures favoring the latter, and (*c*) more exposed heterogeneous sites[6] may produce syndiotactic polymers, even at relatively high temperatures, if crowding about the center is such as to combine features of Cossee's mechanism with ours. For example, crystal geometry might favor a particular monomer orientation but not the postulated rearrangement of R and vacancy between growth steps, or methyl–methyl interactions may determine monomer orientation while crystal geometry might be responsible for a very large barrier to rotation about the V—R bond.

Intuitively, we feel that the mechanisms for iso- and syndiotactic Ziegler polymerization of α-olefins should be very similar. Although the ideas expressed above require much further development, they do begin to show how subtle changes in catalyst structure and attendant changes in one basic mechanism can account for highly isotactic, to atactic, to highly syndiotactic propagation.

CHARACTERIZATION OF SYNDIOTACTIC POLYPROPYLENE

The polymers prepared as described in the foregoing were characterized in a number of ways.

Infrared Absorption

Like Zambelli et al., we have used the infrared absorbance ratio, $A_{11.53\mu}/ {}^1/_2(A_{2.32\mu} + A_{2.35\mu})$, to provide a relative index of syndiotacticity. Figure 6 presents the spectrum of a 66% crystalline sample, IR syndio index = 2.4; values for other samples ranged from 0 to 2.6. A different IR index, r_B, em-

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* Equal numbers of isotactic and syndiotactic diads distributed randomly.

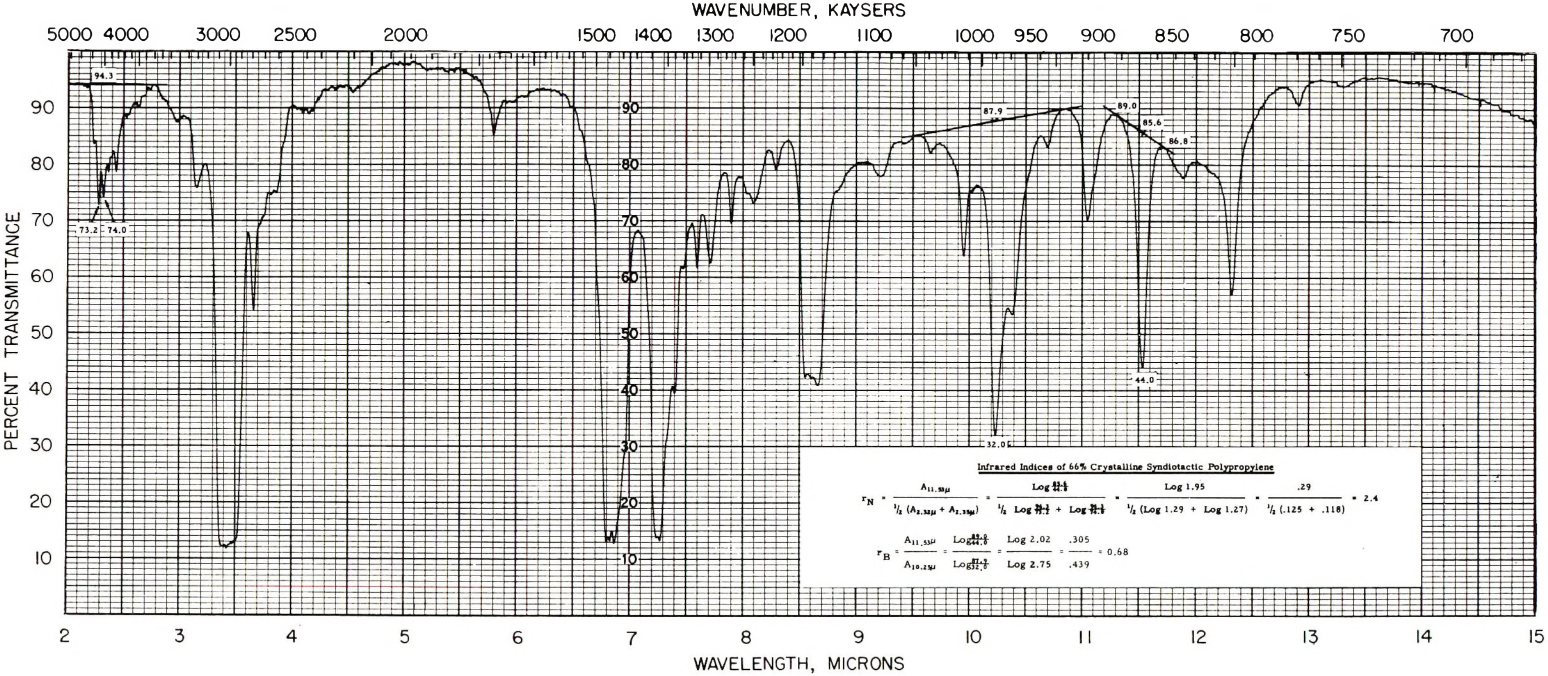

Fig. 6. Infrared spectrum of 66% crystalline syndiotactic polypropylene. Indices: $r_N = A_{11.53\mu}/{}^1/_2\,(A_{2.32\mu} + A_{2.35\mu}) = \log\,(85.6/44.0)/{}^1/_2\,[\log\,(94.3/73.2) + \log\,(94.3/74.0)] = \log 1.95/{}^1/_2\,(\log 1.29 + \log 1.27) = 0.29/{}^1/_2\,(0.125 + 0.118) = 2.4$; $r_B = A_{11.53\mu}/A_{10.25\mu} = \log\,(89.0/44.0)/\log\,(87.9/32.0) = \log 2.02/\log 2.75 = 0.305/0.439 = 0.68$.

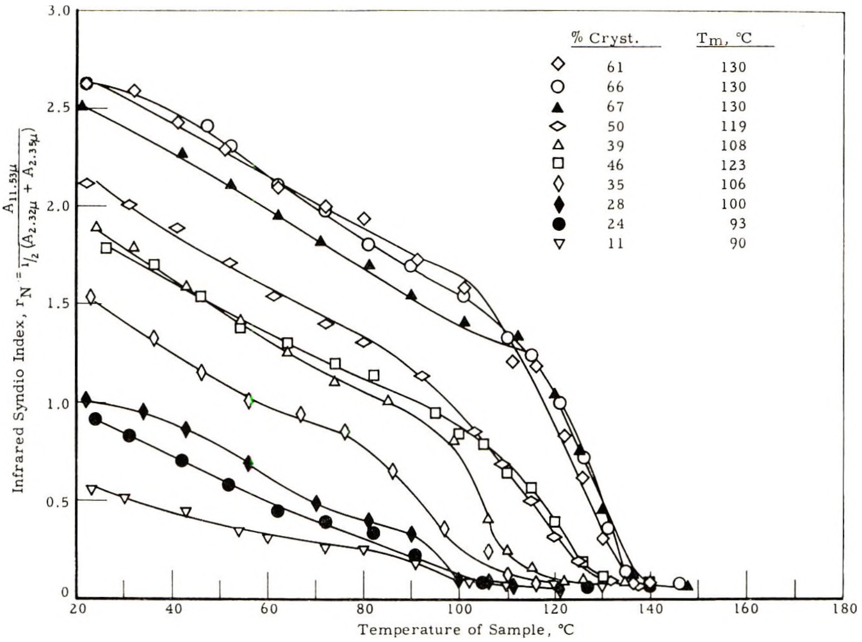

Fig. 7. Changes in IR syndio index with increasing sample temperature. Crystallinity from density assuming unit cell density = 0.90; T_m is the temperature at which 88% of 11.53 μ band intensity is lost.

