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Aminobutadienes. X. Polymerization and Copolymerization of 2-Phthalimidomethyl-1,3-butadiene

KENICHI MURATA and AKIRA TERADA,*
Government Industrial Research Institute,
Osaka, Midorigaoka, Ikeda, Osaka, Japan

Synopsis

The polymerization and copolymerization of 2-phthalimidomethyl-1,3-butadiene were investigated. This monomer was easily polymerized by benzoyl peroxide catalyst in bulk or in solvent, and by γ-radiation in the solid state to give polymers having a softening point of 135–145°C. Although these resulting polymers did not give x-ray diffraction patterns, they showed crystalline patterns by electron diffraction. On the other hand, cationic polymerization with the use of boron trifluoride diethyl etherate in chloroform was attempted, but no formation of the polymer was observed. Also, this monomer was easily copolymerized with styrene in *N*,*N*-dimethylformamide. The monomer reactivity ratios and Alfrey-Price Q and e values calculated from the copolymerization data of this monomer (M_1) with styrene (M_2) were $r_1 = 2.0 \pm 0.13$, $r_2 = 0.15 \pm 0.02$, and $Q_1 = 2.78$, $e_1 = 0.30$.

INTRODUCTION

In previous papers[1–3] of this series, the polymerizations and copolymerizations of 1-phthalimido-1,3-butadiene (1-PB), 2-phthalimido-1,3-butadiene (2-PB), and 1-succinimido-1,3-butadiene (1-SB) have been discussed. These results may be summarized as follows: (*1*) These monomers were easily polymerized by radical catalysts, and their polymerizability was in the order of 2-PB > 1-SB > 1-PB. (*2*) The monomer reactivity ratios and Alfrey-Price Q and e values calculated from the copolymerization data of these monomers with styrene were shown.

Some of the polymers thus obtained were converted into a new type of effective anion exchange resins after hydrolysis of the imido group.[4] The higher reactivity of these imidobutadiene monomers toward either homopolymerization or copolymerization was also applied to prepare graft copolymers with polyethylene[5] and polypropylene[6] for the purpose of improving the dyeability of the latter polymers.

We also reported the synthesis of a new butadiene monomer, 2-phthalimidomethyl-1,3-butadiene (2-PMB), in which the imido group was separated from the butadiene chain by a methylene group.[7]

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* Present address: Department of Industrial Chemistry, Kyushu Institute of Technology, Tobata-ku, Kita-kyushu, Japan.

The present paper deals with the polymerization and copolymerization of 2-PMB, of its polymerizability compared to that for the previously reported imidobutadienes, and also the solid-state polymerization of 2-PMB by γ-radiation.

EXPERIMENTAL

Materials

2-Phthalimidomethyl-1,3-butadiene (2-PMB) was synthesized from isoprene according to the method reported previously, yielding colorless crystals melting at 114.5–116°C.[7] Styrene (St) was purified by the usual method.[8] The catalysts, benzoyl peroxide (BPO) and boron trifluoride diethyl etherate, and the solvents, *N*,*N*-dimethylformamide (DMF), acetylene tetrachloride (ATC), and chloroform were carefully purified by the methods previously reported.[2]

Radiation Source

The radiation was γ-radiation from a ^{60}Co source, and the dose rate was measured by the use of a Toshiba dosimeter, Model RCD-43101.

Polymerization Procedure

Polymerization and copolymerization with benzoyl peroxide or boron trifluoride diethyl etherate were carried out as previously reported.[2] The reduced viscosity of the resulting polymer as a 0.50% solution in acetylene tetrachloride was determined at 30 ± 0.01°C by using an Ostwald viscometer.

Solid-state polymerization by γ-radiation was carried out according to the following method. The required amount of monomer was irradiated under atmospheric pressure. The irradiated monomer was immersed in a large amount of methanol for one week at room temperature to extract the remaining monomer. The resulting polymer was collected on a filter, washed with methanol, and then dried under vacuum.

Infrared Spectra

Infrared spectra were measured with a Hitachi infrared spectrophotometer, Model EPI-S, in potassium bromide disk or in Nujol paste.

X-Ray and Electron Diffraction Patterns

The monomer, irradiated monomer, and two kinds of polymer were studied by both x-ray and electron diffraction methods. For the x-ray diffraction study, the samples were finely powdered, packed into glass capillaries, and exposed to x-rays (CuKα, 1.542 Å) in a Debye-Scherrer camera using a nickel filter for approximately 5 hr. Electron diffraction patterns from the samples were taken at 100 KeV and measured against β-tin as a reference.

Nitrogen Analysis

The copolymers were purified by repeated precipitations, and the copolymer composition was determined by Micro-Dumas method.

RESULTS AND DISCUSSION

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

The results of the bulk polymerization of 2-PMB by the use of benzoyl peroxide or γ-radiation are shown in Table I, together with those of some other imidobutadienes for comparison. Polymerization with benzoyl peroxide was attempted at the melting point of each of these monomers. The 2-PMB polymer obtained was a transparent resin having a softening point of 135–145°C and soluble in several solvents, such as chloroform, ethylene dichloride, acetylene tetrachloride, and *N,N*-dimethylformamide. While 2-phthalimido-1,3-butadiene (2-PB) had a much greater tendency to crosslink on bulk polymerization,[2] 2-PMB, like 1-phthalimido-1,3-butadiene (1-PB) and 1-succinimido-1,3-butadiene (1-SB), did not show any gelation phenomenon.

TABLE I
Bulk Polymerization of 2-Phthalimidomethyl-1,3-butadiene and Some Imidobutadienes

Monomer	Catalyst	Temperature, °C	Time, hr	Yield, %
2-PMB	BPO, 0.5 mole-%	116	1.0	88.6[a]
2-PB	BPO, 0.1 mole-%	85	2.5	gelled
1-PB	BPO, 0.5 mole-%	116	1.0	80.5[b]
1-SB	BPO, 0.5 mole-%	76	1.0	59.9[c]
2-PMB	γ-ray, 1.1×10^5 R/hr	5–10	99	42.2
1-PB	γ-ray, 1.1×10^5 R/hr	5–10	554	8.2
1-SB	γ-ray, 1.1×10^5 R/hr	5–10	144	7.2

[a] Reduced viscosity, 0.57 dl/g.
[b] Reduced viscosity, 3.00 dl/g.
[c] Reduced viscosity, 0.24 dl/g.

Radical polymerization in the solid state was also carried out under atmospheric pressure by the use of γ-radiation. The 2-PMB polymer obtained from this process looked like the original monomer crystals and was colorless. This polymer was also soluble in the solvents mentioned above. The rate of polymerization of 2-PMB by γ-rays was much faster than those of 1-phthalimido- and 1-succinimido-1,3-butadienes.[5]

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

The polymerization of 2-PMB in acetylene tetrachloride was carried out with the use of benzoyl peroxide as in the cases of the other imidobutadienes.[1,2] The results are summarized in Figure 1, in which the polymerization rate of 2-PMB is faster than those of 1-imidobutadienes, but far slower than that of 2-phthalimido-1,3-butadiene. This fact agrees with the conclusion of Carothers obtained in a discussion of the influence of structural variations on the relative rates of various diene polymerizations.[9] Since the phthalimidomethyl group of this monomer is located on the 2 position on the internal side of the butadiene chain, it must have less steric hindrance to the reactive centers of the butadiene chain on polymerization than in 1-imidobutadienes.

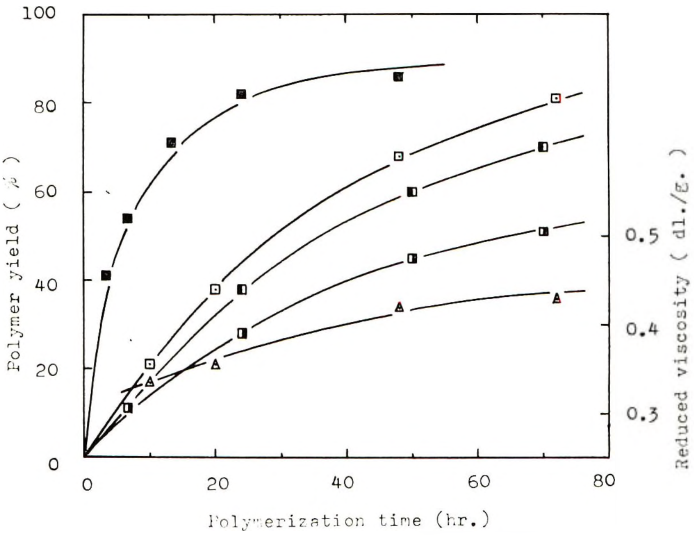

Fig. 1. Solution polymerization of 2-phthalimidomethyl-1,3-butadiene and some imidobutadienes: (⊡) 2-PMB; (■) 2-PB; (◨) 1-PB; (◧) 1-SB; (△) reduced viscosity of poly-2-PMB. Monomer, 300 mg; BPO, 1.0 mole-%; ATC, 1.00 ml; temperature, 60°C.

TABLE II
Cationic Polymerization of 2-Phthalimidomethyl-1,3-butadiene and Some Imidobutadienes in Solution State

Monomer	Monomer wt, mg	BF_3Et_2O, mole-%	Solvent Type	Solvent Vol, ml	Temperature, °C	Time, hr	Yield, %
2-PMB	300	10	$CHCl_3$	2.00	20	210	0
2-PB	271	10	ATC	1.18	20	212	Trace
1-PB	300	10	$CHCl_3$	2.00	20	210	51.5

The reduced viscosity of 2-PMB polymer slightly increased with increasing polymerization time (Fig. 1).

The cationic polymerization of this monomer in the presence of boron trifluoride diethyl etherate was attempted in chloroform at 20°C but, as in the case of 2-phthalimido-1,3-butadiene polymer,[2] no formation of 2-PMB polymer was observed, although 1-phthalimido-1,3-butadiene could easily polymerize under the same conditions[10] (Table II).

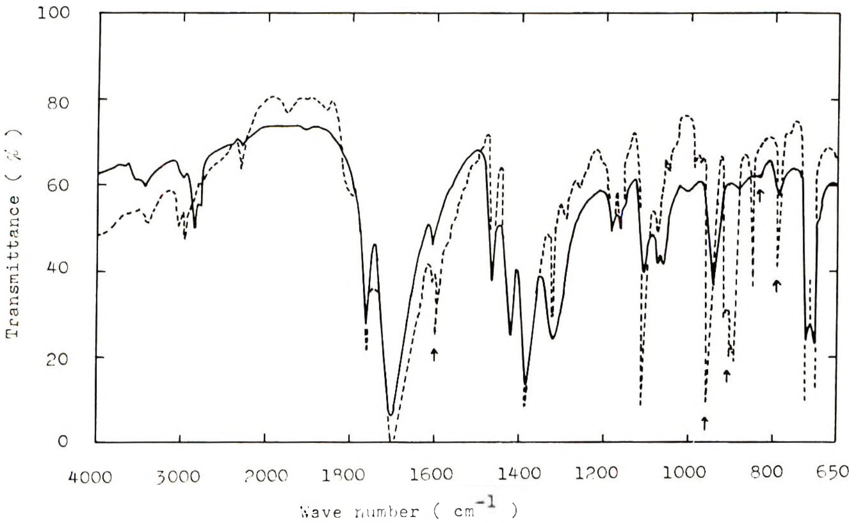

Fig. 2. Infrared spectra of (- - -) 2-phthalimidomethyl-1,3-butadiene monomer and (——) polymer; KBr disk.

Structure of 2-Phthalimidomethyl-1,3-butadiene Polymer

The infrared spectra of 2-PMB monomer and polymer are illustrated in Figure 2. In the polymer spectrum, no absorption at 1600 cm^{-1} due to conjugated diene nor at 912 and 958 cm^{-1} due to the vinyl group in the monomer spectrum can be found. Moreover, the absorption intensity at 895 cm^{-1} due to the vinylidene group in the polymer spectrum is far weaker than in the monomer spectrum. The infrared spectra of the polymer and the copolymer (Fig. 5) have absorption at 840 cm^{-1} assignable to the trisubstituted ethylenic linkage in the main chain.

From these facts above mentioned, it is reasonable to consider that the possibility of 1,2 (or 2,1) addition is eliminated, and that 4,1 (or 1,4) addition substantially exceeds 4,3 (or 3,4) addition, as has already been discussed in the case of 2-phthalimido-1,3-butadiene.[2] Although the infrared data could not be used to decide between 4,1 and 1,4 additions, the steric arguments lead us to the conclusion that 4,1 addition was preferred.

The infrared spectrum of the polymer obtained by γ-radiation was essentially identical with that of the polymer obtained with benzoyl peroxide.

On the other hand, since these polymers obtained with benzoyl peroxide and γ-radiation were both anisotropic from the polarization microscope studies, an x-ray diffraction study was made of the original monomer, the irradiated monomer, and both the polymers in order to confirm the possibility of their crystallinity. The results are shown in Table III. Although the original monomer shows many sharp Debye-Scherrer rings, the irradiated monomer shows only relatively strong ones having almost the same spacings as the original one has.

TABLE III
X-Ray Diffraction Patterns from Monomer, Irradiated Monomer, and Polymers of 2-Phthalimidomethyl-1,3-butadiene

Monomer		Irradiated monomer[a]		Polymers[b]	
Lattice spacing, Å	Intensity	Lattice spacing, Å	Intensity	Lattice spacing, Å	Intensity
2.17	w				
2.66	w				
2.79	w				
2.91	w				
3.12	s	3.12	w		
3.28	w				
3.41	s	3.38	w		
3.55	vs	3.58	m		
3.84	m	3.5	w	3.5	s
4.32	w				
4.70	vs	4.75	m		
5.11	vs	5.13	m		
5.73	m	5.83	w		
6.51	s	6.48	w		

[a] Monomer was irradiated in air for 99 hr at 5–10°C by γ-radiation of 1.1×10^5 R/hr.

[b] Polymers were prepared both by benzoyl peroxide and by γ-radiation.

The polymer obtained by extracting the unpolymerized monomer after irradiation and the polymer obtained by using benzoyl peroxide have only one halo near 3.5 Å. Table IV shows the electron diffraction maxima from the monomer and the two polymers mentioned above. The lattice spacings calculated from the net patterns of single crystal of this monomer are, as a matter of course, very close to those from x-ray diffraction. The lattice spacings of the two polymers are, however, quite different from those of the original monomer.

Since evidence for crystallinity of the polymer could be found only by electron diffraction and not by x-ray diffraction, it may be inferred that the 2-PMB polymers contain very fine microcrystalline parts in the amorphous region which occupies most volume, though the reason is not presently understood.

TABLE IV
Electron Diffraction Patterns of Monomer and Polymers of 2-Phthalimidomethyl-1,3-butadiene

Monomer		Polymer (γ-ray)		Polymer (BPO)	
Lattice Spacing, Å	Intensity	Lattice Spacing, Å	Intensity	Lattice Spacing, Å	Intensity
2.146		1.159	w		
2.229		1.266	w		
2.281		1.405	w		
2.376		1.627	w	1.622	w
2.410				1.759	w
2.529				1.882	w
2.636		2.007	m	2.072	m
2.831		2.226	m	2.231	m
2.865				2.360	w
3.178				2.486	m
3.219		2.829	w		
3.412		2.943	w	2.987	w
3.538	s			3.746	s
3.615	s	4.135	m	4.145	s
3.951					
4.718					
5.058	s				
6.438	s				
7.077					
7.230					
14.153					

Copolymerization of 2-Phthalimidomethyl-1,3-butadiene

The copolymerization of 2-PMB with styrene was carried out with the use of benzoyl peroxide in *N*,*N*-dimethylformamide at 60°C, in order to determine the monomer reactivity ratios. The results are shown in Table V, where M_1 and M_2 represent the monomer feeds of 2-PMB and styrene,

TABLE V
Copolymerization of 2-Phthalimidomethyl-1,3-butadiene (M_1) with Styrene (M_2)[a]

Monomer feed		Polymer yield, %	Nitrogen in polymer, %	Copolymer composition	
$M_1 \times 10^{-4}$, mole	$M_2 \times 10^{-4}$, mole			m_1, mole-%	m_2, mole-%
5.0	45.0	10.9	3.50	35.7	64.3
10.0	40.0	8.0	4.13 4.48	48.1	51.9
15.0	35.0	7.2	4.81	57.1	42.9
20.0	30.0	10.5	5.40 5.03	65.4	34.6

[a] Solvent, DMF; BPO, 1.0 mole-%; temperature, 60°C.

respectively, and m_1 and m_2 indicate the molar fractions of the monomer units in resulting copolymer calculated from the nitrogen analysis. Figure 3 shows the plots for determining the monomer reactivity ratios by the Fineman-Ross method.[11] Thus, we obtained r_1 (2-PMB) = 2.0 ± 0.13, r_2 (St) = 0.15 ± 0.02.

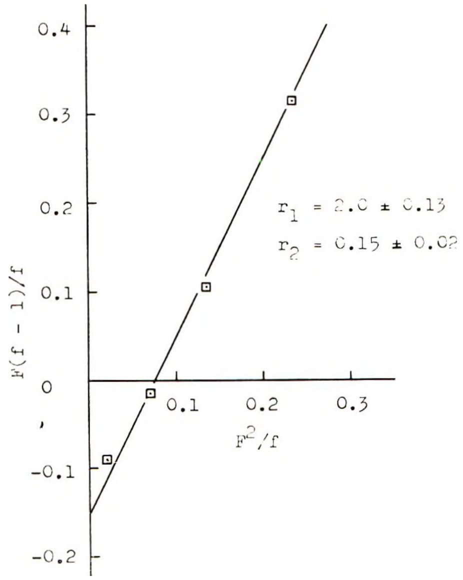

Fig. 3. Fineman-Ross plots for determining the monomer reactivity ratios.

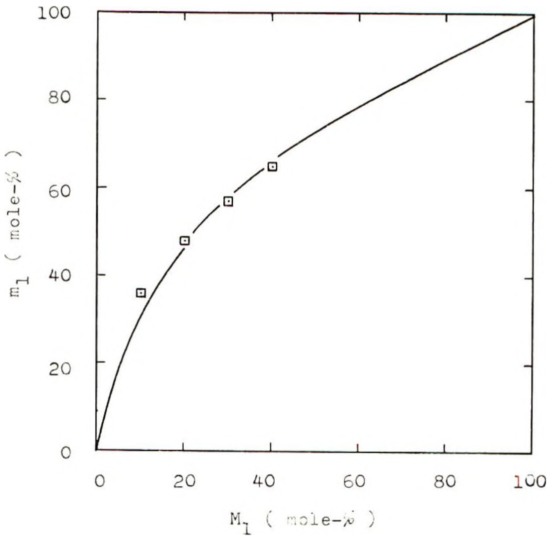

Fig. 4. Composition curve for the copolymerization of 2-phthalimidomethyl-1,3-butadiene (M_1) with styrene.

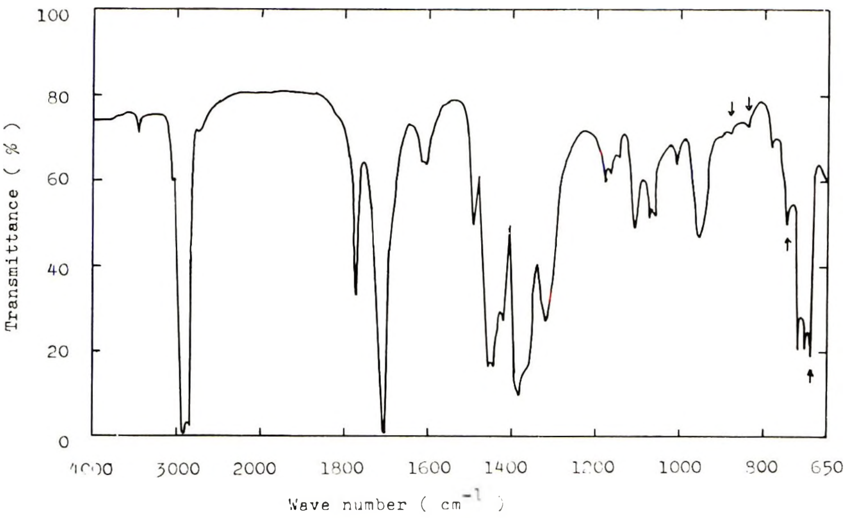

Fig. 5. Infrared spectrum of 2-phthalimidomethyl-1,3-butadiene-styrene copolymer; Nujol mull.

The composition curve for the copolymerization of 2-PMB with styrene calculated from the above r_1 and r_2 values is shown in Figure 4.