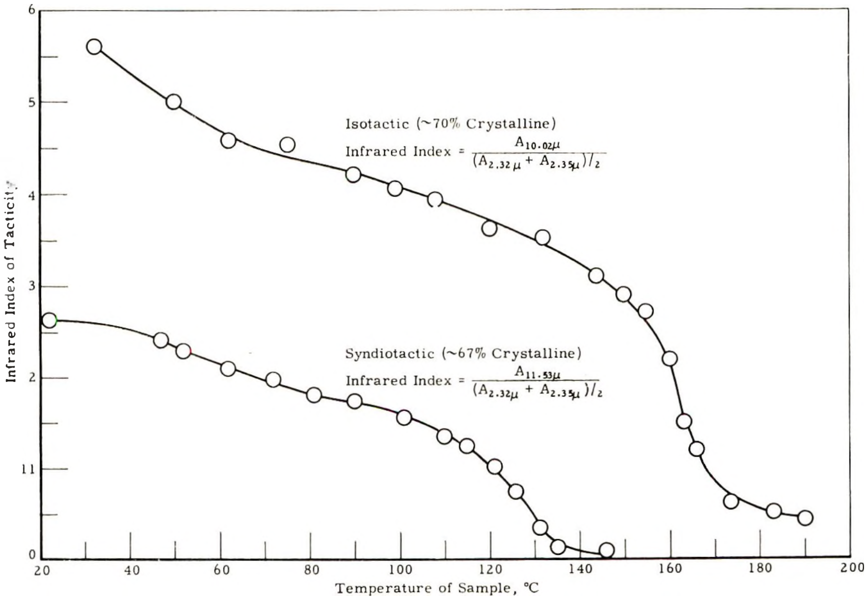

Fig. 8. Changes in the IR isotactic and IR syndio indices with increasing sample temperature.

ploying the band at 10.25 μ as reference for the 11.53 μ band, is also shown in Figure 6. This index is less satisfactory, as the 10.25μ band intensity is temperature-sensitive and the range of index values for various samples was smaller (0–0.7). The complete absence of absorption at 995 cm.$^{-1}$ (10.02 μ) where isotactic samples absorb strongly was confirmed by high-resolution infrared spectra. Figure 7 shows the indices for a number of samples as a function of sample temperature. Because the samples tended to flow and distort near the melting point, the temperature at which 88% of the original band intensity disappeared was arbitrarily taken as the melting point. The true infrared melting points are probably somewhat higher.

Figure 8 compares the changes in the IR indices for isotactic and syndiotactic samples as a function of temperature. Both samples were about 68% crystalline. The temperature for 88% loss of the respective tacticity band intensities was 130°C. for syndiotactic and 169° for isotactic polypropylene.

Syndiotactic polypropylene sample density and infrared index correlated well.[5,15]

Nuclear Magnetic Resonance (NMR)

Figure 9 is the NMR spectrum (100 Mcycles/sec.) of a 30% crystalline syndiotactic sample; more crystalline samples had very similar spectra. It was not possible to discriminate quantitatively among the samples. Until

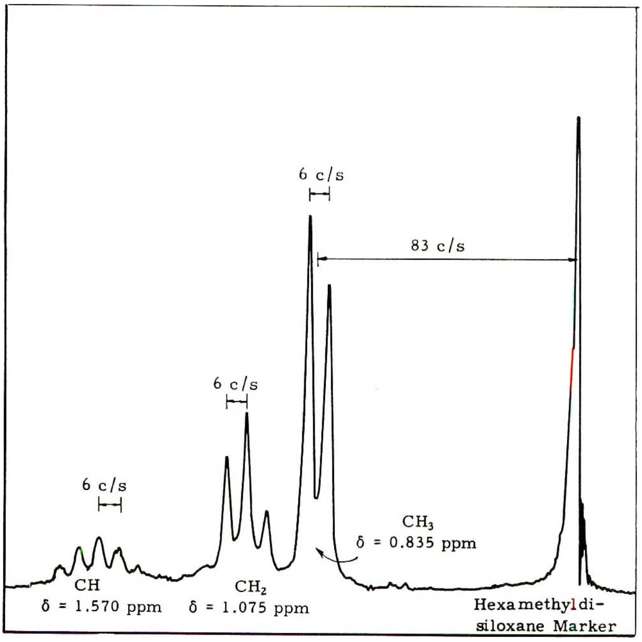

Fig. 9. NMR spectrum (100 Mcycle/sec.) of 30% crystalline syndiotactic polypropylene (sample 7964–406). Varian spectrometer; 30 wt.-% solution in *o*-dichlorobenzene; analysis at 170°C.

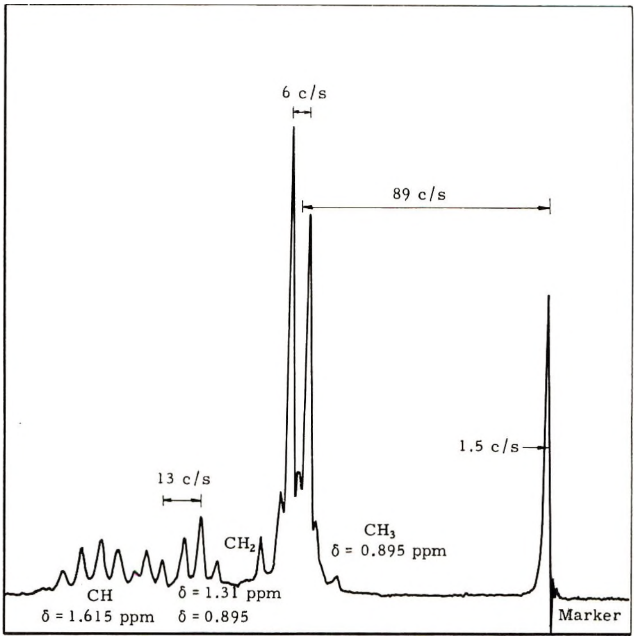

Fig. 10. NMR spectrum (100 Mcycle/sec.) of 65% crystalline isotactic polypropylene. Varian spectrometer; 30 wt.-% solution in *o*-dichlorobenzene; analysis at 170°C.

better resolution is achieved, NMR spectra serve only to show that the samples are highly syndiotactic and free of detectable isotactic or even heterotactic resonances (see Figure 10, the spectrum of a highly isotactic sample, and Natta et al.[16]).

Solubility

Unlike isotactic polypropylene, highly crystalline syndiotactic polypropylene samples were readily soluble in ether and in aliphatic or aromatic hydrocarbons at 40°C. or below. Like Natta, Zambelli, and Pasquon,[2,3] we were unable to isolate more crystallizable fractions from the whole sample by solvent fractionation.

Crystallinity Measurements

Highly syndiotactic polypropylene samples closely resembled highly isotactic polymer in physical appearance. Both were obtained from the polymerizations as white, free-flowing powders. Spherulitic crystallization was observed only with the most regular samples (IR indices of 2.0 or higher).

The crystallinities of annealed samples, as calculated from the densities were between 0 and 68%, assuming a unit cell density of 0.90 g./cc.[2] and an amorphous density of 0.854 g./cc.[15].

Birefringence

Melting points from disappearance of birefringence could be obtained only with the most crystalline samples. Figure 11 shows the loss of birefringence with temperature for an isotactic and a syndiotactic sample.

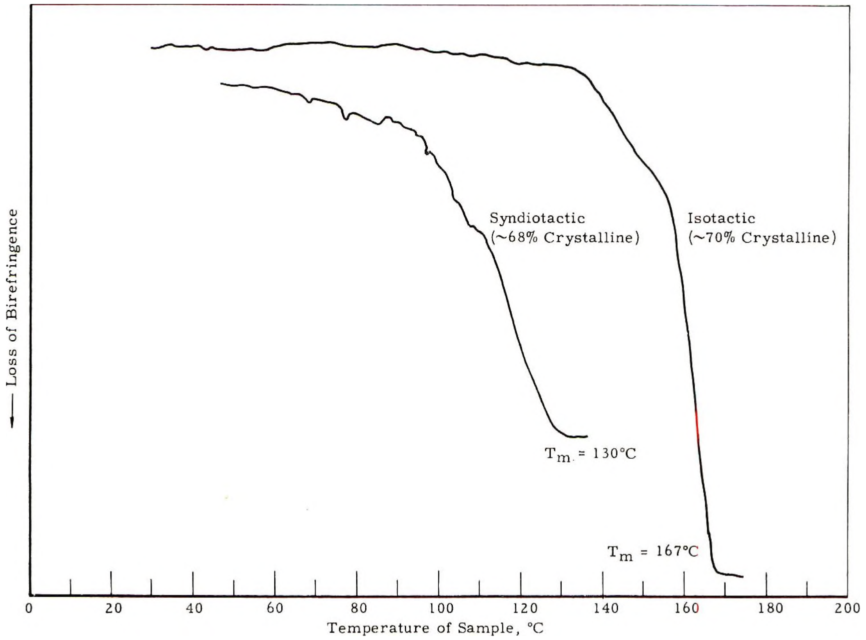

Fig. 11. Loss of birefringence with increasing temperature for isotactic an syndiotactic polypropylenes.

Differential Thermal Analysis

We examined the entire family of syndiotactic polypropylene samples by differential thermal analysis (DTA). The maximum temperature of the melting endotherm was taken as the melting point (Fig. 12).

With all of the polymers we observed two maxima. The intensity of each peak depended on the crystallinity of the sample. The higher-melting peak was more intense for the more crystalline samples while the lower-melting peak was more intense for less crystalline samples. We attribute the high-melting peak to the helical form and the lower-melting peak to the planar[17] form of the syndiotactic polypropylene. However, we have no direct evidence on this point. Both forms have been established by Natta and co-workers.[1,17] Melting points of 130°C. (helical peak) were found for samples having about 68% crystallinity. Finally, that the above values (infrared, birefringence, and DTA) were true crystalline melting points was confirmed by x-ray diffraction analysis (Fig. 13). Changes in the reflection intensity at $2\theta = 12.2°$ were noted during heating of a highly crystalline

(68%) syndiotactic sample. At 127 ± 2°C., this reflection became very weak; when the temperature was raised a few degrees more the sample lost its shape and flowed. The above value is very close to that found by the other methods.

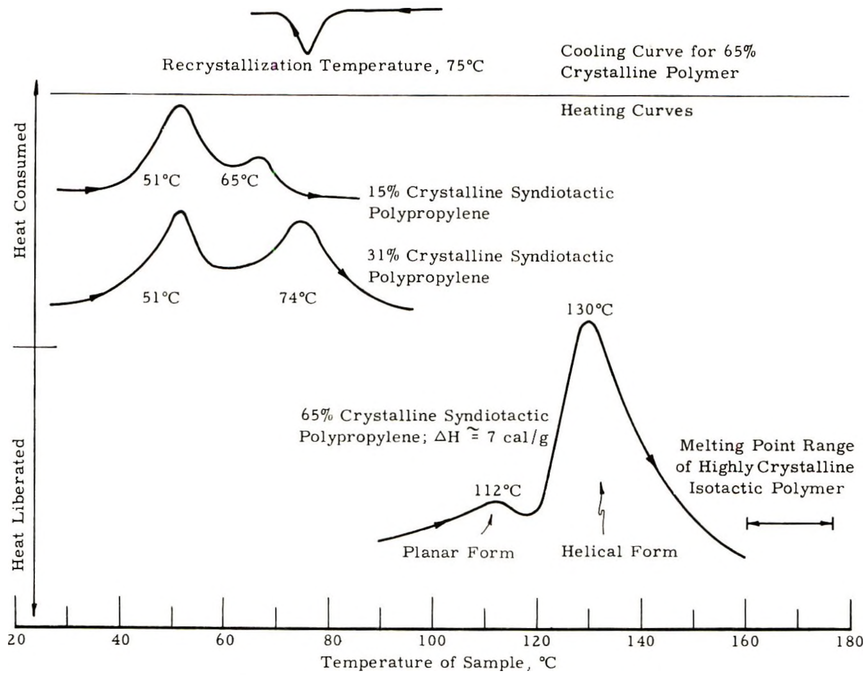

Fig. 12. Differential thermograms of syndiotactic polypropylenes having different crystallinities.

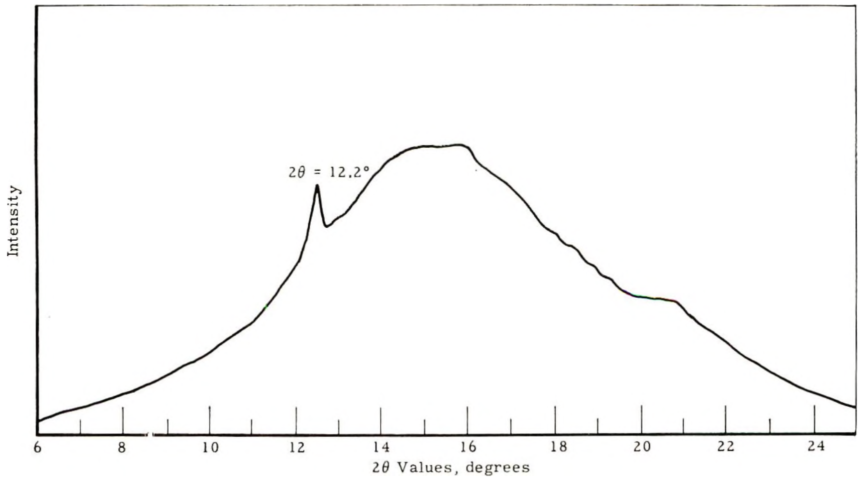

Fig. 13. X-ray diffraction trace of 68% crystalline syndiotactic polypropylene heated to and maintained at 127 ± 2°C.

Heat of Fusion

The heat changes on melting and recrystallizing syndiotactic polypropylene samples were quite low. For example, a 7 ± 1 cal./g. endotherm was observed for the melting of a sample having a density of 0.884 g./cc. Assuming amorphous and unit cell densities of 0.854[15] and 0.90,[2] respectively, calculated crystallinity is 65% and the calculated heat of fusion is 450 ± 65 cal./mole of monomer repeat units. This compares with a value of 2150 ± 100 cal./mole of repeat units obtained by us for isotactic samples and a value of 2400 ± 300 cal./mole obtained by Kershenbaum et al.[18] by essentially the same method.

The extremely low heat of fusion for syndiotactic polypropylene is not understood and deserves further study.

Melting Points of Syndiotactic Polypropylene

As seen in the last section, even the most crystalline syndiotactic polypropylene samples had relatively low melting points. In Figure 14 the melting points for our syndiotactic samples (from DTA and infrared data) and for Newman's[19] isotactic samples (from dilatometry) are plotted against the corresponding crystallinities. The syndiotactic samples melt about 40°C. below their isotactic counterparts. We reached the same conclusion earlier[5] from a different treatment of the data.

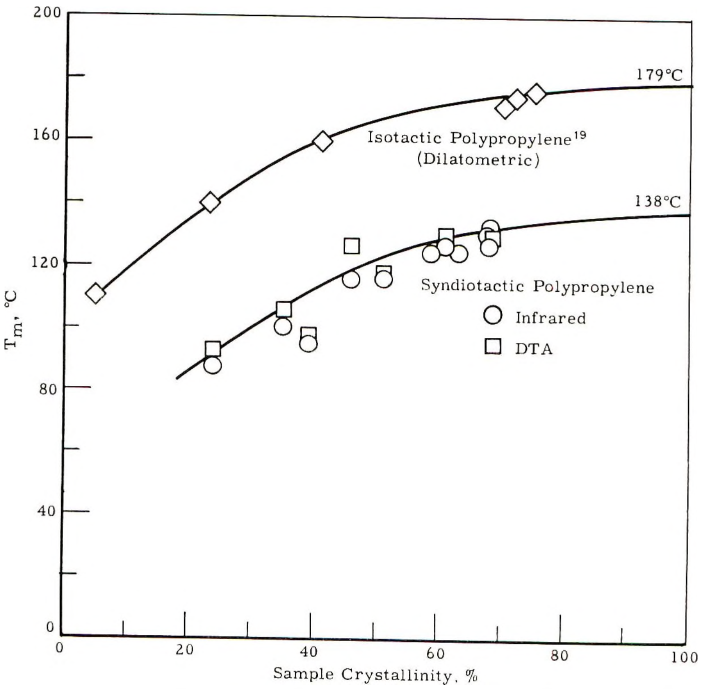

Fig. 14. Extrapolated melting point of syndiotactic and isotactic polypropylenes from a plot of per cent crystallinity vs. temperature.

Glass Transition Temperature

The glass transition temperature at a frequency of about 1 cps (torsion pendulum) was very near 0°C., the same as for isotactic polypropylene.

Overall Comparison Between Isotactic and Syndiotactic Polypropylene

Syndiotactic and isotactic polypropylene differ in that the former has (*a*) a lower unit cell density (0.90 versus 0.94 g./cc.)[1,2] (*b*) a much lower heat of fusion (ca. 450 versus 2350 cal./unit), (*c*) a lower perfect crystal or ultimate melting point (ca. 160°C. versus 189–200°C.)[5] and lower melting points at the same crystallinity, and (*d*) a much higher solubility in ether and aliphatic hydrocarbons.[1–3] These differences are mutually consistent and indicate a large difference in the intermolecular forces present in syndiotactic and isotactic polypropylene.

EXPERIMENTAL

Polymerization Procedure

The polymerizations were carried out in two types of reaction vessels: (*1*) 8-oz. bottles which were sealed with Hycar rubber gaskets and metal caps and (2) a glass tube reactor.

All materials were handled under a nitrogen atmosphere.

When bottles were used as reaction vessels (method 1) the reactants were added in amounts specified in the tables and figures of this paper, $AlEt_2Cl$ was always added to VCl_4 in heptane previously cooled to −78°C. unless otherwise indicated. Propylene was added in the condensed form and cooled to −78°C. before being added. The bottles were enveloped with Dry Ice for the −78°C. polymerizations. The bottles were hand-agitated several times in the course of polymerization.