The infrared spectrum of the copolymer is shown in Figure 5. From these results, it is understood that this monomer is able to copolymerize easily with styrene. The infrared spectrum clearly shows also that the copolymer contains a few pendant vinylidene groups, as found in the homopolymer of 2-PMB.

The Q and e values for this monomer were calculated according to the Alfrey-Price scheme,[12]

$$r_1 = (Q_1/Q_2) \exp\{-e_1(e_1-e_2)\}$$
$$r_2 = (Q_2/Q_1) \exp\{-e_2(e_2-e_1)\}$$

by using the values, $Q_2 = 1.0$ and $e_2 = -0.8$, for styrene, and r_1 (2-PMB) and r_2 (St). Thus, we obtain $Q_1 = 2.78$, $e_1 = 0.30$.

Table VI summarizes the monomer reactivity ratios for our imidobutadienes and styrene, and Alfrey-Price Q and e values.

TABLE VI

Monomer Reactivity Ratios and Alfrey-Price Q-e Values

Imido-buta-diene M_1	Co-mono-mer M_2	Monomer reactivity ratios r_1	r_2	Q_1	e_1
2-PMB	St	2.0 ± 0.13	0.15 ± 0.02	2.78	+0.30
2-PB	St	5.2 ± 0.5	0.11 ± 0.02	5.0	−0.05
1-PB	St	1.48 ± 0.08	0.32 ± 0.06	1.57	+0.06
1-SB	St	1.62 ± 0.04	0.28 ± 0.03	1.76	+0.09

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Novel Bridged Anthracene Derivatives and Polyesters and Copolyesters Therefrom

B. H. KLANDERMAN and J. W. H. FABER, *Research Laboratories, Eastman Kodak Company, Rochester, New York, 14650*

Synopsis

9,10-Bis(hydroxymethyl)triptycene, 9,10-dihydro-9,10-bis(hydroxymethyl)-9,10-ethanoanthracene, 9,10-dihydro-9,10-bis(hydroxymethyl)-9,10-(2,3-bicyclo[2.2.1] heptano)-anthracene, 9,10-dihydro-9,10-bis(hydroxymethyl)-*N*-phenyl-9,10-ethanoanthracene-11,12-dicarboximide, and 9,10-bis(carbethoxy)triptycene have been prepared and employed as modifying agents to improve the physical properties of polyesters such as poly(ethylene terephthalate). Especially noteworthy are the high glass transition temperatures (T_g) which can be obtained.

INTRODUCTION

Polymers containing three-dimensional units, such as 9,10-bridged anthracene systems, may exhibit unusual physical properties because of the interference of segmental rotation of the polymer chains by the three-dimensional units. To examine this possibility, properly substituted 9,10-bridged anthracene systems were prepared and used as modifiers for polyesters.

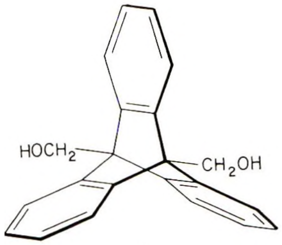
To date, only a limited number of 9,10-disubstituted triptycenes (9,10-dihydro-9,10-*o*-benzenoanthracenes) have been synthesized and these in low yield.[1]

More recently, an improved procedure for the preparation of triptycenes by the reaction of benzyne with anthracene derivatives has been reported.[2] Benzyne is thermally generated *in situ* in aprotic solvents from diazotized anthranilic acid, and thus the highly reactive benzyne intermediate can be effectively trapped by anthracenes, so that good yields of adducts can be obtained. Applying this procedure to difunctional anthracenes, one can then prepare difunctional triptycenes which may be used for polymerization purposes. Polymers containing the triptycene system have not previously been described.

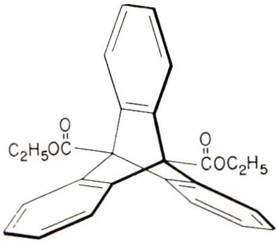
RESULTS AND DISCUSSION

Monomers

9,10-Bis(hydroxymethyl)triptycene (I) and 9,10-bis(carbethoxy)triptycene (II) represent ideal triptycene derivatives to be used as modifying agents for poly(ethylene terephthalate).

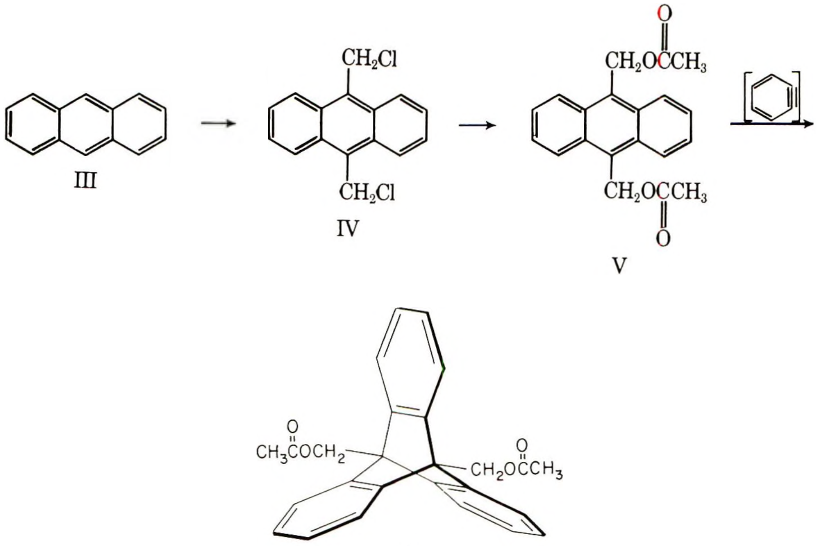


I



II

Compound I can readily be prepared by the following sequence of reactions: Anthracene (III) is converted to 9,10-bis(chloromethyl)anthracene (IV) by chloromethylation with paraformaldehyde and hydrogen chloride.[3,4] Compound IV is easily transformed to 9,10-bis(acetoxymethyl)-anthracene (V) by treatment with potassium acetate and acetic acid.[4] The key step is represented by the transformation of compound V to 9,10-bis-(acetoxymethyl)triptycene (VI) by reaction with the benzyne intermediate. On using the *in situ* procedure for the generation of benzyne, a 72% yield of compound VI was obtained. Hydrolysis of compound VI readily produces compound I in good yield.

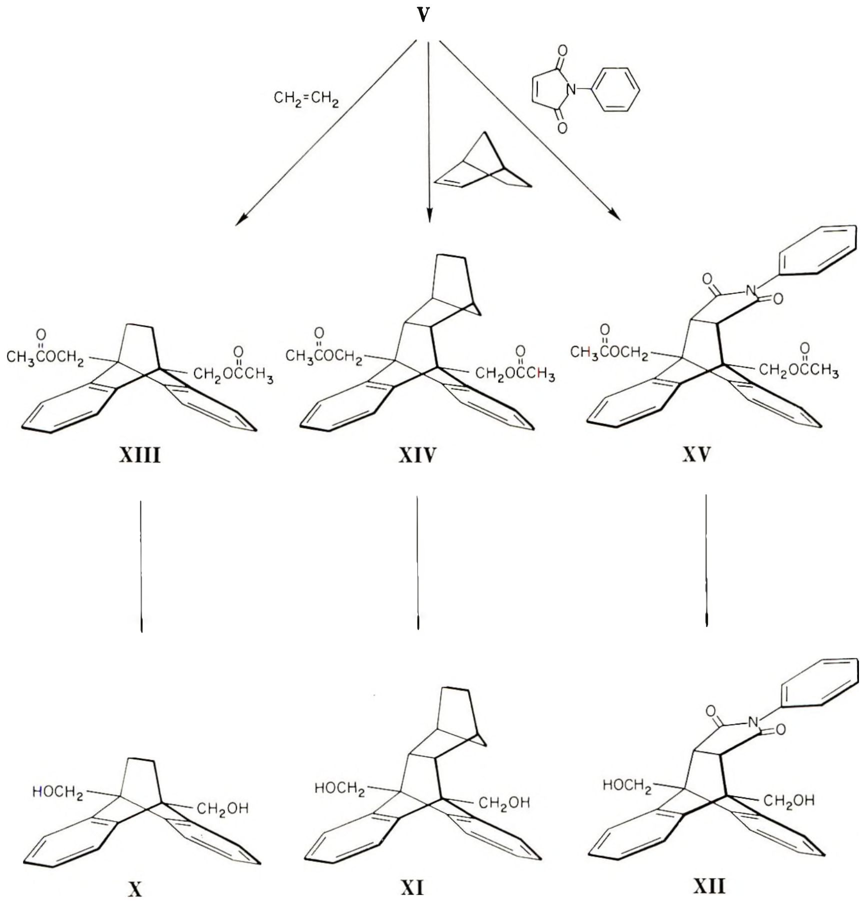


VI

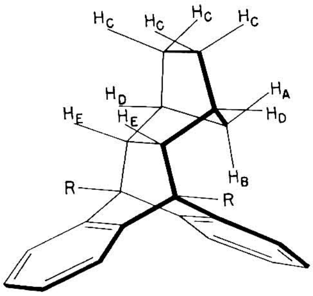
The good yield for the benzyne reaction is significant because it represents a useful entry into 9,10-disubstituted triptycene systems. Not only is compound V a good diene, but it is reasonably soluble in methylene chloride, the aprotic solvent used in the benzyne reaction. It is important that the diene be in solution for an efficient reaction to occur with the short-lived benzyne intermediate. For this reason, 9,10-bis(hydroxymethyl)-anthracene (VII) is unsuitable for the benzyne reaction because it is a relatively insoluble compound.

Compound II is obtained from compound I in the following manner. Compound I is oxidized with chromic acid to 9,10-triptycenedicarboxylic acid (VIII) which is converted by means of thionyl chloride to the acid chloride (IX) which gives the desired diester (II) upon treatment with ethanol.

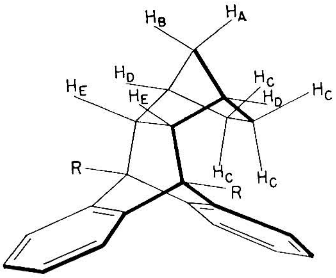
9,10 - Dihydro - 9,10 - bis(hydroxymethyl) - 9,10 - ethanoanthracene (X), 9,10-dihydro - 9,10 - bis(hydroxymethyl) - 9,10-(2,3-bicyclo[2.2.1]heptano)-anthracene (XI), and 9,10 - dihydro-9,10-bis(hydroxymethyl)-*N*-phenyl-9,10-ethanoanthracene-11,12-dicarboximide (XII) are readily prepared by hydrolysis of the appropriate 9,10-bridged anthracene derivatives (XIII, XIV, XV) obtained from the Diels-Alder reaction of 9,10-bis(acetoxymethyl)anthracene (V) with ethylene, bicyclo [2.2.1] heptene, or *N*-phenylmaleimide, respectively.



The configuration of the 9,10-dihydro-9,10-(2,3-bicyclo-[2.2.1]heptano)-anthracene system deserves some comment. Two possible configurations (XVI and XVII) can be formed, depending upon the course of the Diels-Alder reaction. Molecular models indicate



XVI



XVII

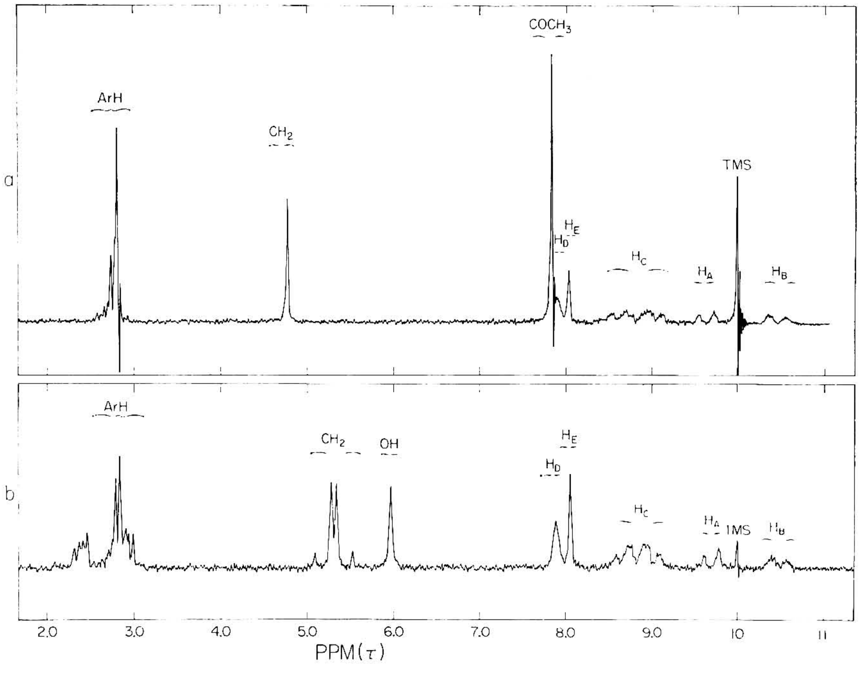


Fig. 1. NMR spectra: (*a*) XIV, in $CDCl_3$; (*b*) XI, in $CDCl_3$–DMSO-d_6.

that XVI would be preferred over XVII but that the preference would not be overwhelming. Nuclear magnetic resonance provides an excellent method for determining the configuration of this adduct. Figure 1 shows the NMR spectra of XI and XIV. The large upfield shift for one proton (H_B) shows that the methano bridge is toward the aromatic ring whose ring current produces this pronounced upfield shift. The bridgehead protons (H_D) can be assigned to the broad peak at τ 7.9 because of the spin coupling of H_D with H_A, H_B, H_C, and H_E protons. The narrowness of the H_E band implies little or no spin coupling to the bridgehead protons (H_D) and therefore that the H_E protons are *endo* hydrogens with respect to the bicyclo[2.2.1]heptano part of the system; this fact further supports the methano bridge being directly over the aromatic ring. Consequently, configuration XVI is the structure for the isolated adducts XI and XIV. Because the total yield for the two-step preparation of XI is greater than 50%, the predominant configuration formed in the Diels-Alder reaction is configuration XVI. Furthermore, reacetylation of diol XI produced material identical to diacetate XIV, thus ruling out structural changes during the formation of XI.

Polymers

Compounds I, II, X, XI, and XII were used to prepare the modified poly(ethylene terephthalates) shown in Tables I and II. The modified polyesters were prepared by replacing various percentages of the usual glycol (ethylene glycol) with I, X, XI, or XII, or the usual diester (dimethyl terephthalate) with II. The polyesters with modified glycol components

TABLE I

Modified Poly(ethylene Terephthalates)

Glycol composition, mole-% for the feed						
Ethylene glycol	I	X	XI	XII	$[\eta]^a$	T_g, °C
100						79
95	5				Insol	89
90	10				0.37	99
80	20				0.26	139
75	25				0.20	140
65	35				0.26	170
83		17			0.60	115
66		34			0.27	135
31		69			0.16	143
83			17		0.49	122
66			34		0.23	153
31			69		0.20	203
83				17	0.23	102
66				34	0.12	108
31				69	0.08	98–102

[a] Determined in phenol–chlorobenzene.

TABLE II
Modified Poly(ethylene Terephthalates)

Diester Composition, Mole-% for the feed			
Dimethyl terephthalate	II	$[\eta]$[a]	T_g, °C
100			79
95	5	0.48	70
90	10	0.48	76
80	20	Insoluble	b

[a] Determined in phenol–chlorobenzene.
[b] Would not quench.

showed the most interesting properties: high heat-distortion temperatures and high glass transition temperatures, T_g, along with decreased crystallizability. These are unique characteristics to be had simultaneously.

Figure 2 shows a plot of the T_g versus the percentages of the various glycols used as glycol components in the modified polyesters. For small amounts of all of the modifying glycols, relatively large increases in the T_g of the modified polymers resulted. However, at higher concentrations for the modifying glycols, various effects were obtained. Glycol I shows a straight line relationship for T_g versus mole per cent modifying glycol, which fact indicates the stability and integrity of the triptycene system. The effects of the other glycols on the T_g fall off with high concentrations of the modifying glycol, indicating that relatively less modifying glycol was incorporated and/or that these glycols were thermally cracking at the reaction temperature to lose ethylene, bicyclo[2.2.1]heptene, or *N*-phenylmaleimide, respectively. These proposals were substantiated by the fact that the modified polyesters with higher percentages of modifier were more highly colored, and yellow solid (probably disubstituted anthracene) appeared on the side arm of the polymerization flask in the later stages of some of the reactions. Other types of 9,10-difunctional-9,10-dihydro-9,10-ethanoanthracenes and polymers therefrom have been reported to thermally change with formation of ethylene and the anthracene moiety at 250–275°C, accompanied by discoloration characteristic of the substituted anthracene system.[5]

Semiquantitative NMR evidence showed that for the case where a high percentage of modifying glycol X was employed, approximately 75% of the modifier was incorporated into the polymer; whereas for the case where a high percentage of glycol I was employed, essentially all of the modifier was incorporated into the polymer. These data further support the relationships observed in Figure 2.

The polyesters with a modified diester component (II) did not show any significant change in thermal properties. The finding that the incorporation of the bridged anthracene system in the diester portion of the polymer

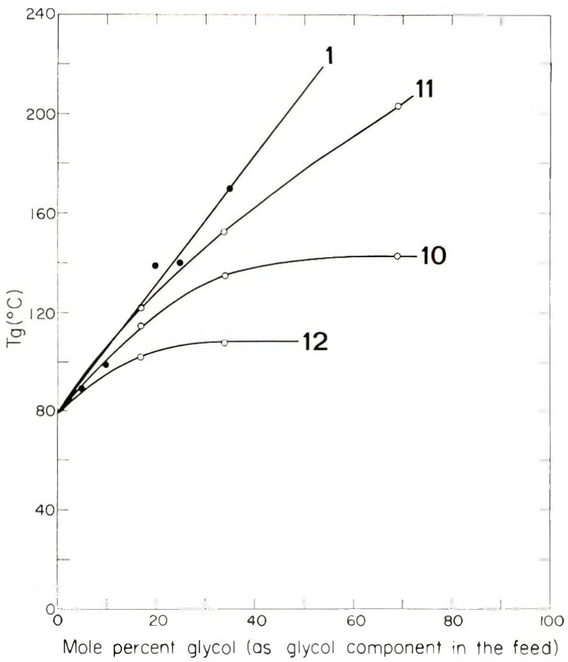


Fig. 2. Glass transition temperatures of modified poly(ethylene terephthalates).

did not increase the T_g may be attributed to the fact that in this case the bridged anthracene system is not adjacent to a terephthalyl group as in the cases for modifying glycols. Moreover, in the modifying diester case, the modifier is replacing a more bulky group (terephthalyl) than in the replacement of ethylene groups; and thus less effect on the thermal properties might well be expected.

EXPERIMENTAL*

9,10-Bis(acetoxymethyl)triptycene (VI)

To a refluxing solution of 115 g (0.36 mole) of 9,10-bis(acetoxymethyl)-anthracene (V)[4] in 3 l of methylene chloride were added, slowly and simultaneously, 65 ml (0.48 mole) of isopentyl nitrite and a solution of 58 g (0.42 mole) of anthranilic acid in 600 ml of acetone. The reaction mixture was refluxed for a total of 6 hr, allowed to stand overnight, washed twice with 12% aqueous potassium hydroxide, dried with anhydrous sodium sulfate, and evaporated to dryness. The crystalline residue was treated with 500 ml of xylene and 50 g (0.51 mole) of maleic anhydride and refluxed for 10 min. The solution was then cooled, diluted with methylene chloride, washed twice with 12% aqueous potassium hydroxide, dried over anhydrous sodium sulfate, and concentrated until crystallization was heavy. The off-white 9,10-bis(acetoxymethyl)triptycene obtained, mp 281–283°C,

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* The infrared and NMR spectra of all compounds were consistent with the structure.

weighed 85 g. Concentration of the mother liquor afforded an additional 16.5 g of 9,10-bis(acetoxymethyl)triptycene, mp 270–280°C. The total yield obtained represented 72% of the theoretical amount.

ANAL. Calcd for $C_{26}H_{22}O_4$: C, 78.4%; H, 5.5%. Found: C, 78.7%; H, 5.9%.

9,10-Bis(hydroxymethyl)Triptycene (I)

To a boiling solution of 85 g (0.21 mole) of 9,10-bis(acetoxymethyl)-triptycene (VI) in 2 l of dioxane was added slowly a solution of 85 g (1.5 moles) of potassium hydroxide in 500 ml of water. The reaction mixture was boiled for 2 hr until 1 liter of solvents had distilled. Approximately 3 l of water was then added to precipitate crude 9,10-bis(hydroxy-methyl)-triptycene as a white solid, and the mixture was allowed to cool. The product, 66 g, mp 305–308°C, was collected and recrystallized from 2-butanone (Nuchar) to obtain 58 g (87%) of pure 9,10-bis(hydroxymethyl) triptycene, mp 308–309°C.