The second procedure (method 2) utilized a specially designed glass reactor tube which was attached by ground glass contact to a head having the appropriate outlets and inlets. Vertical agitation was accomplished by an air-driven motor. With a constant flow of nitrogen an inert atmosphere was maintained over the reaction mixture. Materials were syringed into the solvent through serum caps.

For the −95°C. experiments a special reactor tube was designed. An inner reaction tube was enveloped with a glass chamber containing isopentane (melting point −160°C.). The −95°C. temperature of the polymerization was maintained by lowering and raising the reactor tube from a Dewar containing liquid nitrogen. The isopentane-filled outer chamber which jacketed the inner tube insulated the reaction mixture and allowed the reaction temperature to remain nearly constant. This temperature was actually measured by means of a thermocouple placed in a thermowell which was immersed into the reaction mixture.

Heptane was purified by passing it through silica gel and then distilling from CaH_2. Toluene was washed with dilute H_2SO_4 and distilled water (until acid-free), dried first with $MgSO_4$, and then distilled from CaH_2.

$ZnEt_2$, $ZnEtCl$, and $Al(C_6H_5)_2Cl$ were purchased from Orgmet, Wenham, Massachusetts. VCl_4 and vanadates were purchased from Stauffer Chemical Company, Richmond, California.

Analytical Methods

Infrared. Films of polymer were compression-molded between aluminum foil sheets or pressed with slight pressure between NaCl plates at 150°C. The samples were maintained at 100°C. for 16 hr. and at about 25°C. for 48 hr. A spectrum of highly syndiotactic crystalline sample showing the backgrounds used to determine absorbance at 2.32–2.35 μ and at 11.53 μ is presented in Figure 6. The IR syndio index is defined as the ratio $A_{11.53\mu} / {}^1/_2(A_{2.32\mu} + A_{2.35\mu})$, in accordance with the suggestion of Zambelli et al.[3] Unless noted otherwise, the analyses were made at ambient temperatures. For analyses at higher temperatures the samples were placed between NaCl plates placed in an insulated box maintained within ±1°C. of the desired temperature. A Beckman IR-4 spectrophotometer was used.

Birefringence. A polarizing microscope with hot stage, a sensitive photometer, and an X–Y recorder were used to record birefringence as a function of temperature. This instrument was constructed by Dr. H. Lunk of these laboratories, who also helped us in the analyses. A heating rate of 5°C./min. was used. The samples to be examined were prepared by fusing the polymer at 150°C. between thin microscope cover glasses and then maintaining them at 100°C. for over 16 hr. and at about 25°C. for over 48 hr.

DTA. A locally constructed (by Mr. J. Badley) unit called the differential millicalorimeter was used. This is a differential thermal analyzer with high sensitivity and good repeatability in the measurement of heats of transition. Heating rates of about 20°C./min. were used. These measurements were supervised by Mr. J. Badley. The examined samples were prepared by fusing the polymers at 150°C., annealed approximately 30°C. below their melting points, and maintained at room temperature for over 48 hr.

X-Ray. The x-ray diffraction melting point was determined by Dr. T. C. Yao and Mr. J. Holst. The polymer sample was fused at 150°C. and subsequently annealed (100°C., 16 hr.) before analysis.

Densities. Densities were determined at 25°C. by density-gradient methods on similarly fused and subsequently annealed polymer samples. These measurements were supervised by Mr. R. J. Dougherty.

The authors wish to acknowledge the technical assistance of Mr. D. W. Penhale in carrying out the preparative and characterization studies.

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Résumé

La préparation et la caractérization de polypropylène syndiotactique ont été rapportées. L'influence des variables de la polymérisation sur la capacité régulatrice syndiotactique du catalyseur VCl_4–$AlEt_2Cl$ a été étudiée. Des vanadates peuvent être substitués au VCl_4 et $Al(C_6H_5)_2Cl$ ou $AlEt_2Br$ ou $AlEt_2Cl$ dans des conditions appropriées. L'hydrogène fonctionnait comme agent de transfert de chaîne pour le catalyseur $AlEt_2Cl$–VCl_4 et les polymérisations qui étaient terminées avec des alcools tritiés fournissaient des polymères contenant du tritium lié. Le pouvoir syndiorégulateur du catalyseur $AlEt_2Cl$–VCl_4 était accrû dans des conditions spécifiques lorsque le cyclohexène, l'oxygène ou le benzoate de *tert*-butyle y était incorporé. Un mécanisme de polymérisation est proposé. Conformément à ce mécanisme la préférence pour un mode de complexation du monomère qui minimise les répulsions stériques entre les groupes méthyles des dernier et futur unités monomériques est responsable pour la propagation syndiotactique. La caractérisation des polymères comprenait la détermination des indices de syndiotacticité par infra-rouge, les points de fusion (65–131°C), les températures de transition vitreuse, les densités (0.859–0.885 g/cm^3), les spectres de résonance nucléaire magnétique, les biréfringences, les spectrogrammes d'analyse thermique différentielle, la solubilité et la chaleur de fusion $\sim$450 cal/mole).

Zusammenfassung

Die Darstellung und Charakterisierung von syndiotaktischem Polypropylen wird beschrieben. Der Einfluss der Polymerisationsvariablen auf die Fähigkeit des VCl_4–$AlEt_2Cl$-Katalysators zur syndiotaktischen Anordnung wurde untersucht. Unter geeigneten Bedingungen konnten Vanadate für VCl_4 und $Al(C_6H_5)_2Cl$ oder $AlEt_2Br$ für $AlEt_2Cl$ substituiert werden. Wasserstoff wirkte beim $AlEt_2Cl$–VCl_4-Katalysator als Kettenüberträger, und Polymerisationen, welche mit tritiierten Alkoholen abgebrochen wurden, lieferten Polymere mit gebundenem Tritium. Die syndioregulierende Fähigkeit des $AlEt_2Cl$–VCl_4-Katalysators wurde unter spezifischen Bedingungen durch Einbringung von Cyclohexen, Sauerstoff oder *tert*-Butylperbenzoat erhöht. Ein Polymerisationsmechanismus wird vorgeschlagen. Nach diesem Mechanismus ist die Bevorzugung einer Monomerkomplexierung, welche die sterische Abstossung zwischen den Methylgruppen der neuen und der zuletzt addierten Monomereinheit auf ein Minimum bringt, für das syndiotaktische Wachstum verantwortlich. Die Charakterisierung erfolgte durch Bestimmung des Infrarotsyndiotaktizitätsindex, des Schmelzpunkts (65–131°C), der Glasumwandlungstemperatur, der Dichte (0,859–0,885 g/cm³), der kernmagnetischen Resonanzspektren, der Doppelbrechung, der differentielthermoanalytischen Spektrogramme, der Löslichkeit und der Schmelzwärme (~450 cal/Mol).

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NOTES

Selective Polymerization of 1-Pentene in the Presence of 2-Methyl-1-Butene

α-n-Olefins frequently occur with other terminal olefins from which they cannot be readily separated. Such an example is the mixture of 1-pentene (b.p. 30°C.) and 2-methyl-1-butene (b.p. 31.2°C.) which occurs in light catalytic gasoline. It seemed of interest to see if such a mixture could serve as a source for poly-1-pentene.

The Ziegler-catalyzed polymerization of 2-methyl-1-butene is not reported, but that of its lower homolog, isobutylene, is. An early report indicated that isobutylene is polymerized by a Ziegler catalyst, but that a rearranged polymer structure was obtained.[1,2] More recently, Bacskai and Lapporte have found that isobutylene polymerizes in the normal manner with a Ziegler catalyst at −30°C.[2] With some Ziegler catalysts, Al/Ti = 24 at 50°C. or $2AlEt_3$–$TiCl_3$ at −30°C., no polymer formation was observed.

We have found agreement with the latter observation, in that 1-pentene can be selectively polymerized in the presence of 2-methyl-1-butene with a $2AlEt_3$–$TiCl_3$ catalyst at ~50°C. The charged 2-methyl-1-butene does not polymerize and is recovered unchanged or as its 2-methyl-2-butene isomer.