ANAL. Calcd for $C_{22}H_{18}O_2$: C, 84.0%; H, 5.8%. Found: C, 83.8%; H, 5.5%.

9,10-Triptycenedicarboxylic Acid (VIII)

To a solution of 19 g (0.060 mole) of 9,10-bis(hydroxymethyl)triptycene (I) in 1 liter of acetone was added a solution of 19 g (0.19 mole) of chromium trioxide and 20 ml of concentrated sulfuric acid in 175 ml of water. The resulting solution was boiled under reflux for 30 min and then poured into about 3 l of ice water to obtain a white precipitate of 9,10-triptycenedicarboxylic acid, 19 g (92%), mp >475°C.

ANAL. Calcd for $C_{22}H_{14}O_4$: C, 77.3%; H, 4.1%. Found: C, 77.4%; H, 4.5%.

9,10-Bis(carbethoxy)triptycene (II)

To a refluxing mixture of 65.5 g (0.19 mole) of 9,10-triptycenedicarboxylic acid VIII in 800 ml of chloroform was added 80 ml (1.11 mole) of thionyl chloride and 5 ml of dimethylformamide. The mixture was refluxed for 3.5 hr, during which time a 30-ml portion of thionyl chloride was added (after 2 hr). The solvents were removed under vacuum and then 250 ml of absolute ethanol was added. This mixture was boiled for 15 min until all the methylene chloride was removed. After cooling, the product was removed and recrystallized twice from benzene–cyclohexane to give 42.8 g (56%) of 9,10-bis(carbethoxy)triptycene, mp 237–238°C.

ANAL. Calcd for $C_{26}H_{22}O_4$: C, 78.4%; H, 5.5%. Found: C, 78.2%; H, 5.8%.

9,10-Bis(hydroxymethyl)anthracene (VII)

A mixture of 100 g (0.43 mole) of anthracene-9,10-dicarboxaldehyde, 250 g (1.23 mole) of aluminum isopropoxide, and 4 l of isopropyl alcohol was refluxed, with slow distillation, for 15 hr. The cooled reaction mixture was filtered and the pasty product was treated with methylene chloride and dilute hydrochloric acid (2*N*). This mixture was filtered and the yellow precipitate was dried and treated with boiling anisole and allowed to cool. The yellow product was washed with methylene chloride and weighed 72.3 g (72%), mp 248–250°C.

ANAL. Calcd for $C_{16}H_{14}O_2$: C, 80.7 ; H, 5.9%. Found: C, 80.9%; H, 6.1%.

9,10-Dihydro-9,10-bis(acetoxymethyl)-9,10-ethanoanthracene (XIII)

Ethylene (maximum cylinder pressure) and 50 g (0.155 mole) of 9,10-bis(acetoxymethyl)anthracene were heated at 200°C for 48 hr in a sealed bomb. The reaction product was recrystallized twice from benzene to give two crops of white product for a total 73% yield: first crop: 36.5 g, mp 177–179°C; second crop: 2.9 g, mp 175–178°C.

ANAL. Calcd for $C_{22}H_{22}O_4$: C, 75.4%; H, 6.3%. Found (first crop): C, 75.2%; H, 6.4%.

9,10-Dihydro-9,10-bis(hydroxymethyl)-9,10-ethanoanthracene (X)

To a refluxing mixture of 15.2 g (0.043 mole) of 9,10-dihydro-9,10-bis-(acetoxymethyl)-9,10-ethanoanthracene in 100 ml of ethanol was added a solution of 10 g of potassium hydroxide in 10 ml of water. The mixture was refluxed for 16 hr. The solvents were removed and the residue was treated with methylene chloride and dilute hydrochloric acid. The methylene chloride layer was concentrated to dryness, and the residue was recrystallized from acetonitrile to give two crops of white product for a total 77% yield: first crop: 7.7 g, mp 205–206°C; second crop: 1.2 g, mp 204–206°C.

ANAL. Calcd for $C_{18}H_{18}O_2$: C, 81.2%; H, 6.8%. Found (first crop): C, 81.0%; H, 7.1%.

9,10-Dihydro-9,10-bis(acetoxymethyl)-9,10-(2,3-bicyclo[2.2.1]-heptano)anthracene (XIV)

An excess of bicyclo[2.2.1]heptene and 100 g (0.031 mole) of 9,10-bis-(acetoxymethyl)anthracene were heated at 200°C for 48 hr in a sealed bomb. The gummy reaction product was concentrated until most of the solvents were removed. About 200 ml of ethanol was added, along with seed crystals, and the solution was refrigerated overnight. The crude product was removed by filtration. An analytical sample was prepared from a similar smaller run by recrystallization of the crude product from benzene–heptane and 2-butanone. The white product melted at 172–175°C.

ANAL. Calcd for $C_{27}H_{28}O_4$: C, 77.9%; H, 6.8%. Found: C, 78.0%; H, 7.0%.

9,10-Dihydro-9,10-bis(hydroxymethyl)-9,10-(2,3-bicyclo[2.2.1]-heptano)-anthracene (XI)

The crude acetoxymethyl derivative just obtained was dissolved in 2.1 liters of hot ethanol and a warm solution of 100 g of potassium hydroxide in 100 ml of water was added. The mixture was refluxed for 4 hr and the solvent was removed. The residue was treated with methylene chloride and water. The organic solution was treated with dilute hydrochloric acid before it was dried with sodium sulfate and concentrated to dryness. The residue was recrystallized from acetonitrile (Nuchar) to give 58 g, mp 259–261°C, of tan product which was recrystallized twice from 2-butanone to give three crops of white product for a 53% yield for two steps: first crop: 30.0 g, mp 260–261°C; second crop: 12.4 g, mp 259–261°C; third crop: 12.0 g, mp 257–259°C.

ANAL. Calcd for $C_{23}H_{24}O_2$: C, 83.0%; H, 7.3%. Found (first crop): C, 82.8%; H, 7.6%.

Reconversion of XI to XIV

To a solution of 2.0 g of XI in 10 ml of pyridine was added dropwise 20 ml of acetic anhydride. The mixture was heated at 105°C for 16 hr before it was poured into cold dilute hydrochloric acid. The precipitate which formed was removed by filtration, washed with water, and recrystallized from 2-butanone (Darco). The product weighed 1.3 g, mp 173–175°C, mixed mp 173–175°C (with authentic XIV).

9,10-Dihydro-9,10-bis(acetoxymethyl)-*N*-phenyl-9,10-ethanoanthracene-11-12-dicarboximide (XV)

To a warm solution of 65 g (0.20 mole) of 9,10-bis(acetoxymethyl)-anthracene in 2.5 liters of toluene was added a solution of 36 g (0.21 mole) of *N*-phenyl-maleimide in 300 ml of toluene. The reaction solution was refluxed for 4 hr and was then concentrated to about one liter to give 80 g (80%) of product, mp 207–209°C.

ANAL. Calcd for $C_{30}N_{25}NO_6$: C, 72.6%; H, 5.1%; N, 2.8%. Found (first crop): C, 72.6%; H, 5.4%; N, 2.9%.

9,10-Dihydro-9,10-bis(hydroxymethyl)-*N*-phenyl-9,10-ethanoanthracene-11,12-dicarboximide (XII)

To a suspension of 73.5 g (0.15 mole) of XV in 3.5 liters of refluxing ethanol was added a solution of 73.5 g of potassium hydroxide in 184 ml of water. The reaction mixture first became clear, and then a heavy precipitate formed during a reflux period of 1 hr. The precipitate was removed from the cooled solution and was then suspended in 1 liter of boiling water. The solid was removed and recrystallized from acetonitrile to give two crops of white product for a total 88% yield: first crop: 50.0 g, mp 302–303°C; second crop: 3.4 g, mp 294–297°C.

ANAL. Calcd for $C_{26}H_{21}NO_4$: C, 76.0%; H, 5.1%; N, 3.4%. Found (first crop): C, 75.7%; H, 5.1%; N, 3.5%.

Preparation of Poly(ethylene Terephthalate) modified with 9,10-Bridged Anthracene Derivatives

A copolyester was derived from 1.0 part ethylene glycol, 0.9 part dimethyl terephthalate, and 0.1 part 9,10-bis(carbethoxy)-triptycene (II). A 50-ml polymerization flask equipped with a stillhead, fractionating column, and a gas insert tube was charged with 17.64 g (0.09 mole) of dimethyl terephthalate, 3.92 g (0.01 mole) of 9,10-bis(carbethoxy)triptycene, 6.6 g (0.106 mole) of ethylene glycol, and one drop of triisopropyl titanate, and heated for 3 hr at 250°C, while a gentle stream of nitrogen was bubbled through the solution. Transesterification began at once. After distillation of methanol had ceased, the stillhead and fractionating column were removed, a stainless-steel stirrer was inserted into the mixture, high vacuum was applied, and the mixture was stirred at 275°C for 1 hr to obtain a highly viscous polymer.

Other modified poly(ethylene terephthalates), the composition and properties of which are shown in Tables I and II, were obtained in the same manner by the two-stage melt process at 225–250°C, except that dibutyltin oxide was used as the catalyst instead of triisopropyl titanate.

CONCLUSION

A number of 9,10-bridged anthracene glycols can be prepared by convenient syntheses. Pronounced effects upon the thermal properties, especially the T_g, of polyesters prepared with the incorporation of these modifying glycols have been observed. Thus, the "paddle-wheel" effect of 9,10-bridged anthracene systems is a significant factor in determining the thermal properties of polyesters containing these moieties. It is reasonable to assume that these rigid bulky systems interfere with the segmental rotation of the polymer chain.

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Syntheses and Properties of Photochromic Polymers of the Azobenzene and Thiazine Series*

HIROYOSHI KAMOGAWA, MASAO KATO,
and HIROKO SUGIYAMA, *Textile Research Institute, Kanagawa, Yokohama, Japan*

Synopsis

Photochromic polymers of the azobenzene and thiazine series were synthesized via two routes: (*1*) synthesis of vinyl photochromic monomers and subsequent polymerization and (*2*) chemical reactions of the substrate polymers with photochromic components. Polyvinylaminoazobenzenes, polyvinylhydroxyazobenzenes, polyacrylamidomethylaminoazobenzenes, and polyacrylamidomethylthionine were thus prepared and their photochromic behavior investigated. In the case of azobenzene polymers, irradiations from a 100-W projection lamp are enough to induce reversible changes in absorption spectra both in benzene solutions and film states, their absorption maxima being located around 400 mμ in the dark. Better results are obtained for some polymers as compared with the corresponding low molecular weight compounds; in the case of the thionine polymer (absorption maximum, ca. 600 mμ), the presence of ferrous ion remarkably enhances the photosensitivity in aqueous solutions, but incorporation of some polymers containing hydroxyl groups, such as poly(vinyl alcohol), are preferable for film states.

There have been found numerous photochromic substances, both organic and inorganic, since the first discovery of this phototropy or photochromism phenomenon by Marckwald in 1899.[1] A review by Exelby and Grinter[2] covers the literature to June 1964, and gives an organized list of photochromic compounds together with the properties, conditions, and theories involved. In 1963, in the course of synthetic studies on oxidation–reduction polymers, Kamogawa suggested the possibility that thionine, when introduced into polymer chains and combined with suitable reductants such as ferrous ion, might show excellent photochromic properties.[3] Later, Lourien and Waddington[4] reported that copolymers of 4-acrylamidoazobenzene derivatives with acrylic and methacrylic acid in solutions showed photochromis; polystyrene partially substituted in the *para* position by bis(4-dimethylaminophenyl)methanol, sandwiched between two glass plates, was also found to be photochromic.[5]

In this report will be described the results of the synthetic studies on the photochromic polymers of the amino-, dimethylamino-, and hydroxyazobenzene and thiazine series and their photochromic properties in film states as well as in solutions.

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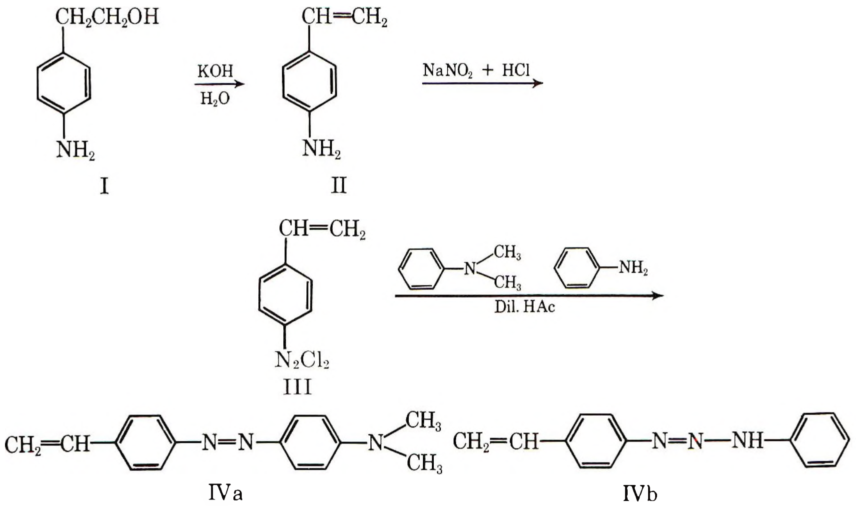
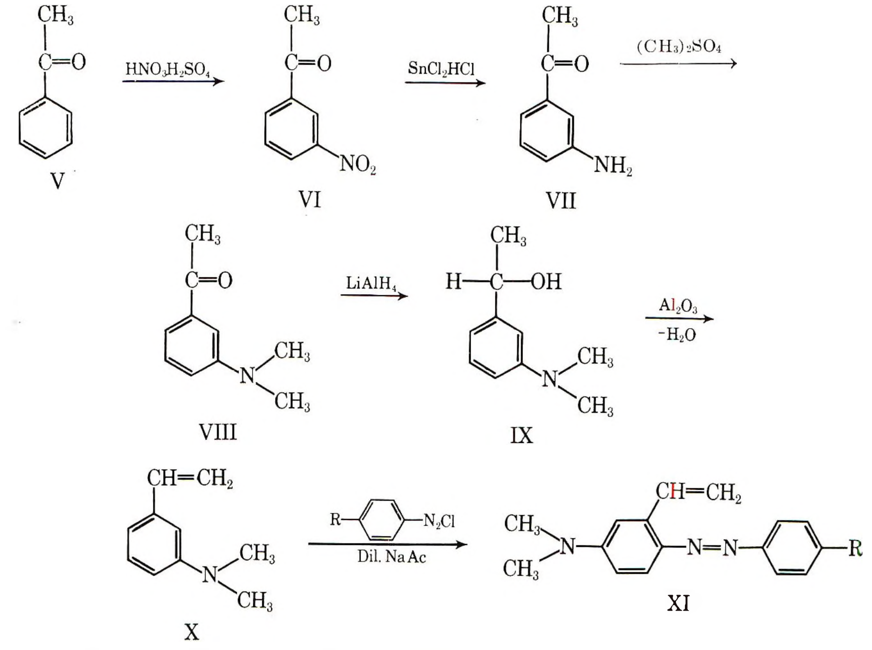
The synthesis of photochromic polymers were carried out via the following route: (*1*) synthesis of photochromic monomers from original vinyl monomers, followed by polymerizations; (*2*) chemical reactions of the substrate polymers with photochromic components.

Four kinds of photochromic vinyl monomers were synthesized. Thus, to prepare 4-vinyl-4′-aminoazobenzene derivatives, the reaction sequence (1) was employed, starting with *p*-aminophenethyl alcohol.



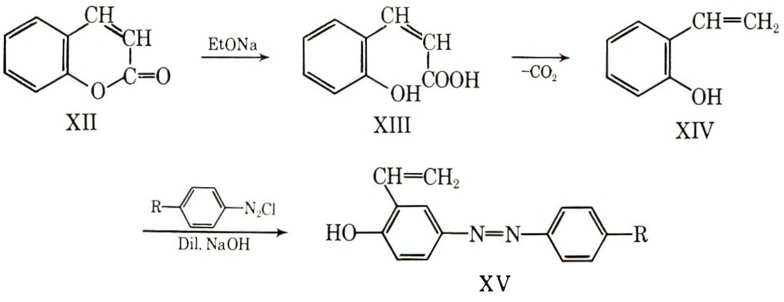
(1)

To prepare 2-vinyl-4-dimethylaminoazobenzene derivatives, the reaction sequence (2) was employed, starting with acetophenone.



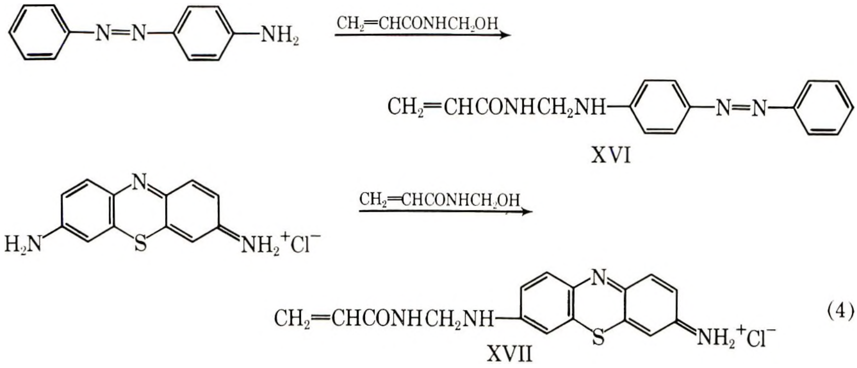
where R is H, CH_3, *p*-$C_6H_4NH_2$, or NO_2.

3-Vinyl-4-hydroxyazobenzene derivatives were prepared according as follows, starting with coumarin.



where R is H, CH_3, or Cl.

N-Acrylamidomethylaminoazobenzene and *N*-acrylamidomethylthionine were prepared by using the condensation reactions of *N*-hydroxymethylacrylamide, starting with 4-aminoazobenzene and thionine.



(4)

The same principles as for the monomer syntheses were applied for chemical modifications of the substrate vinyl polymers. Thus, poly-3-vinyl-4-hydroxyazobenzene derivatives were prepared by the reactions of poly-*o*-hydroxystyrene with the diazonium salts of aniline derivatives; *N*-acrylamidomethylaminoazobenzene and *N*-acrylamidomethylthionine polymers were prepared by the reactions of *N*-hydroxymethylacrylamide copolymers with the corresponding 4-aminoazobenzene derivatives and thionine.

EXPERIMENTAL

Materials

***p*-Aminostyrene** (I).[6] A 10-g portion of 4-aminophenethyl alcohol and 30 g of potassium hydroxide pellets were heated to 220–240°C under 10 mm Hg to distil out 9 g of crude *p*-aminostyrene. A colorless liquid was obtained in approximately 70% yield by redistillation (81°C/25 mm Hg), which solidified upon standing in a refrigerator (absorption maximum in ethanol, 280 mμ).

***m*-Nitroacetophenone (VI).** Corson and Hazen's procedure[7] was modified as follows.

In a one-liter, three-necked flask, immersed in a Dry Ice–methanol bath, was placed 150 ml of concentrated sulfuric acid. The flask was equipped with an efficient mechanical stirrer, a small dropping funnel, and a thermometer reaching the liquid. The stirrer was started at once, and, when the sulfuric acid was cooled to 0°C or below, 59 ml (0.5 mole) of pure acetophenone was added dropwise from the dropping funnel at such a rate (ca. 5 min for the addition) that the temperature did not rise above 0°C. After the reaction mixture was cooled, this time to about −10°C, the nitrating mixture, consisting of 40 ml (0.65 mole) of nitric acid (specific gravity, 1.38) and 60 ml of concentrated sulfuric acid, was added through the dropping funnel at such a rate that the temperature of the reaction mixture remained below 0°C. (usually −2 to −10°C). It takes about 30 min. After the nitrating acid was added, stirring was continued for several minutes until the temperature went up to 0°C, without the bath. The contents of the flask were then poured with vigorous manual stirring into a mixture of 750 g of cracked ice and 1500 ml of water.

The separated product was washed with water, then with a small amount of ice-cold ethanol, and recrystallized from ethanol. A slightly colored crystal of mp 76–78°C was obtained in 50 g yield (61%). The infrared spectrum indicates new absorption bands at 1540 and 1360 cm^{-1} (nitro group).

***m*-Aminoacetophenone (VII).** A conventional procedure for the reduction of the nitrogroup[8] was employed. Thus from 16.5 g (0.1 mole) of VI, 102.4 g (0.5 mole) of stannous chloride, and 95 ml (ca. 1 mole) of concentrated hydrochloric acid in 180 ml ethanol there was obtained a light yellow crystal (plate) of mp 98–99°C (lit.[8] mp, 99.5°C) in 78% yield. The absorption at 1540 cm^{-1} for *m*-nitroacetophenone disappears in the infrared spectrum, whereas a doublet for the amino group appears at 3500 cm^{-1}.

***m*-Dimethylaminoacetophenone (VIII).** In a 500-ml three-necked flask equipped with a reflux condenser, a dropping funnel, and a thermometer, were placed 6.8 g (0.05 mole) of *m*-aminoacetophenone, 100 ml (0.1 mole) of a strong anion exchange resin (Diaion-SA, #100, Mitsubishi Chem. Prod. Co., Ltd.), and 100 ml of water. A magnetic stirrer was fitted, 16 ml (0.16 mole) of dimethyl sulfate added through the dropping funnel, and, after 1 hr stirring at ambient temperature, the mixture was warmed up to 60°C, followed by further one hour stirring. After decomposing unreacted dimethyl sulfate with sodium hydroxide, ether extraction was carried out, followed by dehydration with anhydrous sodium sulfate. Ether was then removed by evaporation, and the resulting red-brown liquid was purified by fractional distillation under reduced pressure to yield a yellow liquid of bp 98°C/4 mm; yield, 61.3%. A new absorption band in the infrared spectrum is recognized at 3000 cm^{-1} (methyl group).

Since this liquid was known to contain some monomethyl compound from infrared evidences and the properties of the polydimethylaminostyrene and the azomonomer derived from it, the removal of the monomethyl compound by acetylation was carried out. Thus, the product was refluxed for 2 hr with a threefold volume of acetic anhydride. Upon cooling, the reaction mixture was dissolved in ether and dimethylaminoacetophenone was extracted with dilute hydrochloric acid. The extract was neutralized with sodium hydroxide, then extracted with ether, followed by purification by fractional distillation.

α-(*m*-Dimethylaminophenyl)ethanol (IX). In a 500-ml three-necked flask, equipped with a reflux condenser, a magnetic stirrer, and a dropping funnel, were placed 200 ml of anhydrous tetrahydrofuran and 7.4 g (0.2 mole) of lithium aluminum hydride. To this was added through the dropping funnel 10 g (0.06 mole) of *m*-dimethylaminoacetophenone in 150 ml tetrahydrofuran, followed by 1 hr refluxing. After decomposing the unreacted lithium aluminum hydride with water and removing tetrahydrofuran by evaporation, ether extraction was carried out, followed by dehydration with anhydrous sodium sulfate and subsequent fractionation. The yield was 47.5%; bp, 126–128°C/2 mm (lit.[9] bp. 130°C/3 mm).

The carbonyl absorption at 1700 cm^{-1} is no longer discernible in the infrared spectrum.

***m*-Dimethylaminostyrene (X).** A procedure analogous to that adopted by Manecke and Kossmethl[9] was employed. Thus, from 4.7 g (0.03 mole) of α-(*m*-dimethylaminophenyl)ethanol and 16 g of activated alumina there was obtained a colorless oil of bp 105°C/2 mm (lit.[9] bp, 120°C/10 mm) in 76% yield.

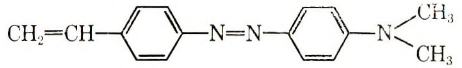
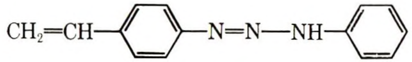
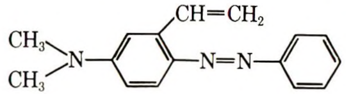
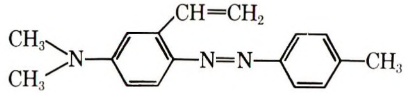
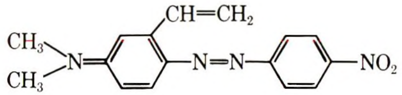
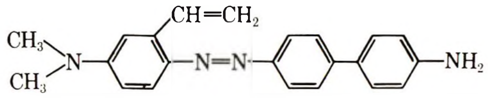
***o*-Coumaric Acid (XIII).** The method of Ebert[10] was employed. From 100 g (0.68 mole) of coumarin and 32 g (1.4 mole) of sodium dissolved in 500 ml of absolute ethanol, there was obtained 84 g (75%) of almost colorless product after recrystallization from water; mp, 207–208°C (lit.[10] mp, 208°C).

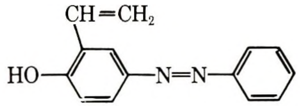
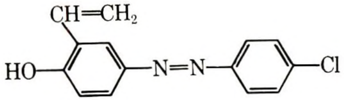
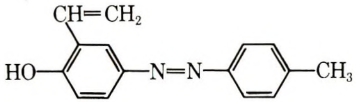
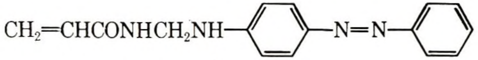
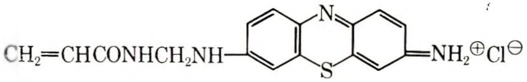
***o*-Hydroxystyrene (XIV).** *o*-Coumaric acid was decarboxylated according to the procedure of Fries and Fickwirth[11] under reduced pressure (ca. 5 mm). From 70 g (0.43 mole) of *o*-coumaric acid, there was obtained 30 g (58%) of colorless oil after redistillation (bp, 58–59°C, 1 mm), which solidified upon standing to a white crystalline mass of mp 28°C.

4-Vinyl-4′-dimethylaminoazobenzene(IVa). A 1.19-g portion (0.01 mole) of *p*-aminostyrene was dissolved in water containing ca. 2 ml (0.02 mole) of concentrated hydrochloric acid with cooling. To the resulting solution under cooling was added 0.69 g (0.01 mole) of sodium nitrite in aqueous solution to provide a yellowish turbid solution, followed by the immediate addition of 1.2 g (0.01 mole) of dimethylaniline in glacial acetic acid to yield an orange-red colored turbid solution. The reaction mixture was then made basic with aqueous ammonia to precipitate an orange-brown colored coupling product, which was filtered and rinsed with water several times.

Recrystallization from ethanol–water afforded fine orange crystals of mp 132–134°C in 70% yield; absorption maximum in benzene, 428 mμ.

TABLE I
Properties of the Photochromic Monomers Synthesized

Monomer	Mp, °C	λ_{max} in benzene, mμ	
	132–134	428	(1)
	75–77	373	
	—	420	(2)
	Oily	423	
	—	465	
	55–57	429	

	105–106	350	(3)
	134–135	358	
	138–139	355	
	115–117	380	(4)
	—	603	

4-Vinyl diazoaminobenzene (IVb). This monomer was prepared from *p*-aminostyrene and aniline via the diazotization of the former and the subsequent coupling in acetic acid with the addition of equivalent sodium acetate to remove hydrochloric acid; mp, 75–77°C; absorption maximum in benzene, 373 mμ. This monomer was subjected to rearrangement procedure with aniline hydrochloride using aniline as diluent. In spite of the readiness observed in the corresponding model compound 4-methyldiazoaminobenzene, however, this diazoamino monomer could not be rearranged to the expected azo monomer, presumably due to the presence of the vinyl double bond conjugate to the diazo group.

2-Vinyl-4-dimethylaminoazobenzene (XI). Aniline (0.093 g., 0.001 mole) was dissolved in water containing 0.2 ml (ca. 0.002 mole) of concentrated hydrochloric acid with cooling. To the resulting solution under cooling was added 0.069 g (0.001 mole) of sodium nitrite in aqueous solution, followed by the immediate addition of 0.143 g (0.001 mole) of *m*-dimethylaminostyrene in glacial acetic acid to yield an orange-red turbid solution. The reaction mixture was then made basic with aqueous sodium hydroxide to precipitate an orange-red coupling product, which was filtered and rinsed with water several times. The orange-colored mass thus obtained was extracted with benzene. The orange-red extract was then treated with dilute hydrochloric acid to remove unreacted aniline derivatives, followed by neutralization with ammonia water. A bright red mass was obtained by freeze-drying from benzene solution. The mass was recrystallized from ethanol–water to provide orange-red crystals; absorption maximum in benzene, 420 mμ.

2-Vinyl-4-dimethylamino-4′-methylazobenzene, 2-vinyl-4-dimethylamino-4′-(*p*-amino)phenylazobenzene, and 2-vinyl-4-dimethylamino-4′-nitroazobenzene were synthesized according to the same procedure, their properties being listed in Table I.

3-Vinyl-4-hydroxyazobenzene (XV). A diazonium salt solution, prepared by mixing 5.18 g (0.04 mole) of aniline hydrochloride in 50 ml of 1% hydrochloric acid with 2.67 g (0.04 mole) of sodium nitrite in 30 ml water, was added dropwise under cooling to a solution of 4.81 g (0.04 mole) of *o*-hydroxystyrene in 2.5% aqueous sodium hydroxide. After 1 hr stirring and subsequent filtration, Dry Ice was added to the filtrate to produce a deep-orange precipitate in 57% yield, which was then recrystallized from a benzene–ligroin (1:1) mixture to provide lustrouso range–yellow crystals of mp 105–106°C.

ANAL. Calcd: N, 12.48%. Found: N, 12.41%.

3-Vinyl-4-hydroxy-4′-methylazobenzene and 3-vinyl-4-hydroxy-4′-chloroazobenzene, as listed in Table I, were synthesized in a similar manner.

4-(*N*-Acrylamidomethyl)aminoazobenzene (XVI). A 1.5-g portion of *N*-hydroxymethylacrylamide (0.015 mole) and 1.97 g (0.01 mole) of 4-aminoazobenzene were dissolved in 30 ml acetonitrile, a small amount of hydroquinone being added. The solution was refluxed for 1.5 hr. Upon cooling, it was poured into a large quantity of water to precipitate a brownish yellow mass, which was recrystallized from ethanol–water. Repetition of recrystallization provided a brownish-yellow crystalline substance of mp 115–117°C in 86% yield; absorption maximum in benzene, 380 mμ.

ANAL. Calcd: N, 20.02%. Found: N, 20.80%.

The infrared spectrum indicates the carbonyl absorption attributable to the acrylamidomethyl group at 1650 cm^{-1}.

***N*-Acrylamidomethylthionine (XVII).** Thionine (2.6 g, 0.010 mole) and 1.5 g (0.015 mole) of *N*-hydroxymethylacrylamide were dissolved in 50 ml water, a small amount of hydroquinone being added. The resulting solution was kept at 80°C for 1 hr, followed by precipitation into a large quantity of ethanol. Recrystallization from water provided a deep-violet crystalline mass in 54% yield; absorption maximum in water, 603 mμ.

ANAL. Calcd: S, 9.28%. Found: S, 8.99%.

the infrared spectrum also indicates the carbonyl absorption at 1650 cm^{-1}.

The model azo compounds employed were prepared according to conventional procedures, except 4-aminoazobenzene, which was commercially obtained.

Polymerization

The azo monomers were polymerized in sealed ampules under vacuum or in an inert atmosphere with tetrahydrofuran as solvent and azobisisobutyronitrile as initiator. For *N*-acrylamidomethylthionine, water was used as solvent and potassium persulfate as initiator. From practical standpoints, copolymers were prepared exclusively. As regards *N*-acrylamidomethylthionine, the copolymerization with 10-fold acrylamide afforded only a trace of polymer. Styrene, methyl methacrylate, and acrylic esters were employed as comonomers in the azo copolymerizations. A typical example is as follows.

A solution of 0.05 g of 4-vinyl-4′-dimethylaminoazobenzene, 0.45 g of styrene, 0.5 g of tetrahydrofuran, and 0.002 g of azobisisobutyronitrile was put into a Pyrex glass ampule, which was then evaluated and sealed off. Upon standing 48 hr at 80°C, a viscous red solution resulted. It was precipitated into petroleum ether, followed by redissolution in benzene and successive reprecipitation into petroleum ether. This reprecipitation procedure was reiterated at least twice. The purified polymer was freeze-dried from benzene to provide an orange powder in 96% conversion; intrinsic viscosity $[\eta]$ in benzene at 20°C, 0.13.

Preparation of Photochromic Polymer by Chemical Reaction of Polymer Via Diazocoupling Reactions of Poly-*o*-hydroxystyrene. A typical example is as follows.

An aqueous solution containing 0.083 mole of *p*-chlorobenzenediazonium chloride was added dropwise, with stirring at 5°C, to an aqueous solution containing 10.0 g (0.083 mole) of poly-*o*-hydroxystyrene($[\eta]$ = 0.11) and 25 g of sodium hydroxide.

Stirring was continued for 1 hr longer, followed by neutralization with hydrochloric acid to yield a brown precipitate. It was purified by dissolving in tetrahydrofuran and subsequent precipitation into water. The extent of reaction was 86%.

Via Reactions of *N*-Hydroxymethylacrylamide Polymers with Aminoazobenzene Derivatives. *N*-Hydroxymethylacrylamide copolymers with inert vinyl monomers such as acrylic and methacrylic esters and styrene were combined with aminoazobenzene derivatives via the condensation reactions of *N*-methylol with amino groups. Thus, in a typical example, 2.5 g of *N*-hydroxymethylacrylamide, 5 g each of butyl acrylate and methyl methacrylate, 0.15 g of benzoyl peroxide, and 0.1 ml of dodecyl mercaptan were dissolved in 30 ml tetrahydrofuran, and polymerization was carried out at 70°C for 5 hr. The resulting polymer solution was diluted with tetrahydrofuran so as to afford 10% concentration, excess 4-aminoazobenzene being added, followed by 15 hr refluxing. The resulting deep orange-colored solution was poured into water. The precipitate thus produced was dissolved in tetrahydrofuran and reprecipitated into water. This operation was reiterated several times. The extent of reaction as calculated from the result of elementary analysis was 61.4% of the *N*-hydroxymethyl group. $[\eta]$ = 0.33 (acetone, 20°C); absorption maximum in benzene, 381 mμ (sample 11).

Via reaction of *N*-Hydroxymethylacrylamide Polymer with Thionine. Almost the same procedure was employed as for aminoazobenzene derivatives, except that water was used as solvent. In a typical procedure, to 10 ml of 5% aqueous solution of the *N*-hydroxymethylacrylamide–acrylamide copolymer (1:5 by weight; $[\eta]$ in water at 30°C, 1.2) were added 0.4 g of thionine in 5 ml of water, the mixture being heated 5 hr at 90°C. The resulting solution was precipitated into ethanol, followed by several repetitions of dissolution in water and subsequent precipitation into ethanol. The purified solution was then freeze-dried to give a fluffy violet polymer. Redox titration of this polymer in aqueous solution with titanous chloride indicates that the reaction was almost quantitative.

Measuring Instrument

An irradiation (ca. 80 000 lux) at a distance of 30 cm from a 500-W tungsten lamp spotlight was employed for the acrylamidomethylthionine polymer films. However, since the spectral changes with light irradiations are usually too fast to permit taking of exact spectra, an instrument with a rotating shutter working upon a principle similar to that proposed by Gould and Brode[12] was devised in order to effect the measurements under irradiation (Fig. 1). The instrument was attached to the cell compartment of a Hitachi recording spectrophotometer (Model EPS-3T). Thus, a polymer solution in an optical cell, which is transparent on all sides, was placed in the sample compartment, which was then exposed to intermittent irradiation from a 100-W projection lamp with the rotating shutter, the

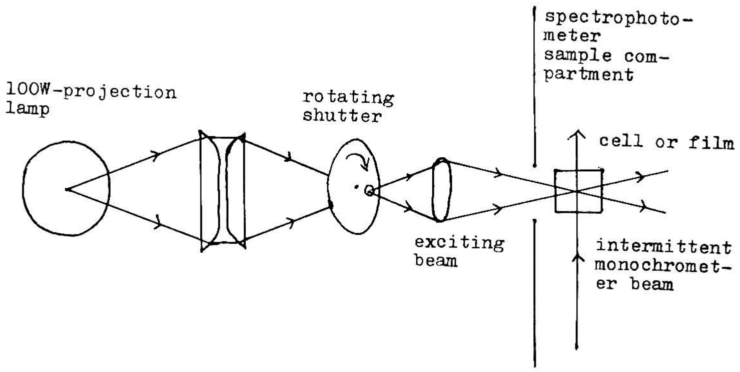


Fig. 1. Schematic representation of the measuring instrument with rotating shutter device.

light being directed at right angles to the monochrometer beam and the shutter being so adjusted as to admit the exciting and monochrometer beams alternately. In the case of films, polymer solutions were evaporated to films 0.01–0.1 mm in thickness on thin glass plates which are almost transparent over a range of 350–500 mμ. The glass plates were then inserted diagonally into the sample cell holder to effect irradiation.

Photochromic Behavior

Aminoazobenzene Polymers. Figures 2 and 3 indicate typical spectral changes in vinylaminoazobenzene polymers with 10 min irradiation with

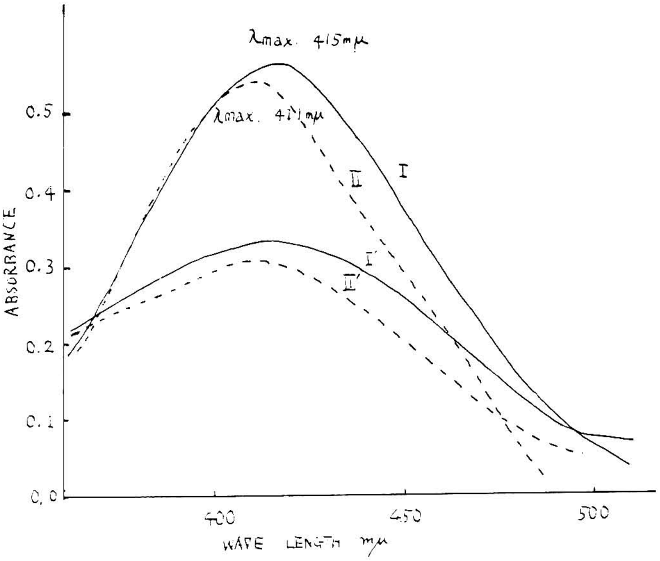
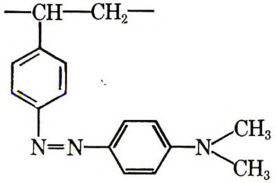
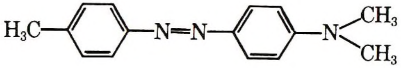
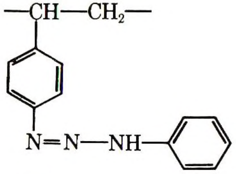
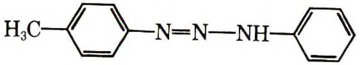
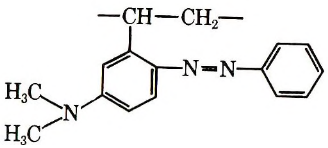
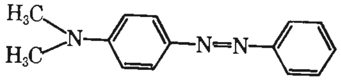
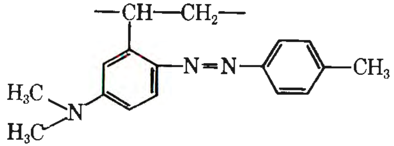
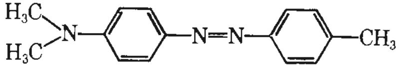
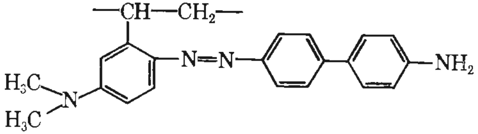
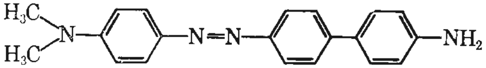


Fig. 2. Absorption spectra of (——) 4-vinyl-4′-dimethylaminoazobenzene (copolymer with styrene (1:9 by weight) and (- - -) 4-methyl-4′-dimethylaminoazobenzene in benzene solutions, exposed to: (I, II), darkness (*I′*, *II′*) the exciting beam (no filter). Concentration of the polymer, 3×10^{-2} g/l.