The Ziegler catalyst was prepared by adding 2.3 g. (0.02 mole) of triethylaluminum to 1.6 g. (0.01 mole) of titanium trichloride (aluminum-reduced, Stauffer Chemical Company) in 50 cc. of *n*-heptane in a dry box according to a procedure previously described.[3] After the catalyst was prepared, the reaction flask was removed from the dry box and equipped, under a blanket of repurified nitrogen, with a paddle stirrer and a condenser fitted with a Dry Ice cold trap. A mixture of 10 g. (0.14 mole) of 1-pentene and 10 g. (0.14 mole) of 2-methyl-1-butene in 20 cc. *n*-heptane was added to the catalyst suspension with stirring. The reaction mixture exothermed from about 23°C. to 50°C. in about 15 min. When it was apparent that the exotherm had subsided, heat was applied and the reaction mixture was maintained at a temperature of 52–54°C. for 16.5 hr. At the end of this period, additional *n*-heptane was added to dissolve the polymer that had formed, and the insoluble catalyst was removed by centrifugation. Part of the *n*-heptane polymer solution was then distilled, and 52.2 g. of a cut distilling between 25 and 90°C. was collected. This fraction was analyzed by gas chromatography on a F & M 609 instrument equipped with 2 m. of 25% 2,4-dimethyl sulfolane on Chromosorb P maintained at 21°C. and showed no 1-pentene remaining. Calculations showed 2.6 g. of 2-methyl-1-butene and 7.4 g. of 2-methyl-2-butene were recovered, and this accounts for 100% of the charged 2-methyl-1-butene.

The remaining *n*-heptane solution was washed with dilute HCl and then added to methanol to precipitate the polymer. After drying, 10.0 g. of polymer was recovered. The intrinsic viscosity, determined in benzene at 26°C., was 0.94.

In another experiment utilizing the same amounts of catalyst and solvent, 5 g. (0.07 mole) of 1-pentene and 15 g. (0.21 mole) of 2-methyl-1-butene was added to the catalyst slurry. The reaction mixture again exothermed from about 23°C. to about 52°C. in a period of about 3.75 hr. At the end of this period more *n*-heptane was added to dissolve the polymer, and spent catalyst was removed by centrifugation. A distillation cut weighing 50.0 g. was taken at 25–90°C. Gas chromatographic analysis showed that the cut contained no 1-pentene, but did contain 11.45 g. of 2-methyl-1-butene and 4.10 g. of 2-methyl-2-butene. This accounts for 103% of the charged 2-methyl-1-butene.

The remaining *n*-heptane solution was added to methanol to precipitate the polymer. After drying for 2 days in the atmosphere and for about 13 hr. in a vacuum oven maintained at about 40°C., the polymer was found to weigh 5 g. This accounts for the 1-pentene charged.

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Proton Magnetic Resonance Spectra of Cyclopentadiene Polymers

It has been shown[1,2] that certain cyclopentadiene polymers, containing 1.0 ± 0.1 double bonds per C_5H_6 base unit, are characterized by unusual properties. In order to gain more information about the nature of the base units we have measured the proton magnetic resonance spectra of three typical members of this series. The polymers which were investigated and the signal positions of the proton magnetic resonance spectra (τ values) are given in Tables I and II. The τ values 4.26 and 4.29 are assigned to hydro-

TABLE I
Cyclopentadiene Polymers

Polymer	Method of preparation	Mol. wt. $\times 10^{+3}$	Color	λ_{max}, mμ	Proton acceptor properties	Electrical conductance[a]
E[b,c]	Catalysis by $SnCl_4$	3.5 ± 0.6	—	<235	–	–
F[b]	Polymer E + Cl_3CCOOH	2.3 ± 0.4	Brown-red	320	+	+
A[b]	Catalysis by Cl_3CCOOH	1.2 ± 0.1	Brown-red	360	+	+

[a] Of protonated polymers in solvent benzene.
[b] Data of French and Wassermann.[1]
[c] Data of French et al.[2]

TABLE II
Position of Proton Magnetic Resonance Signals and Ratios of Signal Areas, β (observed) in Carbon Tetrachloride, 33.5°C.

Polymer	τ values	β (observed)
E	4.26, 7.34, 7.75, 8.30	2.3 ± 0.2
F	4.29, 7.35, 7.77, 8.33	2.5 ± 0.3
A	4.26, 7.38,[a] 7.78, 8.33	4.6 ± 0.5

[a] Shoulder.

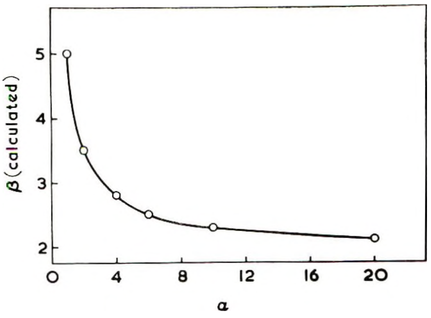
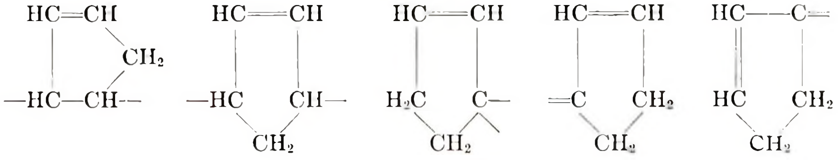


Fig. 1. Plot of α (= number of type A C_5H_6 units of polymer/number of type B C_5H_6 units of polymer) vs. β (calculated) = number of hydrogens of polymer bound to nonolefinic carbons/number of hydrogens bound to olefinic carbon.

gens bound to olefinic carbons and the other τ values in the range 7.34–8.33, to hydrogens bound to nonolefinic carbons.[3] The β (observed) in the last column of Table II are defined as the ratio of the number of hydrogens of polymer bound to nonolefinic carbons to the number of hydrogens of polymer bound to olefinic carbons; the β values are obtained by integration of the relevant signal areas. Figure 1 shows a plot of the ratios β (calculated) against the polymer composition in terms of types of C_5H_6 units.



Type A units

Type B units

Type A units contain two hydrogens attached to olefinic carbons, while type B units contain olefinic carbons without hydrogens. Both types of base units are compatible with the observed unsaturation of these polymers. The β (observed) values of polymers E and F are in the range 2.1–2.8, which indicates (see Fig. 1) that there are between 4 and 20 C_5H_6 units of type A per unit of the alternative type. In polymer A, on the other hand, the ratio β (observed) is at least 4.1, so that there should be about equal numbers of type A and type B units. It is not suggested that all the units of the latter type are aligned in such a manner as to give rise to only one sequence of conjugated double bonds. It is clear, on the other hand, that the formation of the polymer involves significant migration of hydrogens, as postulated before.[2]

Experimental

The polymers, prepared as described,[1,2] were purified and dried in a high vacuum, shortly before recording the spectra at 60 Mc./sec. on a Perkin-Elmer instrument. Exposure of the polymers to air was as short as possible. A typical spectrum is shown in Figure 2.

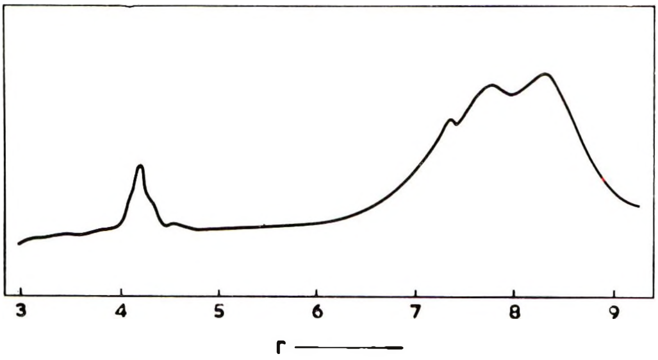


Fig. 2. Proton magnetic resonance of cyclopentadiene polymer A in carbon tetrachloride at 33.5°C. Concentration of polymer and tetramethylsilane about 10% and 1% respectively.

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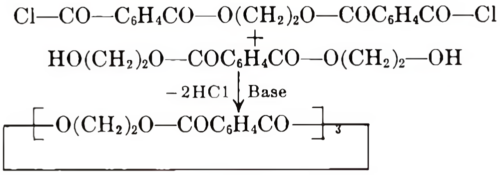
Synthesis of Cyclic Tris(ethylene Terephthalate)

In 1954 Ross et al.[1] isolated a crystalline substance with a melting point of 325–327°C. from trichloroethylene extracts of poly(ethylene terephthalate) films. Because of its properties the authors attributed to this compound the formula of a cyclic tris(ethylene terephthalate). This structure was confirmed later by Goodman and Nesbitt.[2]

Until recently attempts[3–5] to synthesize the cyclic tris(ethylene terephthalate) had failed. We have now succeeded in synthesizing the cyclic trimer by reacting the dichloride of the monomer dicarboxylic acid[6] with terephthalic acid–diethylene glycol under dilution conditions:[7]



$$\mathrm{Cl{-}CO{-}C_6H_4CO{-}O(CH_2)_2O{-}COC_6H_4CO{-}Cl}$$
$$+$$
$$\mathrm{HO(CH_2)_2O{-}COC_6H_4CO{-}O(CH_2)_2{-}OH}$$
$$-2\mathrm{HCl}\;\Big\downarrow\;\text{Base}$$
$$\left[\mathrm{O(CH_2)_2O{-}COC_6H_4CO}\right]_3$$

The starting materials were of high purity, and all experiments are carried out in the absence of moisture and carbon dioxide under nitrogen. *o*-Dichlorobenzene was used as solvent and *N*,*N*-dimethylaniline as base. From the resulting reaction mixture we isolated the cyclic trimer by extraction with trichloroethylene.

$(C_{10}H_8O_4)_3$ melted at 315–316°C. after recrystallization from ethyl acetate, *N*,*N*-dimethylformamide, and benzene. The mixed melting point with the isolated trimer was not depressed.

Analysis showed C, 61.96%; H, 4.37% (calculated: C, 62.5%; H, 4.2%).

Vapor pressure osmometry yielded values of 561, 535, 568, and 554 (average 554.5) for the molecular weight (calculated, 576).

Thin-layer chromatography in benzene–dioxane 10:1 gave an R_f value of 0.45. The material isolated from the polymer showed the same value.

Bands corresponding to hydroxyl and carbonyl groups were absent in the infrared spectrum.

Experimental

o-Dichlorobenzene (3.5 liters) was heated in a three-necked flask in a nitrogen atmosphere to 145–150°C. Then the following two solutions were added dropwise in equimolecular amounts during 1 hr.: (a) 1.580 g. $\mathrm{Cl{-}CO{-}C_6H_4CO{-}O\,(CH_2)_2O{-}COC_6H_4CO{-}Cl}$ (4×10^{-3}mole) in 250 ml. *o*-dichlorobenzene; (b) 1.016 g. $\mathrm{HO(CH_2)_2O{-}COC_6H_4CO{-}O(CH_2)_2{-}OH}$ (4×10^{-3} mole) plus 1.064 g. *N*,*N*-dimethylaniline (excess) plus 10 ml. hexamethylphosphoric acid triamide in 240 ml. *o*-dichlorobenzene. After the addition of the reactants, heating was continued for 3.5 hr. The reaction mixture was evaporated, and the oily residue was treated with cold water and kept for several hours at 0°C. The solid material (0.45 g.) was filtered off, dried, and extracted with trichloroethylene (Soxhlet) several times. After evaporation of the solvent, the residue was dissolved in dioxane–trichloroethylene, and the cyclic trimer was precipitated by addition of ether. On recrystallization from benzene or ethyl acetate the cyclic trimer (0.16 g.) separated in a highly crystalline form. The synthesis of other cyclic esters of the same type is now in progress.

We thank the Bundesministerium für Wirtschaft, Bonn and A.I.F. Köln, (Research Project 1033), for support of this work.

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Sulfonation of Polystyrene Crosslinked with Pure m*-Divinylbenzene*

We have previously reported[1] the rates of sulfonation of polystyrene crosslinked with pure *para*, 2:1/*m*:*p*-, and commercial divinylbenzenes. We have extended these studies to obtain data for the sulfonation of polystyrene crosslinked with pure *m*-divinylbenzene.

Experimental

The *m*-divinylbenzene used in the present studies was prepared from commercial divinylbenzene (Koppers 50–60%) by the method previously described.[2] Vapor-phase chromatograpic analysis (Perkin-Elmer Model 154-D, R column) showed the material to be 99.4% pure. The difficulty encountered previously[3] in the preparation of bead copolymers of polystyrene crosslinked with 8 mole-% *m*-divinylbenzene was eliminated by careful distillation of the divinyl monomer over potassium hydroxide to remove the traces of inhibitor used during chromatographic separation. The sulfonation was followed as previously described.[1] The capacities at different time intervals for 2 and 4 mole-% *meta* crosslinked beads are given in Tables I and II. The values reported are for one batch of each resin. The sulfonation data at 100°C. for the 8 mole-% crosslinked beads are given in Table III. The capacities were determined as previously described.[3]

Discussion

The kinetic studies on the sulfonation of polystyrene crosslinked with pure *p*- and pure *m*-divinylbenzenes show that under comparable conditions, the 8 mole-% *para* crosslinked beads sulfonate faster than do those crosslinked with 8 mole-% *m*-divinylbenzene. Thus at 100°C., the 8 mole-% *para* crosslinked beads sulfonate to a capacity of 5.12 meq./g. in 2 hr.,[3] whereas the corresponding *meta* crosslinked beads acquire a capacity of 4.5–4.9 meq./g. in 20 hr. at 100°C. At 80°C. the *para* crosslinked beads reach a capacity of 4.01 meq./g. in 4 hr. of sulfonation[1] while the *meta* crosslinked beads do not sulfonate during the same period.

We have reported an apparent activation energy for the sulfonation process of 40,190 cal./mole[1] for the 8 mole-% *para* crosslinked beads. The activation energy for the corresponding *meta* beads should be much greater than this value. The activation energies calculated for the 2 and 4 mole-% *meta* crosslinked beads by the method previously described[1] are 12,030 and 15,370 cal./mole, respectively. These values are not much different from those reported[1] for the corresponding *para* crosslinked beads.

The structural interpretations of the results obtained must take into account the differences in the reactivity ratio values in the copolymerization of styrene with each isomeric divinylbenzene. On the basis of values reported previously[4,5] for the styrene–*m*-divinylbenzene system, $r_1r_2 = 0.39$; for styrene–*p*-divinylbenzene, $r_1r_2 = 0.07$. The r_1r_2 values show that the alternating tendency should be more for styrene–*p*-divinylbenzene copolymer than it is for styrene–*m*-divinylbenzene copolymer. This alternating tendency in copolymerization involving small amounts of divinyl monomer should result in rapid exhaustion of the available divinyl monomer long before styrene is consumed.

The overall effect appears to be that the copolymerization of styrene with *p*-divinylbenzene results in a structure with a tightly crosslinked nucleus to which long chains of polystyrene are attached and in which much more pure polystyrene may be imbedded. In comparison, the styrene–*m*-divinylbenzene copolymer would be expected to have a structure in which the crosslinks are more widely distributed than in the styrene–*p*-divinylbenzene copolymer, and there is presumably less pure polystyrene forming in the last stages of polymerization.

In the sulfonation of 8 mole-% *para* crosslinked beads the sulfonating species is apparently able to permeate the polystyrene portion of the chain, if not the cluster of crosslinkages. With 8 mole-% *meta* crosslinked beads, the overall distribution of the cross-

TABLE I

Rates of Sulfonation of Polystyrene Crosslinked with 2 mole-% *m*-Divinylbenzene[a]

Temperature of sulfonation, °C.	Capacity, meq./g.[b]									
	5 min.	10 min.	15 min.	20 min.	30 min.	40 min.	60 min.	80 min.	100 min.	120 min.
80	0.56	1.95	3.15	3.87	4.77	5.17	5.36	—	—	—
60	—	0.12	—	0.70	1.58	2.36	3.60	4.23	3.83	5.19

[a] Bead copolymer prepared with 0.5% by weight dibenzoyl peroxide as initiator.

[b] Capacity after times stated. It is to be noted that capacity of the resin measures the extent of sulfonation and its rate of change is directly related to the rate of sulfonation.

TABLE II

Rates of Sulfonation of Polystyrene Crosslinked with 4 mole-% *m*-Divinylbenzene

Temperature of sulfonation °C.	Capacity, meq./g.												
	5 min.	10 min.	15 min.	20 min.	30 min.	40 min.	45 min.	60 min.	75 min.	90 min.	120 min.	150 min.	180 min.
80	0.44	1.33	1.88	2.45	3.61	4.35	—	5.11	—	5.25	—	—	—
60	—	—	0.093	—	0.76	—	1.33	1.86	2.44	3.01	3.82	4.53	5.17

TABLE III
Data on Sulfonation of Polystyrene Crosslinked with 8 mole-% *m*-Divinylbenzene at 100°C.

Dispersion agent used in copolymerization[a]	Initiator, concn. in copolymerization, %[b]	Capacity, meq./g.[c]
CMC	0.1	4.49
CMC	2.0	4.74[d]
PVA	0.5	4.88
CMC/PVA	0.5	4.73

[a] CMC: 0.5 g. of sodium salt of carboxymethyl cellulose ether in 250 ml. of distilled water; PVA: 1 g. of poly(vinyl alcohol) in 250 ml. of distilled water; CMC/PVA: 0.5 g. each of sodium salt of carboxymethylcellulose ether and poly(vinyl alcohol) in 250 ml. distilled water.

[b] Dibenzoyl peroxide used.

[c] Capacity after 20 hr. of sulfonation.