TABLE II

Photochromic Properties of Copolymers of Vinylaminoazobenzenes with Styrene (1.9 by weight) and their model Compounds

Sample	Compound	State[a]	Absorbance maximum, mμ	Irradiation time, min	E^{L}_{max}/E^{D}_{max}	50% Recovery, min
1		Soln	415	10	0.593[b] 0.753[c] 1.000[d] 1.000[e]	30
		Film	415	10	0.711	150
2		Soln	411	10	0.588	90
		Film[f]	414	10	0.613	240
3		Soln	365	45	0.860	30
4		Soln	360	30	0.863	10
5		Soln	420	30	0.737	15
		Film	420	10	0.870	7

6		Soln Film[f]	420 419	30 10	0.517 0.767	30 8
7		Soln Film	424 424	10 10	0.823 0.863	12 10
8		Soln Film[f]	420 418	10 10	0.740 0.650	2 40
9		Soln Film	398 400	10 —	0.949 —	2 —
10		Soln Film[f]	445 446	10 10	0.699 0.808	5 7

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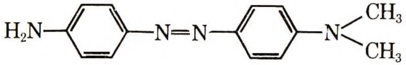
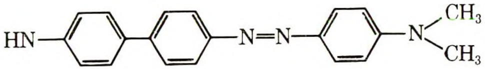
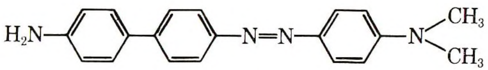
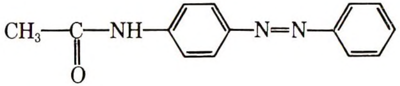
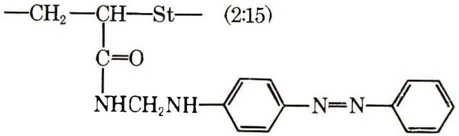
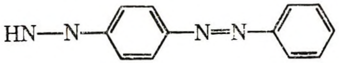
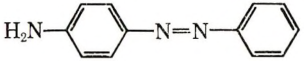
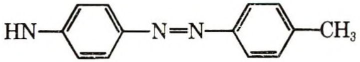
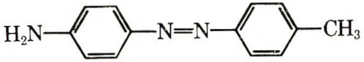
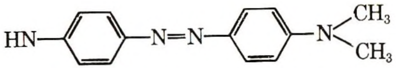
[a] Soln denotes benzene solution.
[b] No filter.
[c] Toshiba blue filter.
[d] Toshiba green filter.
[e] Toshiba red filter.
[f] Embedded in polystyrene film.

TABLE III
Photochromic Properties of 4-Acrylamidomethylaminoazobenzene Polymers and Related Model Compounds

Sample	Azobenzene component in polymer or model compound	State	Absorbance maximum, mμ	Irradiation time, min	$E^{L}_{max}\lambda/E^{D}_{max}$	50% Recovery, min
11		Soln Film	381 391	10 10	0.641 0.712[a]	10 5
12		Soln Film[b]	378 381	10 10	0.677 0.783	10 15
13		Soln	377	20	0.722	5
14		Soln Film[c] Film[d] Film[e]	379 381 388 390	10 10 10 10	0.738 0.668 0.672 0.886	8 30 10 1
15		Soln	413	10	0.711	4
16		Soln	412	10	0.660	3

17		Soln	426	10	0.735	10
18		Soln	427	10	0.662	10
19		Soln Ethanol–water(NaHCO₃)	354 347	60 20	0.642 0.872	Very long 80
20		Soln Film	384 390	10 10	0.763 0.793	7 90
						

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[a] 0.843, 0.908, and 0.921 are obtained for Toshiba blue, green, and red filters, respectively.

[b] Embedded in BA-MMA(1/1) copolymer.

[c] Embedded in polystyrene film.

[d] Embedded in BA-MMA(1/1) copolymer.

[e] Embedded in MAM-BA-MMA(1/2/2) terpo'ymer.

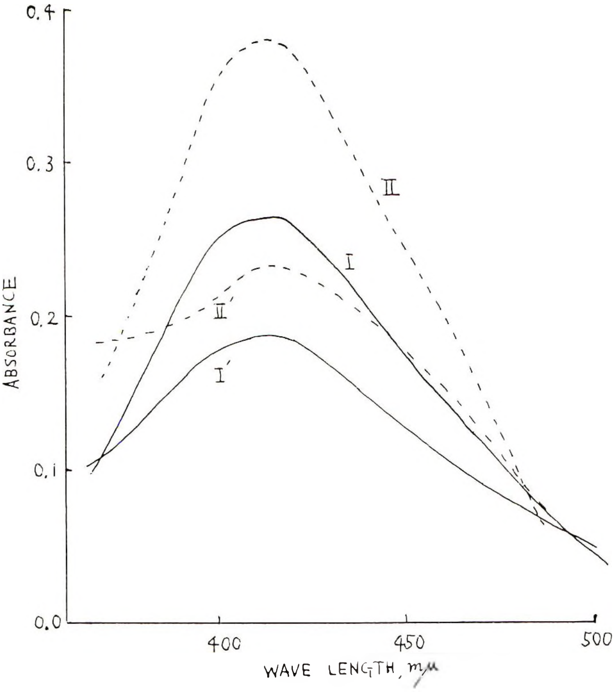


Fig. 3. Absorption spectra of 4-vinyl-4′-dimethylaminoazobenzene polymer and 4-methyl-4′-dimethylaminoazobenzene embedded in polystyrene: (*I*, *II*) exposed to darkness; (*I′*, *II′*) exposed to the exciting beam in film states (ca. 0.01 mm thickness). Notations are the same as for Fig. 2.

the use of the rotating shutter. As seen from these curves, absorption peaks for both 4-vinyl-4′-dimethylaminoazobenzene polymer (sample 1) and its model compound, 4-methyl-4′-dimethylaminoazobenzene, when irradiated, shift towards shorter wavelengths, absorbances at the original wavelengths being decreased simultaneously. Isosbestic points are also found in each case, denoting that new absorption peaks appear with irradiation. In Figure 4 are shown, for this polymer, the changes of transmittance at the original peak sites with irradiation and its recovery in dark. As far as this polymer and its model compound are concerned, the rate of recovery after exposure for the polymer is greater than that for the corresponding model compound.

Table II summarizes numerical data for this system, other related polymers, and their model compounds.

In Table II, $E^{\mathrm{L}}_{\max}/E^{\mathrm{D}}_{\max}$ denotes the ratio of absorbances (light/dark) at the peak wave length in dark. The results obtained on another series of aminoazobenzene polymers, prepared by the condensation reactions of a terpolymer of *N*-hydroxymethylacrylamide(MAM)–butyl acrylate(BA)–methyl methacrylate(MMA) (1:2:2 by weight) with aminoazobenzene derivatives are given in Fig. 5 and Table III. To this table were also added the data for a 4-(*N*-acrylamidomethyl)aminoazobenzene copolymer

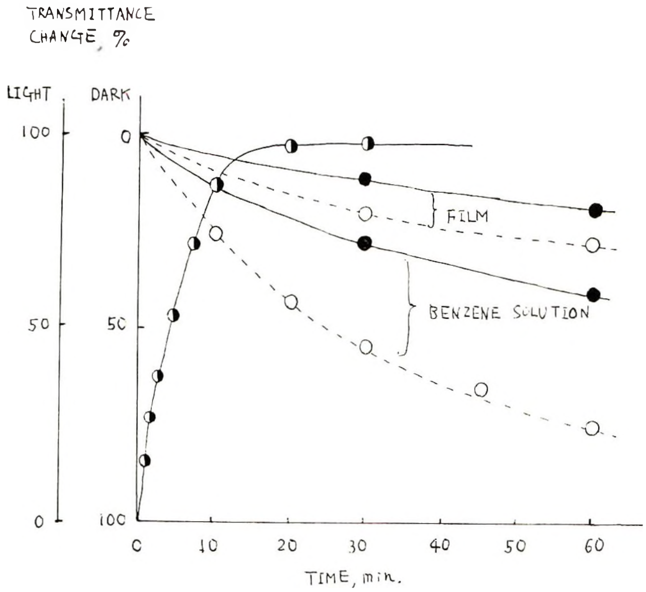


Fig. 4. Rates of the changes of transmittances at absorption maxima (dark); (◑) exposed to the exciting beam for 4-vinyl-4′-dimethylaminoazobenzene–styrene (1:9) copolymer in benzene solution; (○, ●) exposed to darkness after 20 min irradiation for the polymer and 4-methyl-4′-dimethylaminoazobenzene, respectively.

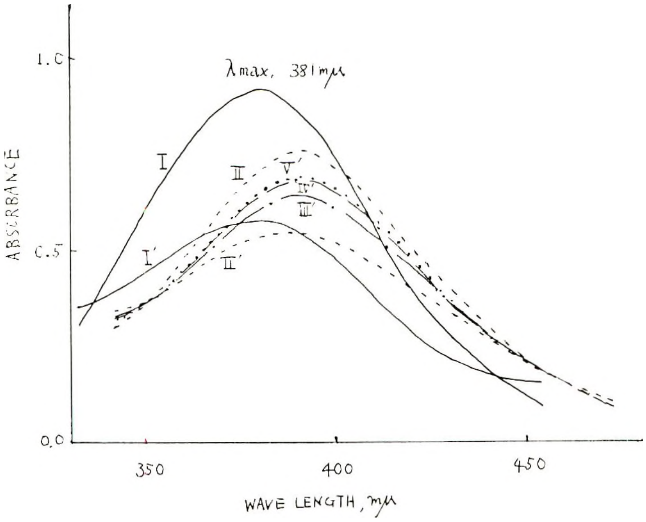
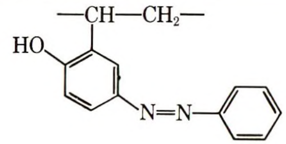
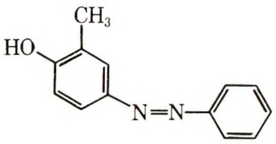
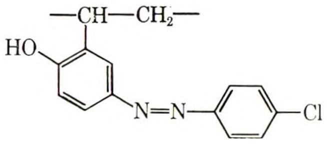
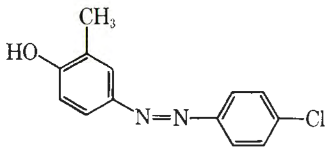
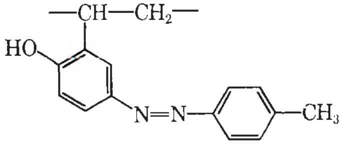
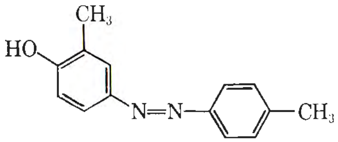


Fig. 5. Absorption spectra of a 4-acrylamidomethylaminoazobenzene –MMA–BA (1:2:2) terpolymer, exposed to: (*I*, *II*) darkness; and (*I′*, *II′*, *III′*, *IV′*, *V′*) the exciting beam; (——) benzene solution (polymer concentration, 0.136 g/l); (--) 0.1 film, without filter, (—·—) film with blue filter (max. transmittance 460 mμ); (– – · – –) film with green filter (530 mμ); (· · ·) film with red filter (700 mμ).

TABLE IV
Photochromic Properties of Vinylhydroxyazobenzene Polymers and Related Model Compounds[a]

Sample	Compound	State	Absorbance maximum, mμ	Irradiation time, min	E^{L}_{max}/E^{D}_{max}	50% Recovery min
21		Soln Film	355 358	60 60	0.72 0.81	— —
22		Soln	350	60	0.79	—
23		Soln Film	362 364	60 60	0.64 0.79	60 —

24		Soln Film[b]	358 358	60 60	0.72 0.81	60 420
25		Soln Film	357 359	60 60	0.72 0.82	— —
26		Soln	352	60	0.77	—

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[a] Copolymers with methyl methacrylate and ethyl acrylate (1:5:5 by weight).
[b] Embedded in polystyrene film.

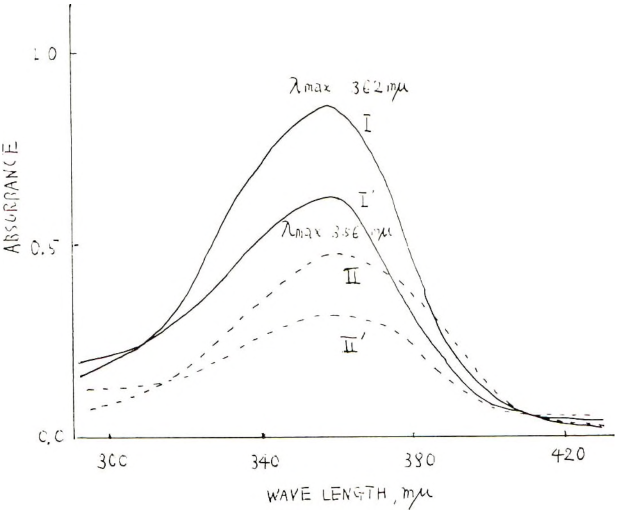


Fig. 6. Absorption spectra of (——) 3-vinyl-4-hydroxy-4′-chloroazobenzene–methyl methacrylate–ethyl acrylate (1:5:5) by weight terpolymer and (- -) 3-methyl-4-hydroxy-4′-chloroazobenzene, exposed to: (*I*, *II*) darkness; (*I′*, *II′*) the exciting beam.

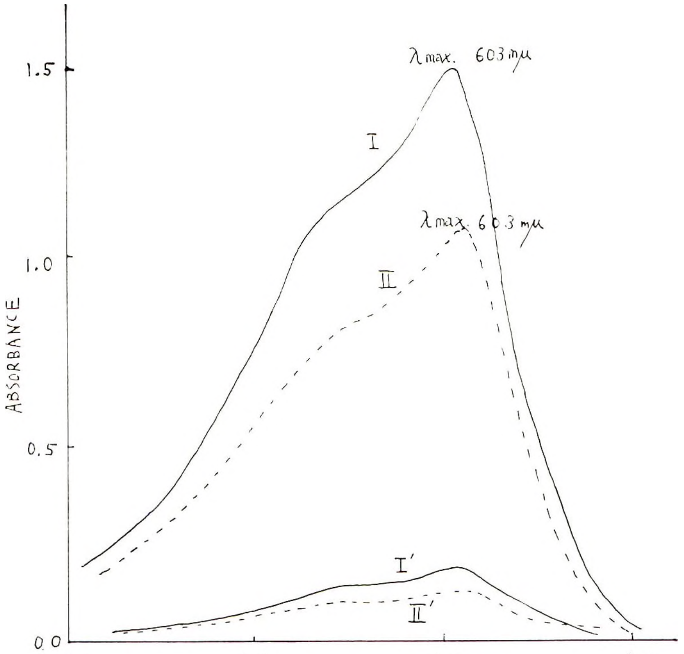


Fig. 7. Absorption spectra of (——) *N*-acrylamidomethylthionine–acrylamide (1:7 mole/mole) copolymer and (- -) thionine in aqueous solutions exposed to: (*I*, *II*) darkness; (*I′*, *II′*) the exciting beam. Aqueous solutions contain 0.1 mole/l phosphoric acid and 0.001 mole/l ferrous ammonium sulfate; polymer concentration, 10 mg/l.

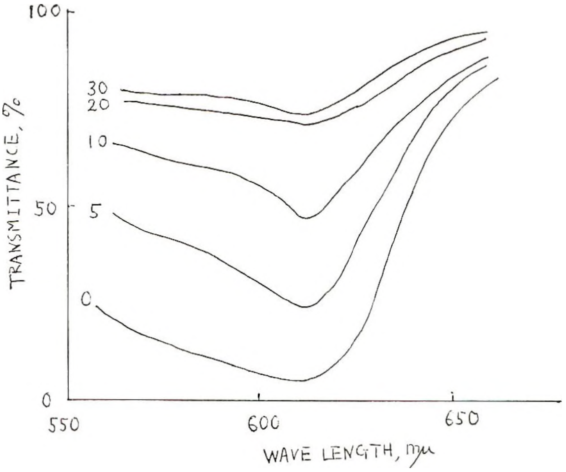


Fig. 8. Change of the absorption spectrum of a *N*-acrylamido-methylthionine–*N*-hydroxymethylacrylamide–acrylamide (0.02/1/7 mole/mole/mole) terpolymer with irradiation. Figures in the diagram denote the irradiation time in minutes from a 500-W spot reflector lamp at a distance of 30 cm. Film was prepared with the addition of equal amount of poly(vinyl alcohol) (DP, 500) in ca. 0.01 mm thickness.

with styrene (2:15 by weight), prepared by the copolymerization of the azomonomer (sample 20).

It is to be noted that blue light is most effective for the photochromic excitation, that compounds without polar substituents in the 4′ positions (samples 11 and 13) are superior to the corresponding model compounds (samples 12 and 14), and that marked effects of comonomers and matrix polymers are observed.

Hydroxyazobenzene Polymers. Figure 6 and Table IV indicate the results obtained for 3-vinyl-4-hydroxyazobenzene polymers and their model compounds. In this series, it can be generally said that absorption peaks are located at lower wavelengths, as compared with the aminoazobenzene series, and that it takes more times in reaching equilibrium under irradiation as well as for recovery.

Thionine Polymers. In Figures 7 and 8 and in Table V are indicated the reversible color fadings of *N*-acrylamidomethylthionine polymers by redox mechanisms.

The presence of some additives, including reductants and active surfaces, is required to enhance the sensitivity of the photo-induced reduction of the blue thionine component in polymer. Ferrous ion in aqueous solutions and poly(vinyl alcohol) in the film states were found to be the most useful for this, sensitivities being strongly dependent upon the amounts of the additives employed. Thus, in dilute acid solutions, the thionine polymer–ferrous ion system induces rapid and strong color fading even with the irradiation from the 100-W tungsten lamp (Fig. 7). In film states, however, the incorporation of low molecular compound is unfavorable from a practical standpoint, so that polyvalent alcohols in the form of polymer,

TABLE V
Photochromic Properties of *N*-Acrylamidomethylthionine Polymers

Sample	Composition	State	Absorbance maximum, mμ	Irradiation time, min	E^{L}_{max}/E^{D}_{max}	50% Recovery, min
27	*N*-Acrylamidomethylthionine–AM(1/7) copolymer[b]	Aqueous[a]	603	10	0.162	5
28	*N*-Acrylamidomethylthionine–MAM–AM(0.02/1/7)[b] terpolymer + PVA(DP, 500) (1:1)[c]	Film	612	30[d]	0.083	400
29	*N*-Acrylamidomethylthionine–AM(1/7)[b] copolymer + PVA(DP, 500) (1:10)[c]	Film	612	5[d]	Colorless	60

[a] 0.1 mole/l HPO_4; 1.8×10^{-3} mole/l ferrous ammonium sulfate; polymer concentration, 10 mg/l.
[b] Molar ratio.
[c] Weight ratio.
[d] 500-W spot reflector lamp.

such as poly(vinyl alcohol), were employed. In order to induce the reversible photobleaching on this case, higher light intensities necessitating the use of the 500-W lamp, were required.

DISCUSSION

As is well known for low molecular weight azobenzene derivatives,[13,14] the azobenzene groups in the polymer molecule are considered to contain the *cis* and *trans* isomers in equilibrium with each other, and irradiation causes partial isomerization to unstable *cis* isomer and subsequent standing in the dark results in reversal to the stable form, *trans* isomer. This *cis–trans* isomerization affects the coplanarity of the azobenzene molecule, thereby causing changes in absorption spectrum. This change of coplanarity is, of course, subject to steric conditions, making solutions of polymer more advantageous than films. Moreover, in film states, flexible inert components such as acrylates are preferred to rigid ones such as styrene. This relationship can be recognized from the comparison between the data for 4-amino-4′-methylazobenzene embedded in polystyrene and that for the same compound in a butyl acrylate–methyl methacrylate copolymer film (sample 14). It was also seen in the copolymers of *p*-(*N*-acrylamidomethyl)aminoazobenzene (samples 11 and 20). As regards the effects of polar groups in the matrix, the hydroxyl group is found to hamper the

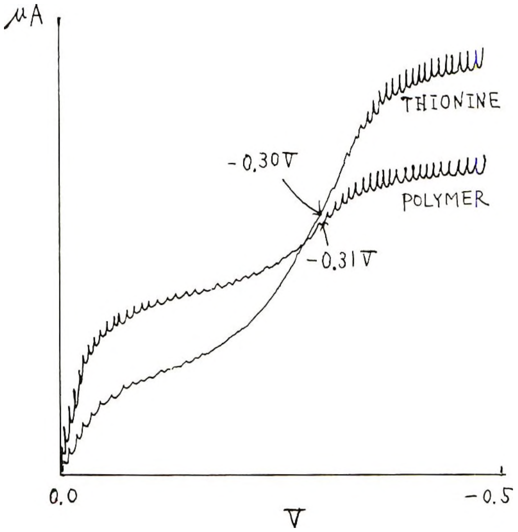


Fig. 9. Polarographic reduction wave for the thionine polymer (sample 27) with the dropping mercury electrode in an aqueous buffer (pH 5; 0.1*M* sodium acetate with the addition of acetic acid).