[d] Data of Wiley et al.[3]

links makes the permeation of the network rather difficult. Thus, the 8 mole-% *para* crosslinked beads sulfonate faster than the corresponding *meta* crosslinked beads at least under the conditions studied, and to higher levels with less degradation. As pointed out earlier,[1] a diffusion-controlled process is indicated in the sulfonation of these bead copolymers.

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Chain Transfer in Ethylene Polymerization. II.

In the first paper of this series,[1] a description was given of a technique for obtaining chain-transfer constants in ethylene polymerization at 1360 atm. and 130°C. Inasmuch as the ethylene–polyethylene bulk polymerization system is heterogeneous at these conditions (which are, except for this one drawback, very good conditions for making measurements) the technique involved using propane as a cosolvent to render the system homogeneous. Because propane is also a chain-transfer agent it was necessary to fit the data on other transfer agents to eq. (1), where $\overline{\mathrm{DP}}$ is the degree of polymerization, $\overline{\mathrm{DP}}_0$ is the degree of polymerization in the absence of chain transfer agent, [S] is the concentration of transfer agent, [M] is the ethylene concentration, and C_s is the transfer constant.

$$(1/\overline{\mathrm{DP}}) - (1/\overline{\mathrm{DP}}_0) = C_{s1}\,[\mathrm{S}_1]/[\mathrm{M}] + C_{s2}/[\mathrm{S}_2]/[\mathrm{M}] \qquad (1)$$

However, there are two disquieting factors which were not given specific consideration previously. First, although adequate theoretical justification for using eq. (1) was given, no experimental demonstration of its validity was presented. The second and more important point is that the use of eq. (1) for ethylene polymerization assumes that the reaction kinetics can be analyzed by means of transition state theory in the form applicable to liquid-phase systems, an approach considered adequate by Symcox and Ehrlich[2] but inadequate by Laird[3] and Gilchrist.[4]

This paper will report the work done to establish whether the transfer constants previously reported are indeed fundamental quantities or whether they are in fact numbers whose magnitude depends on the amount of propane used.

Experimental

All experimental procedures were identical to those previously described.[1,5] The data are given in Table I. Chain-transfer constants were calculated by using eq. (1), as described previously.[1] The base conditions for each calculation were the runs made with the corresponding per cent of propane as implied in Table I. The C_s values are given in Table II.

Discussion

Applying the statistical *t* test to the data of Table II leads to the conclusion that the changes in xylene and cyclohexane C_s values from 12% to 14% propane have possible statistical significance whereas the other changes are definitely not significant. The major change (if it is real) in the C_s values clearly occurs between 12 and 14% propane, with little or no change taking place as the propane concentration is raised further. This is not the behavior to be expected if either of the points under consideration were responsible for the differences in values.

It is therefore concluded that the technique for determining C_s at 130°C. is valid, and that the propane concentration *per se* has little or no effect on the values.

There is an alternate reason why the C_s values might appear to change between 12 and 14% propane. The reaction system is very close to the point of phase separation[6] and may, in fact, be heterogeneous at 12% propane. This could account for the observed results.

The C_s value for acetone at 14.4% propane is different from the previously reported value.[1] Acetone was included in this study because of apparently anomalous behavior in earlier, unpublished experiments. It is now seen that no anomaly exists; rather, the earlier C_s value is wrong. It is not entirely clear why it was incorrectly measured, but it happens that acetone was chronologically the first transfer agent studied. Perhaps our techniques were not yet perfected. There is no reason to suspect other such errors in the earlier work, however, inasmuch as the data on the second-studied compound, *p*-xylene, are completely consistent with our most recent data.

TABLE I
Polymerizations Conducted at 1360 atm. and 130°C. with 2.07×10^{-4} mole/l. Di-*tert*-butyl Peroxide

	Feed composition, mole-%[a]				
Transfer agent	Ethylene	Propane	Transfer agent	Reaction system	Melt index[b]
(Base point)	87.82	12.02		2	0.0818
"	"	"		2	0.0824
"	87.93	11.92		2	0.0525
Cyclohexane	84.55	12.02	3.27	2	12.2
"	"	"	"	2	15.0
p-Xylene	86.67	"	1.15	2	17.1
"	"	"	"	2	16.4
Acetone	85.90	"	1.93	2	11.6
"	"	"	"	2	12.0
(Base point)	85.42	14.43		2	0.410
"	"	"		2	0.553
"	"	"		2	0.502
Cyclohexane	82.15	"	3.27	2	21.8
"	"	"	"	2	19.0
Acetone	83.81	"	1.60	2	12.5
"	"	"	"	2	16.0
"	"	"	"	2	14.2
(Base point)	85.42	"		1	0.162
"	"	"		1	0.131
p-Xylene	85.26	"	0.29	1	0.555
"	84.96	"	0.57	1	2.38
"	84.69	"	0.86	1	6.63
"	84.40	"	1.15	1	15.1
(Base point)	79.81	20.04		2	7.60
"	"	"		2	9.52
"	"	"		2	6.54
Cyclohexane	78.72	"	1.09	2	21.7
"	"	"	"	2	20.2
p-Xylene	79.46	"	0.34	2	17.0
"	"	"	"	2	19.5
Acetone	79.34	19.93	0.58	2	19.0
"	"	"	"	2	18.0

[a] The balance of the feed, usually less than 0.2%, was benzene used as initiator solvent.

[b] See refs. 1 and 5 for the use of melt index data to estimate $\bar{M}_n$.

TABLE II
Chain-Transfer Constants Measured at 1360 atm. and 130°C.

	Chain transfer constants at various propane concentrations		
	12.0%	14.4%	20.0%
Cyclohexane	0.0106 ± 0.0006	0.0091 ± 0.0006	0.009 ± 0.002
p-Xylene	0.034 ± 0.002	0.030 ± 0.002	0.026 ± 0.005
Acetone	0.018 ± 0.001	0.0165 ± 0.0010	0.016 ± 0.003

As a test of internal consistency, the C_s value for propane was recalculated from the base runs in Table I (system 2 only). The value 0.0031 ± 0.0002 is identical with that previously calculated.[1]

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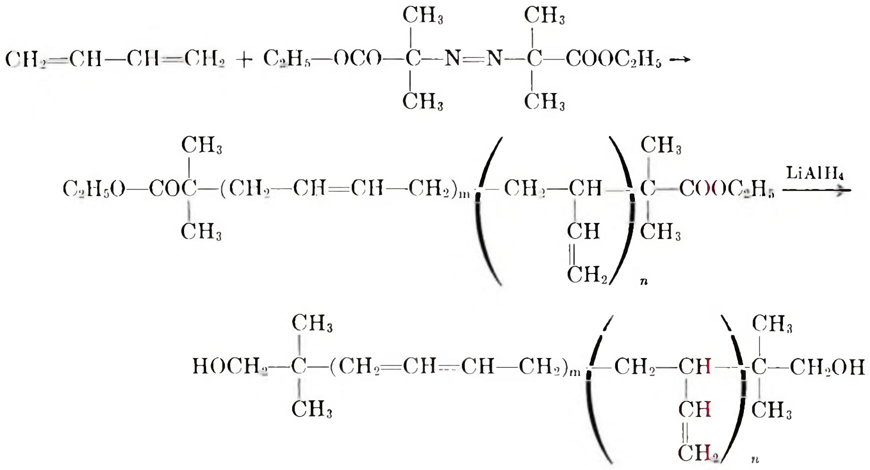
α,ω-Glycols from Butadiene

The preparations of α,ω-glycols of polybutadiene,[1] polyisoprene,[1] and polyisobutylene[2,3] have been reported by workers from this laboratory. This paper is an extension of the above program and involves α,ω-glycols of polybutadiene with a high content of 1,4 units.

The polybutadiene glycols were prepared by free-radical polymerization of butadiene with diethyl 2,2′-azobisisobutyrate[4] in benzene solvent followed by reduction of the resultant diesters with lithium aluminum hydride.



$$CH_2{=}CH{-}CH{=}CH_2 + C_2H_5{-}OCO{-}\overset{CH_3}{\underset{CH_3}{C}}{-}N{=}N{-}\overset{CH_3}{\underset{CH_3}{C}}{-}COOC_2H_5 \rightarrow$$

$$C_2H_5O{-}CO\overset{CH_3}{\underset{CH_3}{C}}{-}(CH_2{-}CH{=}CH{-}CH_2)_m\left({-}CH_2{-}\underset{\underset{CH_2}{\|}}{\underset{CH}{CH}}{-}\right)_n\overset{CH_3}{\underset{CH_3}{C}}{-}COOC_2H_5 \xrightarrow{LiAlH_4}$$

$$HOCH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}(CH_2{=}CH{=}CH{-}CH_2)_m\left({-}CH_2{-}\underset{\underset{CH_2}{\|}}{\underset{CH}{CH}}{-}\right)_n\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2OH$$

Bamford, Jenkins and Wayne[5] have described the preparation of bifunctional polymers by a similar technique.