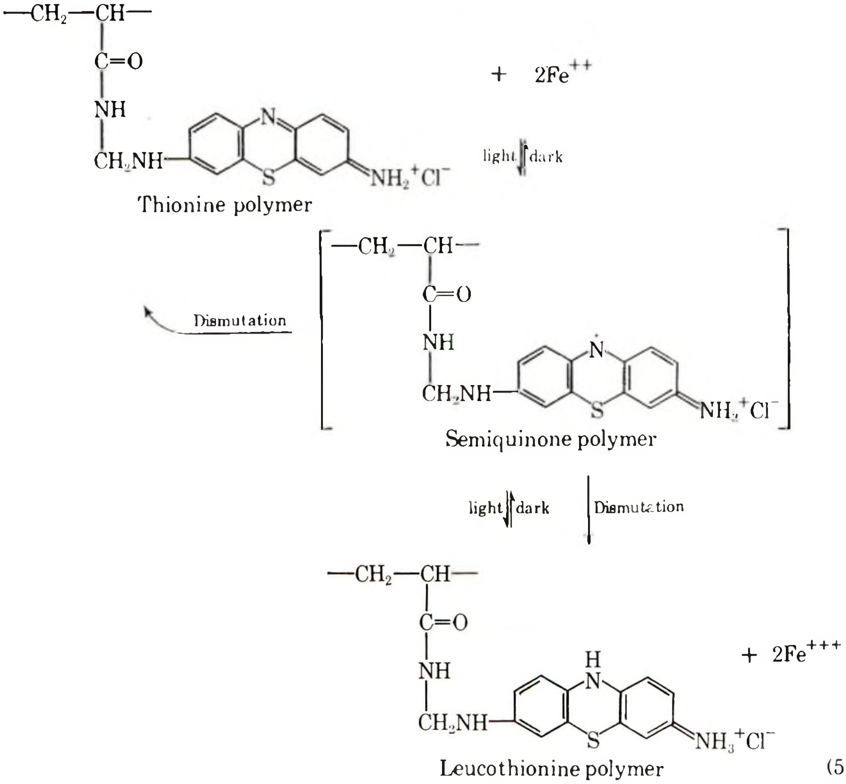
cis–trans isomerization, probably due to the formation of hydrogen bond, as clearly known from the data for 4-amino-4′-methylazobenzene embedded in a *N*-hydroxymethylacrylamide–butyl acrylate–methyl methacrylamide terpolymer (sample 14).

The fact that more favorable results were obtained for some polymers, as compared with the corresponding model compounds, might relate to the problem of the aggregations of azobenzene molecules in film or solution states. Thus, while the fixation of an azobenzene component to a copolymer chain causes steric hindrance for the *cis–trans* isomerization, the isolation of each component from others by inert comonomer components, thus attained, might prevent their aggregations through hydrogen bondings. The former effect is contrary to the latter and practical data are considered to indicate the balances of the two. The best results in this connection are hence observed for the polymers the azobenzene components of which contain no hydrogen-bond-forming substituents other than those for the connections with the polymer substrates (e.g., samples 1 and 11).

It is well known that thiazine derivatives in the oxidized forms, such as thionine, methylene blue, and azure A, B, and C, indicate reversible photobleachings for themselves or in the presence of a sensitizer or a reductant. Thus, Parker[15] indicated that, when oxygen-free solutions of methylene blue or thionine in dilute sulfuric acid are subjected to flash photolysis, reversible bleaching of the dyestuffs occurs, both the long-lived species likely to be semiquinone and produced by wavelengths shorter than 250 mμ and the short-lived species at longer wavelengths, which appear to be triplet levels, being observed.

Sensitizers such as silica gel and zinc oxide have also been reported.[16] Ferrous and stannous ions, ascorbic acid, phenylhydrazine, etc.[17,18] have been known to be effective reductants for reversible photobleachings of methylene blue or thionine.

The absorption changes observed with ferrous ion as reductant in the polymer can be interpreted in terms of the reaction scheme (5).



(5)

Thus, the thionine polymer excited by irradiation, probably to triplet levels, is reduced by ferrous ion to "half-reduced" semiquinone free radical, which rapidly induces dismutation to provide the leuco- and thionine components or which is further reduced to the leucothionine level. The polymeric character of the thionine polymer might exert some influences upon the extent of the dismutation reaction. However, as well recognized from the polarograms in Figure 9, there are observed no appreciable steps for the semiquinone levels in both the thionine polymer and thionine itself, so that the semiquinones are considered to be very unstable, and their formations transient.

As regards Figure 8 and Table V, whether the hydroxyl groups of poly(vinyl alcohol) added participate themselves in the reduction of the thionine components, or merely play a role of carriers of the activated water molecules adsorbed on them (the water molecules participating in reduction) has not as yet been ascertained. However, excellent reversibility encountered in this system and relatively slow recovery might induce us to adopt the latter mechanism for photobleaching and air oxygenoxidation for recovery of color as principal causes.

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Polymerization of Allyl(vinyl Phenyl) Ethers and Reactions of the Resulting Polymers

MASAO KATO and HIROYOSHI KAMOGAWA, *The Textile Research Institute of the Japanese Government, Yokohama, Japan*

Synopsis

Solution polymerizations of allyl(*o*-vinyl phenyl)ether and allyl(*p*-vinyl phenyl)ether with cationic and radical initiators were investigated. Soluble polymers were formed in polymerizations with boron trifluoride etherate and with benzoyl peroxide. In polymerization with azobisisobutyronitrile the polymerization in dilute solution gave a soluble polymer, whereas that in concentrated solution gave a crosslinked, insoluble one. For information on the polymerization behavior some infrared and ultraviolet spectroscopic investigations of the soluble polymers were made. From these results it appears that polymers with pendant allyl groups are formed in polymerization with boron trifluoride etherate at low temperature, and polymers containing pendant vinyl groups and allyl groups are obtained with the two types of radical initiator. Copolymerizations of these monomers with ethyl vinyl ether and styrene with the use of boron trifluoride etherate were successfully effected. Such reactions as Claisen rearrangement, crosslinking induced with radical initiators, and epoxidation with perbenzoic acid were examined for the polymers prepared in the polymerization with boron trifluoride etherate. Good results were obtained for the former two reactions. However, the latter was unsuccessful.

INTRODUCTION

We have undertaken the preparation of polymers containing hydroxystyrene so as to obtain chemically reactive and photoresponsive polymers. Up to this time hydroxymethylation,[1] epoxidation,[2] and allylation[2] of hydroxystyrene polymers have been studied for the purpose of preparing three-dimensional resins. Polymers from *o*-hydroxystyrene containing azo dye groups have been investigated as photochromic polymers.[3] The polymerization behavior of *o*-hydroxystyrene also has been investigated in detail.[4,5]

In the work reported in this paper the allyl ethers of *o*- and *p*-hydroxystyrene were homopolymerized with cationic and radical initiators and were copolymerized with ethyl vinyl ether and styrene with cationic initiators for the purpose of preparing linear polymers. Such reactions as Claisen rearrangement, crosslinking induced with radical initiators, and epoxidation with perbenzoic acid were investigated in the polymers thus obtained.

While this work was being carried out the polymerization behavior of allyl(*p*-vinyl phenyl)ether with anionic catalysts was reported by D'Alelio and Hoffend.[6]

EXPERIMENTAL

Materials

o-Hydroxystyrene was prepared from coumarin, according to the method reported in the previous paper,[4] and distilled before use; b.p. 58–59°C at 1 mm.

p-Hydroxystyrene was synthesized by the procedure of Coroson and others.[7] In this work *p*-hydroxyacetophenone was used as starting material. From 15.5 g of *p*-acetoxystyrene there was obtained 9.9 g (86%) of pale-brown crystalline mass (without recrystallization); m.p. 64–66°C (lit.[8] 71–72°C).

Allyl phenyl ether was synthesized from phenol and allyl bromide according to the method described in the literature;[9] b.p. 82–83°C at 18mm (lit.[8] 85°C at 19 mm).

Allyl(*o*-vinyl phenyl)ether (I) was prepared by the following procedure. A mixture of 12.0 g (0.100 mol) of *o*-hydroxystyrene, 13.3 g (0.110 mol) of allyl bromide, 20 g of anhydrous potassium carbonate, and 25 ml of absolute ethanol were heated at reflux temperature for 4 hr. At the completion of the reaction 100 ml of water and 100 ml of petroleum ether were added. The organic layer was separated and washed twice with 5% sodium hydroxide solution. The petroleum ether solution was dried over anhydrous sodium sulfate, the solvent was removed by distillation, and the residue was distilled under reduced pressure to give 12.2 g (76%) of colorless oil; b.p. 63–66°C at 0.7 mm.

ANAL. Calcd. for $C_{11}H_{12}O$: C 82.47%, H 7.55%. Found: C 82.36%, H 7.28%. The molecular weight determination by means of vapor-pressure osmometry (Mechrolab) gave the value of 168; the theoretical value is 160.2.

Allyl(*p*-vinyl phenyl)ether (II) was obtained by the same procedure as in the preparation of (I). From 8.2 g of *p*-hydroxystyrene there was obtained 7.4 g (68%) of colorless oil; b.p. 74–77°C at 0.7 mm.

ANAL. Found: C 82.16%, H 7.90%. The molecular weight determination gave the value of 157.

Perbenzoic acid was prepared by hydrolysis of benzoyl peroxide according to the method recorded in the literature.[10]

Styrene, α-methylstyrene, and ethyl vinyl ether, used as comonomers, were all commercial products and were purified by distillation just before use. Maleic anhydride was recrystallized from chloroform.

Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO), used as radical initiators, were purified in the usual manner. Boron trifluoride etherate (BTE) and stannic chloride, used as cationic initiators, were of the highest purity commercially available. The latter was purified by distillation after refluxing with phosphorus pentoxide for several hours.

Methylene chloride as solvent for cationic polymerizations was distilled over phosphorus pentoxide. Tetrahydrofuran for radical polymerizations was refluxed over sodium for several hours and then distilled.

Polymerizations

Cationic Polymerizations. A solution of (I) or (II) in methylene chloride was transferred to a flask, which was then sealed with a serum stopper. The flask was cooled to −78°C in a bath of methanol and solid carbon dioxide, and the content was stirred by means of a magnetic stirrer. BTE or stannic chloride was injected through the stopper into the flask, and stirring was continued at this temperature. After polymerization a small amount of methanolic ammonia was added with stirring to the polymer solution, to neutralize the initiator (some solutions were diluted with methylene chloride). The solution was then coagulated by being poured into an excess of vigorously stirred methanol containing a small amount of ammonia. The polymer thus isolated was filtered, rinsed with methanol, and then dried to constant weight in a vacuum oven at 30°C. Polymers obtained from (II) were freeze-dried from benzene.

The general procedure for cationic polymerization described above was also used for preparation of the copolymers. Equimolar quantities of (I) or (II) and a comonomer (ethyl vinyl ether or styrene) were dissolved in methylene chloride, and the solution was subjected to copolymerization at −78°C. The polymers were precipitated in nonsolvent. In the case of copolymers with ethyl vinyl ether a methanol–water (7:1) mixture containing a small amount of ammonium hydroxide was used as nonsolvent. Polymerization of α-methylstyrene and its copolymerization with allyl phenyl ether were also carried out by the same procedure.

Radical Polymerizations. A solution of (I) or (II) in tetrahydrofuran and an initiator (AIBN or BPO) were put into a Pyrex glass tube. The tube was cooled with a bath of methanol and solid carbon dioxide, evacuated, and filled with nitrogen. This operation was repeated twice, after which the tube was flushed with nitrogen and then sealed. Polymerization was carried out in a thermostatted bath at 70 ± 1°C. After polymerization the polymer solution was diluted with tetrahydrofuran and poured into an excess of vigorously stirred methanol, to isolate polymer. The polymer was filtered, rinsed with methanol, and dried under vacuum in an oven kept at 30°C. Copolymerization of allyl phenyl ether and styrene were also done in the same manner as in the radical homopolymerization procedure described above.

Reaction of Linear Polymers

Claisen Rearrangement of Polymers. Eight tenths of a gram of polymer dissolved in 10 ml of diethylaniline (b.p. 215°C) was placed in a 50 ml flask equipped with a reflux condenser, and the solution was refluxed for 3 hr under nitrogen atmosphere. At the end of the reaction the product (a small portion of polymer was isolated from the solution in each case) was diluted with acetone, filtered, and poured into a vigorously stirred 200 ml of water containing 12 ml of concentrated hydrochloric acid. The polymer thus isolated was filtered, dissolved in acetone, and reprecipitated into water. The polymer thus purified was filtered, rinsed with water, and dried under vacuum. After drying the rearrangement product of polymer (I) was soluble in acetone, tetrahydrofran, and pyridine, whereas the rearrangement product of polymer (II) was insoluble.

The degree of rearrangement was determined for the rearrangement product of polymer (I) by the following procedure. The polymer was acetylated with a pyridine–acetic anhydride mixture according to the method reported by Burke and others.[11] The infrared spectrum of the acetylated polymer indicated the absence of the hydroxyl group and showed strong absorption at 1760 cm^{-1} due to the carbonyl group. Determination of acetyl content of the acetylated polymer thus produced was done by a method similar to the one given in the literature[12] (a method used for cellulose acetate). In this work saponification was carried out for 5 days, and titration was conducted with a pH meter equipped with glass and calomel electrodes (the pH value selected as the endpoint was 9.5). Thus, the acetyl content of the acetylated polymer (I) was found to be 29.0%, which value corresponds to the 100% rearranged polymer (29.1%).

Crosslinking of Polymers. Two tenths of a gram of each polymer was dissolved in 1 ml. of tetrahydrofuran; this was followed by addition of 0.01 g of AIBN or BPO and subsequent mixing. The mixture was spread onto a glass plate, the solvent was then allowed to evaporate, and the resulting films were cured at 100°C for 50 min. After that the solubilities of the cured films were determined from the weight differences of the dried samples before and after immersion in tetrahydrofuran for 4 hr at room temperature. Another experiment was done with maleic anhydride as comonomer. In this experiment 0.20 g of each polymer and 0.20 g of maleic anhydride were dissolved in 2 ml of tetrahydrofuran; then 0.02 g of BPO was added to the solutions and followed by mixing and spreading onto a glass plate. Subsequent treatments were carried out in the same way as that described above.

Reaction of Polymers with Perbenzoic Acid. In a 20 ml flask was placed 0.400 g (0.00250 mol) of polymer (I) or (II) or 0.400 g [0.00172 mol as (I) or (II) units] of copolymer obtained from (I) or (II) and ethyl vinyl ether. Approximately equimolar quantity of perbenzoic acid (a solution of 0.469 mol of perbenzoic acid in 1 liter of chloroform) to (I) or (II) ingredient in each polymer was added to the flask with stirring, and the resulting solution was allowed to stand overnight at 20°C. However, no soluble epoxidized polymers were obtained. The homopolymers in solutions led to complete gel formations, whereas the copolymers were partially isolated from the mixtures. When the soluble portions from the latter mixtures were isolated by being poured into a methanol–water (7:1) mixture and dried, they also changed to crosslinked insoluble materials.

Characteristics of Polymers

Viscosity Measurements. The intrinsic viscosities of polymers were measured in tetrahydrofuran solution in an Ubbelohde type of viscometer in a thermostat bath kept at 30 ± 0.05°C.

Measurements of Infrared and Ultraviolet Spectra. Infrared and ultraviolet absorption spectra were taken with Hitachi Recording Spectrophotometers, Models EPI-S_2 and EPS-3T, respectively.

RESULTS AND DISCUSSION

Polymerizations

Monomer (I) and (II) have two different olefinic double bonds in their structures: vinyl and allyl groups. The vinyl group in each monomer should be much more susceptible to cationic initiators at low temperature than the allyl. From this viewpoint the polymerizations of (I) and (II) with some cationic initiators were investigated to obtain linear polymers with pendant, unsaturated groups. At the same time polymerizations of these monomers with radical initiators were also examined.

Table I contains the polymerization conditions and the results of polymerizations of these two monomers. In the case of polymerization with BTE at the temperature of solid carbon dioxide the resulting polymers were soluble in a number of organic solvents, except for a polymer from (I), which was obtained after a long polymerization time (20 hr) and which contained some insoluble portions. Such a tendency was seen even in the case of the cationic polymerization of 2,5-dimethoxystyrene with this same initiator.[13] A polymerization of (I) with stannic chloride afforded polymer containing some insoluble portions. In the polymerization of (II) the use of lower concentrations was more favorable than in that of (I), since the polymerization reaction of (II) was found to proceed more violently than that of (I). The color of the solutions of (II) during polymerizations was dark amber, which disappeared on quenching with methanolic ammonia; the solutions of (I) were colorless during polymerizations.

Unexpected results were obtained in radical polymerizations. When 50% solutions of (I) and (II) in tetrahydrofuran were subjected to radical polymerization with AIBN and BPO, the AIBN gave crosslinked, insoluble polymers, as expected, but BPO gave soluble polymers with higher intrinsic viscosities, although polymer conversions were relatively low. On the other hand, polymerizations of approximately 20% solutions with AIBN gave soluble polymers.

For information on polymerization behavior the infrared absorption spectra of these polymers were investigated. The infrared spectra of (I) and (II) have three strong absorption bands in the region of 900–1000 cm^{-1}: i.e., 905, 923, and 995 cm^{-1}. Styrene has two bands at 905 and 995 cm^{-1}, due to the vinyl double bond.[14] In this region allyl phenyl ether also shows two bands at 923 and 995 cm^{-1} that might be attributable to the double bond in allyl group. As for the polymers prepared by the polymerization with BTE, two absorptions are recognized at the same positions as for allyl phenyl ether in this region; the absorption at 905 cm^{-1} recognized in (I) and (II) disappears in the polymerizations. These two absorptions, however, disappeared by bromination. The infrared

TABLE I

Homopolymerizations of Allyl(*o*-vinyl phenyl) ether (I) and allyl(*p*-vinyl phenyl)ether (II)

Monomer No.	Solvent[a]	Monom. concn., %	Init.,[b] % per monom.	Temp., °C	Time	Convsn., %	[η]
Cationic polymerization:							
I	MC	10	BTE, 3	−78	20 hr	95[c]	0.385
I	MC	10	BTE, 3	−78	1 hr	20	—
I	MC	10	BTE, 6.5	−78	2 hr	97	0.358
I	MC	10	SC, 2.3	−78	35 min	69[c]	0.228
II	MC	10	BTE, 3	−78	3 min	90	3.18
II	MC	3.3	BTE, 3	−78	20 min	84	0.585
II	MC	3.3	BTE, 3	−78	1 hr	91	—
Radical polymerization:							
I	THF	50	AIBN, 1	70	21 hr	gel. (88%)	
I	THF	21	AIBN, 1	65	45 hr	51	0.095
I	THF	50	BPO, 1	70	44 hr	61	0.271
II	THF	50	AIBN, 1	70	21 hr	gel.	
II	THF	19	AIBN, 1	70	44 hr	42	0.096
II	THF	50	BPO, 1	70	44 hr	38	0.227

[a] MC, methylene chloride; THF, tetrahydrofuran.

[b] SC, stannic chloride.

[c] Contains some insoluble portions.

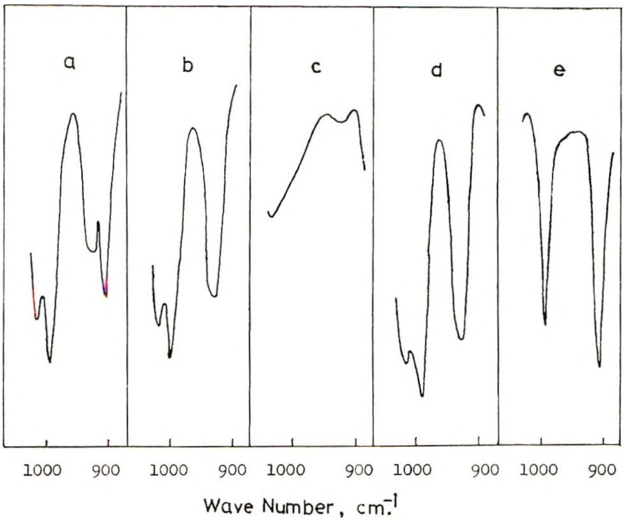


Fig. 1. Infrared spectra (900 to 1000 cm^{-1}): (*a*) allyl(*o*-vinyl phenyl) ether and allyl(*p*-vinyl phenyl)ether; (*b*) poly[allyl(*o*-vinyl phenyl)ether] and poly[allyl(*p*-vinyl phenyl)ether]; (*c*) bromination product of (*b*); (*d*) allyl phenyl ether; (*e*) styrene.

pattern of the soluble polymers formed in the radical polymerization corresponds with that of the polymers formed in the polymerization with BTE. The infrared spectra are compared in Figure 1.