RESULTS AND DISCUSSION

Infrared analysis of the reduced polymer proved the presence of hydroxyl groups, with strong absorption bands appearing at 3350 cm.$^{-1}$. These terminal hydroxyl groups were utilized in determining the molecular weights of the polymers, the hydroxy equivalents being measured using the acetic acid/pyridine method of Ogg et al.[6] These and other results are given in Table I.

Valuable information regarding the structure and molecular weight of polymers was obtained from NMR spectra, an example of which is shown in Figure 1 together with a spectrum of neopentyl alcohol.

In the spectrum of the neopentyl alcohol, the absorption of 6.42τ was attributed to the hydroxyl proton, that at 9.22τ to the methyl proton and at 6.88τ to the methylene protons. The integrated intensities of the absorption were of the correct magnitude, i.e., 1:2:9 = A:B:C.

On comparing the spectrum of the polymer with that of the neopentyl alcohol, the absorptions of 9.20τ and 6.78τ were attributed to the methyl protons (C′) and the methylene protons (B′) respectively, which appear at the chain ends of the polymer. The absorptions at 4.58 and 7.97τ were attributed to the protons (E′) and (D′) occurring in the main chain of the polymer, the absorption at 7.97τ being twice as intense as that at 4.58τ. The exact location of the absorption due to the terminal hydroxyl proton could not be determined because of its extremely low intensity, but is possibly that at 7.30τ. The estimation of the polymer molecular weight was made by comparing the intensity of absorption due to the terminal protons, i.e., (B′) or (C′), with those of protons occurring in the main chain, i.e., (D′) or (E′). The accuracy of these determinations increased with decreasing molecular weight of the polymer.

TABLE I
Polybutadiene Glycols

Glycol	Butadiene, mole/l.	Catalyst, mole/l.	Temp., °C.	Reaction time, hr.	Polymer yield, %	OH equiv.[a]	Mol. wt. (from OH equiv.)	Viscosity[b]	Found		Calculated	
									C, %	H, %	C, %	H, %
P.B.G. 1–3	8.34	2.33×10^{-2}	63	96	21	3570–4150	7140–8300	0.51	86.37	10.90	88.50	11.07
P.B.G. 4	6.01	5.03×10^{-2}	60	96	33	2660	5320	0.428	87.10	11.04	88.37	11.04
P.B.G. 5	3.01	5.03×10^{-2}	60	96	41	1588	3176	0.247	87.46	11.26	87.84	10.99
P.B.G. 7	6.01	1.38×10^{-1}	60	96	50	1502	3004	0.190	86.02	11.28	87.82	11.25
P.B.G. 8	3.01	8.18×10^{-2}	60	96	80	1456	2912	0.165	84.93	11.21	87.66	11.26
P.B.G. 9	6.01	1.89×10^{-1}	80	40	75	—	—	0.181	—	—	—	—
P.B.G. 10	3.01	1.13×10^{-1}	80	40	90	967	1934	0.144	85.93	11.15	87.1	11.20
P.B.G. 11	3.01	1.89×10^{-1}	60	96	69	886	1772	0.113	84.28	11.28	86.96	11.21
P.B.G. 12	3.01	1.13×10^{-1}	80	45	65	866	1732	0.163	—	—	—	—

[a] Hydroxy equivalents determined by acetic acid/pyridine method.[6]

[b] Inherent viscosity measured in the range 0.5–1.0% in toluene as solvent and at 30°C.

Polymerization of dienes with free radicals gives predominately a 1,4 mode of addition. 1,2 addition will give rise to pendant vinyl side chains, such as —CH=CH₂, whose presence can be detected in the NMR spectrum. The absorptions at 4.97 and 5.15τ have been attributed to these vinyl side chain protons.* Comparison of the intensities of these absorptions with those of protons (D′) or (E′) on the main chain leads to a value of 22–25% 1,2-structure. This is in good agreement with the value of 20% 1,2-structure obtained by prebenzoic acid oxidation of the carbethoxy polybutadiene.

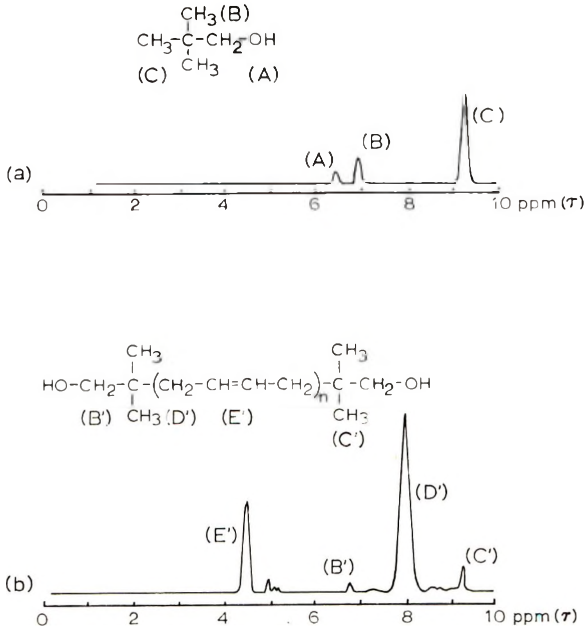


Fig. 1. NMR spectra of (*a*) neopentyl alcohol and (*b*) polybutadiene glycol.

EXPERIMENTAL

Materials

Benzene A. R. grade was obtained from Mallinckrodt Chemical Works and dried by refluxing several times over fresh potassium.

Diethyl ether, A. R. grade, was obtained from Mallinckrodt Chemical Works and dried by refluxing over lithium aluminum hydride.

Methanol, A. R. grade, was supplied by Baker Chemical Company.

Petroleum ether (30–60°C.), A. R. grade was obtained from Mallinckrodt Chemical Works and dried over sodium wire.

Butadiene was supplied by Phillips 66 Company and purified by bubbling through a solution of sodium ethylene glycolate/ethylene glycol and passing the gas through a column of Drierite.

Lithium aluminum hydride was supplied by Metal Hydrides, Inc.

Diethyl 2,2′-azobisisobutyrate was furnished by Dr. A. J. Ultee of the du Pont Company, Benger Laboratory, Waynesboro, Virginia.

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* Compare the spectra of 7-acetoxy-6-allyl-4,8-dimethylcoumarin No. 323, NMR Spectra Catalog, Varian Associates, Palo Alto, California.

Polybutadiene Glycol

In a typical preparation, dry glass pressure bottles were charged with benzene (45.4 ml.) diethyl 2,2′-azobisisobutyrate (0.8 g.; 5.03×10^{-2} mole/l.), and butadiene. Excess butadiene was allowed to boil off, removing oxygen from the system, leaving the required weight of monomer (10 g.; 3.01 mole/l.). The bottles were quickly sealed, vigorously shaken, and placed in a constant temperature bath for 96 hr. at 62°C. After this time had elapsed, the bottles were opened, the unreacted butadiene allowed to boil off, and benzene removed on a rotary evaporator. The carbethoxy-terminated polybutadienes were reduced with lithium aluminum hydride in diethyl ether in the following manner: 21 g. of the polymer was dissolved in dry diethyl ether (100 ml.) and added dropwise over a period of 1 hr. to a gently refluxing diethyl ether solution (300 ml.) containing a large excess of lithium aluminum hydride (4 g.; 0.105 mole) to ensure a complete reduction. Refluxing, with continuous stirring, was continued for 2 hr. and then the solution cooled in ice water before careful addition of 10% hydrochloric acid to destroy the unreacted hydride. Prolonged stirring of the strongly acid mixture (pH 2) finally gave a milk-white liquid which on standing separated into two layers. After separating the organic layer, ether was removed from the glycol. The glycol was then taken up in benzene and precipitated in methanol to remove any impurities. Precipitation of the lowest molecular weight material was accomplished by adding a few drops of concentrated hydrochloric acid to the solution, warming gently and then leaving for several hours. The precipitated glycol was taken up in benzene and 1% of 2,6-di-*tert*-butyl-*p*-cresol (Dupont Antioxidant No. 29) was added. The solution was filtered, and the solvent removed on a rotary evaporator at about 70–80°C., leaving a brown, viscous liquid. In cases where the last traces of benzene were difficult to remove, a more volatile solvent, such as petroleum ether (b.p. 30–60°C.), was used. Hydroxy equivalents, viscosities, etc., are given in Table I.

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