These results suggested that the polymerizations of (I) and (II) proceed through the vinyl double bond without affecting the allyl one, in both cationic and radical polymerizations (only in the case in which soluble polymers are obtained). For the purpose of ascertaining whether this assumption was reasonable or not, a cationic polymerization of α-methylstyrene with BTE and radical polymerizations of styrene with AIBN and BPO in the presence of allyl phenyl ether were examined. If allyl phenyl ether is copolymerized with these monomers under given conditions, it might afford indirect evidence that not only the vinyl but also the allyl double bonds in (I) and (II) participate in polymerization.

The polymerizations were carried out under the conditions listed in Table II. Infrared and ultraviolet spectra were taken for the resulting polymers in order to detect the presence of allyl phenyl ether units in the polymers. The results obtained are indicated in Table II.

The infrared and ultraviolet spectra of the polymers prepared by the polymerizations of α-methylstyrene and the α-methylstyrene–allyl phenyl ether system with BTE at a temperature of solid carbon dioxide showed a perfect correspondence. On the other hand, there are observed some differences between the spectra of polymer formed from styrene and polymer formed from styrene–allyl phenyl ether, as shown in Figures 2 and 3. The infrared spectrum of each of the polymers obtained from styrene–allyl phenyl ether with BPO ("g") and AIBN ("h") revealed a weak absorption band at 1245 cm^{-1}, which is absent in that of polystyrene ("f"). This

TABLE II

Polymerizations of α-Methylstyrene (α-MSt) and Styrene (St) in the Presence of Allyl Phenyl Ether (APE)

Monomer, molar ratio	Solvent	Monom. concn., %	Init., % per monom.	Temp., °C	Time, hr	Convsn., %	APE unit in polymer
α-MSt/APE = 1	MC	10	BTE, 3	−78	1/2	42[a]	no
St/APE = 1	THF	50	BPO, 1	70	24	25	yes
α-MSt/APE = 1	THF	20	AIBN, 1	70	24	14	yes
α-MSt only	MC	10	BTE, 3	−78	1/2	100	
St only	THF	50	BPO, 1	70	24	—	

[a] Corresponds to 90% conversion of α-MSt in the reaction mixture.

TABLE III

Cationic Copolymerizations of Allyl(*o*-vinyl phenyl)ether and Allyl(*p*-vinyl phenyl)ether with Ethyl Vinyl Ether (EVE) and Styrene

Monomer molar ratio	Solvent	Monom. concn., %	Init., % per monom.	Temp., °C	Time, hr	Convsn., %	[η]
(I)/St = 1	MC	10	BTE, 1.5	−78	20	90	0.098
(I)/EVE = 1	MC	10	BTE, 2	−78	20	93	0.362
(I)/EVE = 1	MC	10	BTE, 5	−78	1	86	—
(II)/EVE = 1	MC	6.8	BTE, 3.4	−78	$1^1/_4$	92	0.331

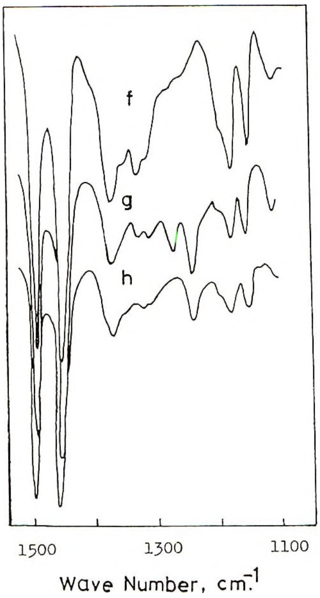


Fig. 2. Infrared spectra: (f) polystyrene; (g, h) polymers prepared in polymerization of styrene–allyl phenyl ether (1:1) with BPO and AIBN, respectively.

absorption should be attributable to the aromatic ether group[14] in the polymers. As for the ultraviolet spectra, there appeared a weak absorption near 279 mμ for each polymer ("g" and "h") obtained in the polymerizations of the styrene–allyl phenyl ether system with BPO and AIBN, whereas for polystyrene ("f") no absorption was recognized in the neighborhood of the region. This absorption possibly is due to the phenolic ether group,[15] indicating the presence of an allyl phenyl ether unit in the polymers.

From the evidence the following conclusions concerning the polymerization of (I) and (II) may be drawn. As regards the solution polymerization with BTE at sufficiently low temperatures, polymerization takes place through the vinyl double bond without affecting the allyl double bond. In the case of polymerization with BPO or AIBN at relatively high temperatures the polymerization proceeds not only through the vinyl double bonds but also through the allyl double bonds, even when soluble polymer is obtained; pendant vinyl groups might exist in minor portions in the polymers in addition to the allyl groups.

D'Alelio and Hoffend[6] indicated that radical (BPO) and cationic (aluminium chloride) polymerizations of undiluted (II) at 60°C and 20°C for 24 hr gave crosslinked, insoluble polymers.

Copolymerizations of (I) and (II) with ethyl vinyl ether and styrene at a temperature of solid carbon dioxide with the use of BTE as initiator were examined. The results are shown in Table III together with the polymerization conditions.

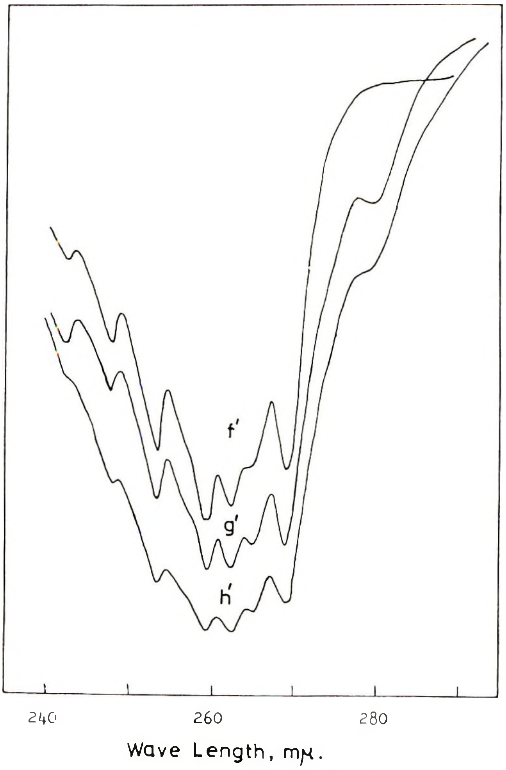


Fig. 3. Ultraviolet spectra: (f') polystyrene; (g', h') polymers prepared in polymerization of styrene–allyl phenyl ether (1:1) with BPO and AIBN, respectively, in dioxane.

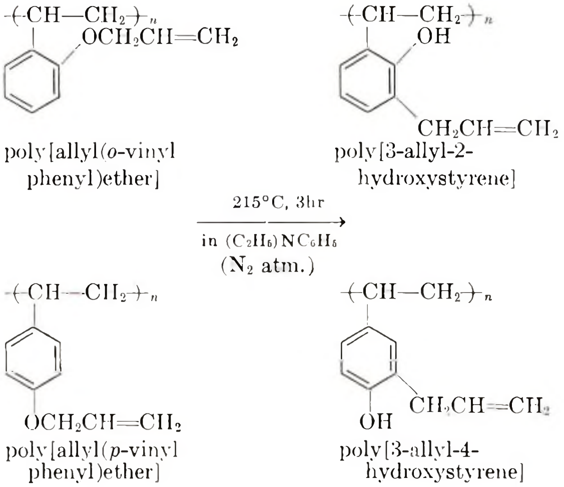
Copolymerizations of (I) for long periods of time with these two comonomers gave perfectly soluble polymers, unlike the homopolymerization of (I). The intrinsic viscosity of the copolymer of (I) with styrene was lower than that with ethyl vinyl ether. The infrared spectra of these polymers also had strong bands at 923 and 995 cm^{-1}.

Claisen Rearrangement of Linear Polymers

The linear polymers obtained in the polymerizations of (I) and (II) with BTE were subjected to a Claisen rearrangement reaction in boiling diethylaniline under nitrogen atmosphere as follows.

A determination of the hydroxyl group indicated that the extent of the rearrangement achieved in the case of polymer (I) was 99.6%. The color of the rearranged polymer was brown, and the polymer was soluble in a number of organic solvents. As regards polymer (II), the rearranged polymer turned to insoluble material in the final drying procedure.

The infrared spectrum of each rearranged polymer showed strong bands at 3550 cm^{-1}, due to the hydroxyl group, at 912 (probably a shifted band from the absorption at 923 cm^{-1} in the unrearranged polymers), and at 995 cm^{-1}, due to the allyl group, and a medium-intensity band near 1320



cm^{-1}, which may be attributable to the phenol group. The absorption at 1240 cm^{-1}, due to the aromatic ether group and occurring in the spectra of the unrearranged polymers, disappeared in the case of the rearrangement product of polymer (I), whereas that for the rearrangement product of polymer (II) was indicated as a weak and broad band. Possibly the degree of rearrangement for polymer (II) was less than that for polymer (I).

Another experiment was carried out for the soluble polymers prepared in the polymerizations with AIBN and BPO. However, the polymers were easily crosslinked and precipitated from solutions while the solutions were being refluxed. This also might suggest that these polymers contain the pendant vinyl groups besides the allyl groups, as already described.

Crosslinking of Linear Polymers

Crosslinked, insoluble films of polymers (I) and (II) obtained in the polymerization with BTE were able to be produced by radical-induced polymerizations of the residual allyl group. The films of the polymers prepared from solutions containing BPO or AIBN were heated at 100°C

TABLE IV
Crosslinking of Polymers with AIBN and BPO[a]

Polymer	Catal., %	Soly., %
Polymer (I)	AIBN, 5	26.0
Polymer (II)	AIBN, 5	4.1
(I)-EVE (1:1) copolymer	AIBN, 5	73.9
II-EVE (1:1) copolymer	AIBN, 5	15.5
Polymer (I)	BPO, 5	6.5
Polymer (II)	BPO, 5	3.4
I-EVE (1:1) copolymer	BPO, 5	28.9
II-EVE (1:1) copolymer	BPO, 5	15.1

[a] Curing: 100 °C, 50 min.

for 50 min. The solubility of the crosslinked films in tetrahydrofuran was measured. The results obtained are summarized in Table IV.

The catalytic action of BPO was apparently stronger than that of AIBN. This is a tendency contrary to that of the solution polymerization already described. The susceptibilities to crosslinking of the homopolymer and copolymer of (II) are significantly greater than those of the polymers of (I). The differences should be attributable to the difference in structure between (I) and (II). Intermolecular crosslinking is considered to be more rapid when the allyl ether group is located in the *para* position with respect to the olefinic group of the allyl(vinyl phenyl)ether unit in the polymer, than when it is located in the ortho position.

Copolymerizations of the polymers with maleic anhydride were successfully effected. The treatments were conducted in a manner similar to that described above. The results are shown in Table V. A difference in crosslinking reactivity is again observed.

TABLE V
Copolymerizations of Polymers with Maleic Anhydride (MA)[a]

Polymer	Weight ratio polymer/MA	Catal., %	Soly., %
Polymer (I)	1:1	PBO, 5	28.6
Polymer (II)	1:1	BPO, 5	9.8

[a] Curing: 100°C, 50 min.

Reaction of Linear Polymers with Perbenzoic Acid

To give epoxidized polymers the homopolymers and copolymers prepared in the polymerization with BTE were subjected to reaction with perbenzoic acid in chloroform at 20°C. However, no soluble polymers were obtained, even though an epoxidation of poly(allyl methacrylate) had proceeded smoothly without gelation under similar conditions.[16] This crosslinking might be related to the etheral oxygen attached to the allyl group, but a reasonable explanation has not been offered yet.

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Soluble High Polymers from Allyl Methacrylate

J. P. J. HIGGINS and K. E. WEALE,
Department of Chemical Engineering and Chemical Technology,
Imperial College of Science and Technology, London, England

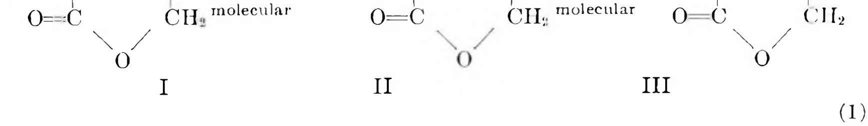
Synopsis

Allyl methacrylate has been polymerized by free-radical methods and found to yield a soluble polymer in carbon tetrachloride, dioxane, and diallyl ether solutions. The overall rate equation in diallyl ether is $R_p = k[\text{In}]^{0.7}[\text{M}]^{1.6}$. It is suggested that propagation and cyclization reactions proceed only via addition to the methacrylyl groups of the monomer. Some degradative chain transfer occurs with the allyl groups, and it is considered that the solvents may ensure the production of soluble polymers by reactions in which allyl-radical side chains are terminated without crosslinking.

INTRODUCTION

It has been shown[1] that 1,6-dienes can, under certain conditions, yield soluble polymers by an alternating inter-intramolecular mechanism. Previous attempts to obtain a soluble polymer from the monomer allyl methacrylate[2,3] have, however, not been successful. Kawai[3] has attributed this to the predominance of the intermolecular reaction and to degradative chain transfer.

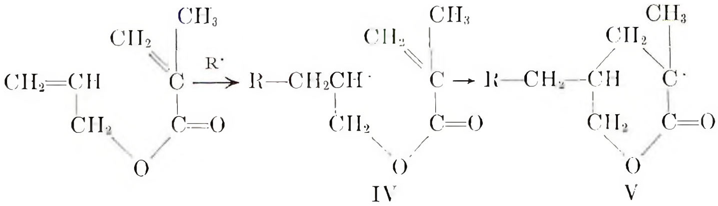
Allyl methacrylate (I), which is an unsymmetrical 1,6-diene, has now been found to produce soluble polymers up to high conversions in solutions of carbon tetrachloride (CCl_4), dioxane, and diallyl ether. Examination of the polymers so produced shows that they are true homopolymers and that in diallyl ether little or no copolymerization occurs with the solvent. The cyclopolymerization reactions may be represented as:



I II III

(1)

where R˙ is an initiator or polymer radical. Normal propagation can take place by the addition of monomer to either structure II or structure III. For reasons which are discussed below and in a forthcoming paper on the kinetics, the alternative reactions through the allyl group as shown in eq. (2) are considered unlikely.



(2)

EXPERIMENTAL

The monomer and all of the solvents were obtained from standard commercial sources and were distilled under vacuum before use. Benzoyl peroxide (Bz_2O_2) was recrystallized from chloroform solution. Polymerizations were carried out in sealed glass ampules in an oil bath at 60°C, and the rate of polymerization R_p was determined gravimetrically. Monomer and diallyl ether which were exposed to air for a few days turned yellow, presumably through absorption of oxygen, and these samples gave relatively low yields when used in polymerizations. However, a few samples prepared by the high vacuum filling technique gave results similar to those obtained from freshly distilled monomer and solvent, but with no special precautions to exclude air. Infrared absorption spectra of the monomer and polymer were obtained on a Hilger H-800 spectrometer with an NaCl prism.

RESULTS

Allyl methacrylate (M) was polymerized in bulk and in solution in toluene, benzene, acetone, CCl_4, isopropyl ether, epoxypropane, dioxane, and diallyl ether, with benzoyl peroxide initiator. With the reactions in bulk, and in the solvents toluene, benzene, acetone, isopropyl ether, and epoxypropane, gelation occurred at very low conversions. The polymers were insoluble in the common organic solvents, in the monomer, and in dimethyl sulfoxide. In CCl_4 solution, at low concentrations, conversions of up to 40% soluble polymer were obtained before gelation occurred. Autoacceleration was also observed and careful purification techniques and the exclusion of oxygen did not prevent its occurrence. In dioxane solutions, at concentrations of up to 2.2 mole/l monomer, high yields of soluble polymer were obtained. In diallyl ether solution very high yields of soluble polymer were also obtained. The gel point occurred at lower conversions as the concentration of the monomer was increased. At very low monomer concentrations almost 100% soluble polymer was obtained. Figure 1 shows the results for the polymerization in three solvents at fixed monomer and initiator concentrations.

In various attempts to homopolymerize dioxane and diallyl ether by free-radical methods[4] at temperatures from 30°C to 100°C and at pressures from 1 to 10 000 atm. it was found that these substances would not polymerize, (diallyl ether is, however, polymerized by cationic catalysts such as boron trifluoride diethyl etherate). Elemental analyses of the polymers

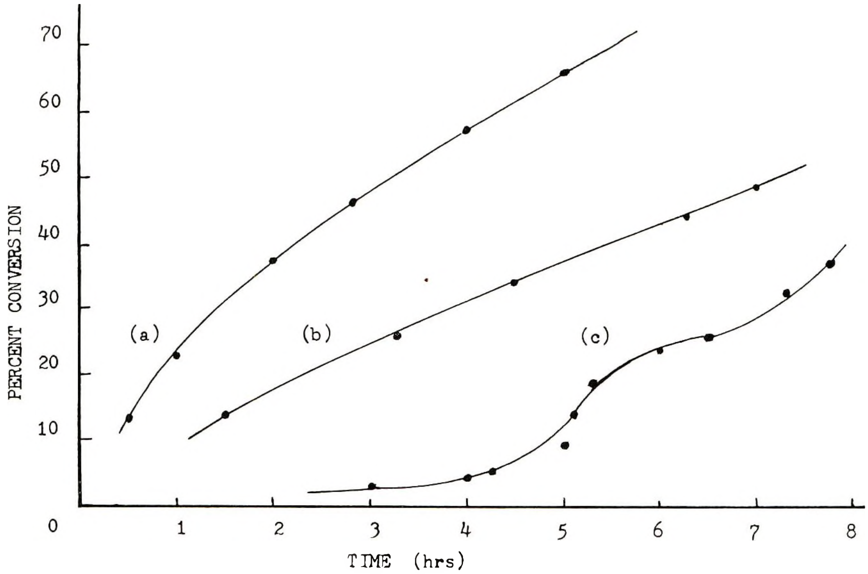


Fig. 1. Polymerization of allyl methacrylate in three solvents at 60°C: (*a*) dioxane; (*b*) diallylether; (*c*) CCl_4. $[Bz_2O_2] = 1.1 \times 10^{-2}$ mole/l; $[M] = 1$ mole/l.

of allyl methacrylate formed in dioxane and diallyl ether solutions confirmed that little or no copolymerization had occurred and that the allyl methacrylate had formed homopolymers. Table I shows the effect on the rate of polymerization of allyl methacrylate in diallyl ether solution as the initiator concentration is varied at constant monomer concentration.

TABLE I
Polymerization of Allyl Methacrylate at 60°C[a]

No.	$[Bz_2O_2] \times 10^3$ mole/l	$R_p \times 10^5$, mole/l-sec
1	1.03	1.01
2	5.80	3.04
3	16.80	5.16
4	27.20	8.49
5	45.20	12.40

[a] Solvent: diallyl ether; [M]: 2.2 mole/l.

The plot of log R_p versus log $[Bz_2O_2]$ is linear and has a slope of 0.7. Table II shows the effect on the rate of polymerization of allyl methacrylate in diallyl ether solution as the monomer concentration is varied at constant initiator concentration.

The plot of log R_p versus log [M] is linear and has a slope of 1.6. Thus the rate of polymerization of allyl methacrylate in diallyl ether solution at 60°C in the range of concentrations studied is given by:

$$R_p = k[Bz_2O_2]^{0.7}[M]^{1.6} \quad (3)$$

TABLE II
Polymerization of Allyl Methacrylate at 60°C.[a]

No.	[M], mole/l	$R_p \times 10^6$, mole/l-sec
1	1.1	27.7
2	1.8	57.6
3	2.2	84.9
4	3.3	172.7
5	3.6	176.9
6	4.4	282.2
7	6.1	580.1

[a] Solvent: diallyl ether; $[Bz_2O_2]$: 1.1×10^{-2} mole/l.

where k is a constant. Such irregular orders with respect to initiator and monomer concentrations are common for allylic and substituted allylic monomers.

Characterization of Polymer

Intrinsic viscosity was measured in an Ubbelohde viscometer at 25°C in toluene solution. The intrinsic viscosity $[\eta]$ varied from 0.1 to 0.5. Because of residual unsaturation the intrinsic viscosity varied with the amount of time the polymer had been exposed to air, and all polymer samples so exposed eventually became insoluble due to crosslinking. Using freeze-dried polymer samples which were immediately dissolved in toluene it was possible to obtain an intrinsic viscosity–molecular weight relationship by comparing intrinsic viscosity results with osmometrically determined molecular weights for the same samples. The Mark-Houwink-Sakurada equation for poly(allyl methacrylate) in toluene at 25°C was found to be:

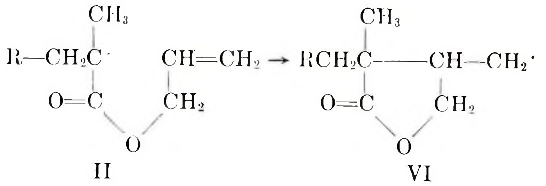
$$[\eta] = 2.4 \times 10^{-4} \bar{M}_n^{0.65} \tag{4}$$

$\bar{M}_n$ is the number-average molecular weight. In the case of poly(allyl methacrylate), formed in diallyl ether solution at 60°C using Bz_2O_2 as the initiator, the molecular weight varied from 70000 to 100000.

Infrared Spectra

The infrared spectra of the monomer and the polymer are given in Figure 2.

In the spectrum of the monomer the carbonyl stretch frequency absorption exhibits a peak at 1725 cm^{-1} but in the polymer this peak is broadened and shifted towards 1740 cm^{-1}. This indicates the presence of δ-lactone units (six-membered rings) in the polymer. The spectrum of the polymer also shows a small absorption at 1775 cm^{-1}. This is attributed to the presence of a small proportion of γ-lactone units (five-membered rings) which may be formed as shown in eq. (5).



(5)

The presence of two types of lactone ring in the polymer is supported by the absorptions at 1230 and 1275 cm^{-1}. These are probably due to the —CO— stretching frequencies in the δ- and γ-lactone rings.

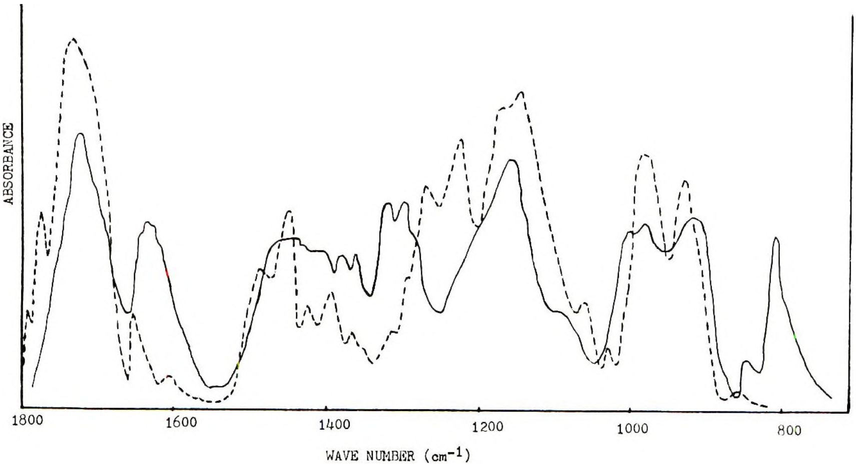
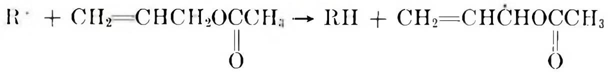


Fig. 2. Infrared spectra of (——) allyl methacrylate and (- -) poly(allyl methacrylate) at 800–1800 cm^{-1}.

DISCUSSION

It has long been known that allylic monomers undergo degradative chain transfer (DCT) reactions.[5,7] In these reactions, which compete with normal propagation, a hydrogen atom is extracted from the monomer by an active radical. In the case of allyl acetate:

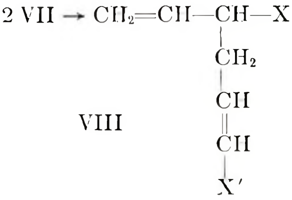


$$R\cdot + CH_2{=}CHCH_2O\underset{\overset{\|}{O}}{C}CH_3 \rightarrow RH + CH_2{=}CH\dot{C}HO\underset{\overset{\|}{O}}{C}CH_3 \qquad (6)$$

The resulting acetoxyallyl radical is resonance-stabilized and does not readily add monomer, although it may terminate by bimolecular combination. If DCT predominates the rate of polymerization varies approximately as the first power of the initiator concentration[5] rather than the 0.5 power found with normal monomers such as styrene and methyl methacrylate. The results for allyl methacrylate show that R_p varies as the 0.7 power of the initiator concentration. This result may be explained if the methacrylyl groups can add to chains and undergo cyclization with the allyl groups as shown in eq. (1), while the allyl groups preferentially undergo DCT rather than the reactions shown in eq. (2). If the allyl group is pendant on a polymer or radical chain, which is denoted by X, the DCT reaction is:

$$\mathrm{R\cdot + CH_2{=}CHCH_2{-}X \rightarrow RH + \underset{VII}{CH_2{\cdots}CH{\cdots}CH{-}X}} \qquad (7)$$

The pendant resonance-stabilized allyl radicals do not propagate further with monomer but may terminate by bimolecular combination in two ways:



$$2\ \mathrm{VII} \rightarrow \mathrm{CH_2{=}CH{-}\underset{\begin{array}{c}|\\ CH_2\\ |\\ CH\\ \|\\ CH\\ |\\ X'\end{array}}{CH}{-}X} \qquad (8)$$

VIII

$$2\ \mathrm{VII} \rightarrow \mathrm{\underset{IX}{X{-}CH{=}CHCH_2CH_2CH{=}CH{-}X'}} \qquad (9)$$

When there are many pendant resonance-stabilized allyl radicals these reactions would quickly lead to crosslinked gel polymers and may account for the formation of insoluble polymers in polymerization in bulk and in the solvents toluene, benzene, acetone, isopropyl ether, and epoxypropane. The formation of soluble polymers in the other solvents suggests that in these the resonance-stabilized allyl radicals are preferentially terminated by a process which does not lead to crosslinking. Carbon tetrachloride is an active chain-transfer agent in some polymerizations[8,9] and ethers and dioxane are known to cause rapid induced decomposition of benzoyl peroxide.[10,11] The allyl groups of the solvent diallyl ether can also take part in DCT reactions. Radical–solvent and radical–initiator reactions will produce small rapidly diffusing radicals which would be expected to react with pendant resonance-stabilized allyl radicals much more rapidly than the latter can combine mutually. The differences between the polymer obtained in the two groups of solvents may thus be explicable in terms of the differing abilities of the solvents to bring about termination of radical side chains before they can react.

It has been shown that methacrylyl groups are much more reactive than allyl groups in the polymerizations of the methacrylic ester of 2-allylphenol[12] and allyl methacrylate.[13] The polymerization proceeds via the methacrylyl groups to give high molecular weight polymer. That fraction of the allyl groups not included in cyclization reactions via the methacrylyl groups are left pendant on the growing chains.

On the view that the allyl group does not enter into chain addition reactions it is possible to make some simplifications in the kinetic equations for the polymerization of allyl methacrylate, and these are discussed in a forthcoming paper.[14]

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Cationic Polymerization of α,β-Disubstituted Olefins. VI. Steric Structure of Poly(methyl Propenyl Ether) Obtained by Cationic Catalysts

Y. OHSUMI, T. HIGASHIMURA, and S. OKAMURA, *Department of Polymer Chemistry, Kyoto University, Kyoto, Japan*, and R. CHÛJÔ and T. KURODA, *Katata Research Institute, Toyobo Company, Ltd., Hon-Katata, Otsu, Japan*

Synopsis

The steric structure of poly(methyl propenyl ether) obtained by cationic polymerization was studied by NMR spectra. From the analysis of β-methyl and α-methoxyl spectra, it was found that the tacticities of the α-carbon were different from those of the β-carbon in all polymers obtained. In the crystalline polymers obtained from the *trans* isomer by homogeneous catalysts, $BF_3{\cdot}O(C_2H_5)_2$ or $Al(C_2H_5)Cl_2$, and from the *cis* isomer by a heterogeneous catalyst, $Al_2(SO_4)_3$–H_2SO_4 complex, the structure of polymers was threo-di-isotactic. Though the configurations of all α-carbons were isotactic, a small amount of syndiotactic structure was observed in the β-carbon. On the other hand, in the amorphous polymer obtained from *cis* isomer by the homogeneous catalyst, the configuration of the α-carbon was isotactic, but that of the β-carbon was atactic. These facts suggest that the type of opening of a monomeric double bond is complicated, or that carbon–carbon double bond in an incoming monomer rotates in the transition state. From these experimental results, a probability treatment was proposed from the diad tacticity of α,β-disubstituted polymers. It shows that the tacticity is decided by a polymerization mechanism different from that proposed by Bovey.

INTRODUCTION

For the investigation of the mechanism of the propagation reaction in the ionic polymerization of vinyl monomers, it is very important to know the type of opening of the monomeric double bond. Natta et al. have shown by x-ray diffraction analysis on the di-isotactic structure of a polymer that the opening of the double bond of monomer is of the *cis* type in cationic polymerization of *trans*-alkenyl ethers[1] and β-chlorovinyl ethers[2] at low temperature.

Recently, information on the double bond opening has been obtained quantitatively for the polymerization of alkyl acrylate-α, β-d_2 by high resolution NMR spectroscopy.[3-5] In radical polymerization the monomer double bond was opened in both *cis* and *trans* type with equal probability, while in anionic polymerization the type of the opening depended on polymerization conditions, e.g., the kind of catalyst and polymerization temperature. Thus, the types of opening of a monomeric double bond seem to be complicated in anionic polymerization.

In the previous paper,[6] we have reported on the NMR spectra of β-methyl protons of poly(methyl propenyl ether) (PMPE) obtained by a homogeneous cationic polymerization. It was found that polymer from the *trans* isomer was a highly crystalline threo-di-isotactic structure and that from *cis* isomer was a mixture of threo- and erythro-di-isotactic structures. From these results, we have assumed that the opening of the double bond of the *trans* isomer was exclusively of the *cis* type and that of *cis* isomer was of both *cis* and *trans* types.

This conclusion was derived only from the analysis of β-methyl protons. We have, however, no complete knowledge of the steric structure of a polymer until structural information is obtained from the α-substituent as well as the β-substituent. The present paper is concerned with the analysis of α-methoxyl spectra which were not elucidated in our previous paper.[6]

EXPERIMENTAL

Methyl propenyl ether was synthesized by the splitting off of alcohol from dimethyl acetal. The crude product was fractionated by distillation on a 45-plate column. The *cis* and *trans* contents of methyl propenyl ether were determined by gas chromatography on a dinonyl phthalate column (3 m), 40°C, with H_2 flow at 50 ml/min. Two kinds of monomer mixture having different mole rations of *cis* and *trans* isomer were used, i.e., *cis*/*trans* ratios of 1/9 and 4/1.

Catalysts and solvents were purified by the usual method. Monomer and solvents were distilled over sodium just before use.

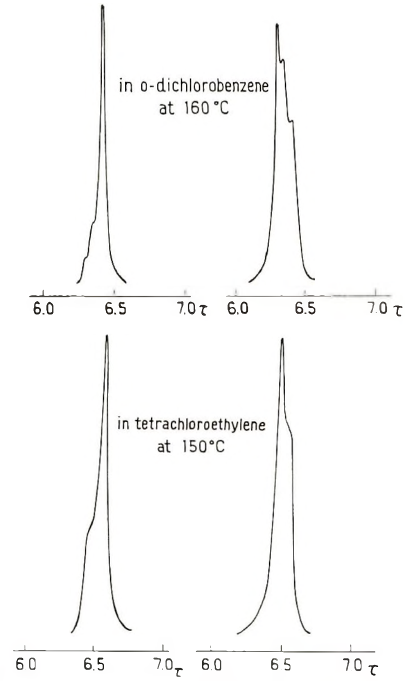
The polymerization with homogeneous catalysts, $BF_3 \cdot O(C_2H_5)_2$ or $Al(C_2H_5)Cl_2$, and with a heterogeneous catalyst, $Al_2(SO_4)_3$–H_2SO_4 complex, were carried out in the same way as described previously.[6]

NMR spectra of polymer were measured mainly in *o*-dichlorobenzene solution (10%, w/v) in a sealed tube at 160°C with a Varian HR-60 instrument. The spin-decoupling experiment was performed by the side-bond method with a phase-sensitive detector operating at 2 kcps. The spectra of methoxyl protons were measured at a slow sweep rate to make the signal separations clear.

RESULTS AND DISCUSSION

NMR Spectra of Methoxyl Protons

Analysis of the configuration of PMPE from the spectra of methoxyl protons as observed in poly(methyl vinyl ether) is anticipated.[6] NMR spectra of PMPE were measured in various solvents, e.g., carbon tetrachloride, chloroform, tetrachloroethylene, nitroethane, and *o*-dichlorobenzene. Figure 1 shows the slow sweep spectra of the methoxyl protons in *o*-dichlorobenzene and in tetrachloroethylene for PMPE obtained by $BF_3 \cdot O(C_2H_5)_2$.



Polymer obtained from trans-rich monomer mixture by BF_3OEt_2

Polymer obtained from cis-rich monomer mixture by BF_3OEt_2

Fig. 1. Effect of solvent on NMR spectrum of methoxy protons in PMPE.

The aromatic solvent seems to increase the resolution of the methoxyl spectrum of this polymer. The slow sweep spectrum of the methoxyl protons was split into three components in *o*-dichlorobenzene solution. In nonaromatic solvents the resolution was rather poor.

It was found in poly(methyl vinyl ether) and poly(methyl methacrylate) that the methoxyl spectra were sensitive to the configuration of the polymer and the resolution of the spectra depended on the kind of solvent.[7–9] Similarly, in NMR spectra of PMPE a solvent effect was observed, as shown in Figure 1. Therefore, it is expected that the signal separations of the methoxyl protons are due to the steric configuration.

Polymers obtained under various conditions showed different spectra of the methoxyl protons. Figure 2 shows the NMR spectra of the methoxyl protons of polymers obtained from a *cis*-rich monomer mixture (*cis*/*trans* = 4/1) and a *trans*-rich monomer mixture (*cis*/*trans* = 1/9) by $BF_3 \cdot O(C_2H_5)_2$ in toluene at various temperatures.

In the crystalline polymers obtained from the *trans*-rich monomer mixture, the intensity at 6.34 τ was much stronger than at 6.26 and 6.30 τ. On the other hand, in the amorphous polymers obtained from the *cis*-rich monomer mixture, the differences among the intensities of three signals were found to be slight. Also, it was found that in the polymers from *trans*-rich monomer the intensity at 6.34 τ increased with decreasing polymerization

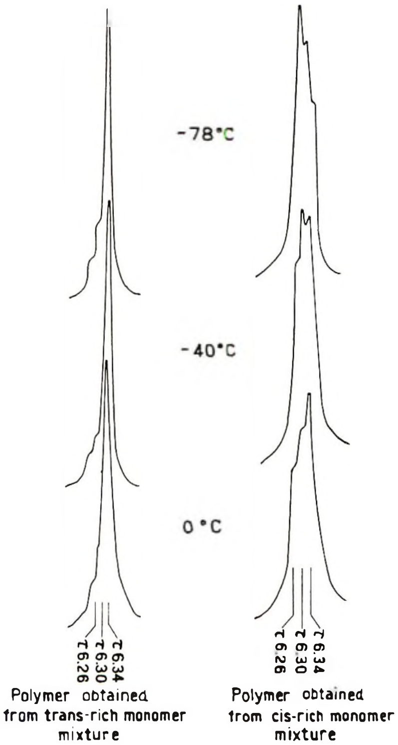


Fig. 2. NMR spectra of methoxyl protons in PMPE obtained by $BF_3 \cdot O(C_2H_5)_2$ in toluene at various temperatures. $[M]_0 = 10$ vol-%; measurement of NMR spectra in *o*-dichlorobenzene at 160°C.

temperature, while in the polymers from *cis*-rich monomer the intensity at 6.34 τ decreased and that at 6.26 τ increased with decreasing polymerization temperature.

TABLE I

Relative Intensity of Methoxyl Proton Triplet of PMPE Obtained under Various Polymerization Conditions ($[M_0] = 10$ vol-%, Toluene)

Monomer	No.	Catalyst	Temperature, °C	Conversion, %	Intensity, % 6.26 τ	6.30 τ	6.34 τ
trans-rich	1	$BF_3 \cdot O(C_2H_5)_2$	−78	32	8	16	76
"	2	"	−40	60	9	13	78
"	3	"	0	61	11	20	69
"	4	$Al(C_2H_5)Cl_2$	−78	80	7	18	75
cis-rich	5	$BF_3 \cdot O(C_2H_5)_2$	−78	65	39	35	26
"	6	"	−40	66	29	37	34
"	7	"	0	68	28	34	38
"	8	$Al(C_2H_5)Cl_2$	−78	88	44	34	22
"	9	$Al(SO_4)_3$–H_2SO_4[a]	0	23	11	19	70

[a] $[M_0] = 20$ vol-%.

Although the spectrum of methoxyl protons changed with the content of geometric isomers and polymerization temperature as described above, the relative intensity of the absorption of methoxyl protons to that of other protons was independent of polymerization conditions and monomer composition. Therefore, it is obvious that the difference in spectra of methoxyl protons is due to the steric structure of polymer.

The relative intensities of the three methoxyl signals of polymers obtained by $BF_3 \cdot O(C_2H_5)Cl_2$, and $Al_2(SO_4)_3$–H_2SO_4 complex are summarized in Table I together with polymerization temperature and the kind of catalyst. As the signals were insufficiently separated for measuring areas, the relative signal heights were determined as relative intensity.

Comparison between Spectra of Methoxyl Protons and of β-Methyl Protons

In the previous paper,[6] we discussed in detail the decoupled spectra of β-methyl protons of PMPE obtained under various conditions. The spectra of β-methyl protons consisted of two signals at 8.78 and 8.89 τ assigned to threo- and erythro-di-isotactic diads, respectively.

As the splitting of methoxyl spectrum was due to the steric structure of polymer as observed in the previous section, it was compared with β-methyl spectrum. The intensity at 8.78 τ of β-methyl protons was strong in the polymers having high intensity only at 6.34 τ of methoxyl protons shown in Table I, e.g., polymers 1, 2, 3, and 4 obtained by homogeneous catalysts and polymer 9, obtained by heterogeneous catalyst. On the other hand, the intensities at 8.78 and 8.89 τ of β-methyl protons were almost same in polymers in which the intensities of the three methoxyl signals were not so different, e.g., polymers 5, 6, 7, and 8 obtained by homogeneous catalysts (Table I). Thus, the intensity of methoxyl absorption at 6.34 τ corresponds to the intensity of β-methyl absorption at 8.78 τ and also that at 6.26 τ, to that at 8.89 τ, irrespective of polymerization conditions.

A shielding effect of adjacent groups on the steric structure represented at 6.30 τ should be intermediate in other two structures, because the signal appears between the signals at 6.26 and 6.34 τ. A half intensity at 6.30 τ was added to the signal intensities at 6.26 and 6.34 τ, respectively. The intensity calculated from methoxyl protons as described above was compared with the intensities of the two β-methyl signals. As shown in Table II, the relationship between methoxyl and methyl spectra was found to be calculated by eqs. (1):

$$\begin{aligned} &\{\text{intensity at } 6.34\,\tau + {}^1/_2\,(\text{intensity at } 6.30\,\tau)\}\ (\alpha\text{-methoxyl}) \\ &\qquad = \{\text{intensity at } 8.78\,\tau\}\ (\beta\text{-methyl}) \\ &\{\text{intensity at } 6.26\,\tau + {}^1/_2\,(\text{intensity at } 6.30\,\tau)\}\ (\alpha\text{-methoxyl}) \\ &\qquad = \{\text{intensity at } 8.89\,\tau\}\ (\beta\text{-methyl}) \end{aligned} \tag{1}$$

The agreement between the intensities of β-methyl protons and the calculated intensities from α-methoxyl protons listed in Table II was too good

TABLE II

Comparison between Intensity of β-Methyl Protons and Calculated Intensity of α-Methoxyl Protons (Calculated from Table I)

Monomer mixture	No.	Catalyst	Temperature, °C	Intensity, %			
				α-OCH$_3$ ($6.34\tau + {}^1/_2 6.30\ \tau$)	α-OCH$_3$ ($6.26\tau + {}^1/_2 6.30\ \tau$)	β-CH$_3$ ($8.78\ \tau$)	β-CH$_3$ ($8.89\ \tau$)
trans-rich	1	$BF_3 \cdot O(C_2H_5)_2$	−78	84	16	85	15
"	2	"	−40	84	16	83	17
"	3	"	0	79	21	76	24
"	4	$Al(C_2H_5)Cl_2$	−78	84	16	84	16
cis-rich	5	$BF_3 \cdot O(C_2H_5)_2$	−78	43	57	44	56
"	6	"	−40	52	48	52	48
"	7	"	0	55	45	54	46
"	8	$Al(C_2H_5)Cl_2$	−78	39	61	38	62
"	9	$Al_2(SO_4)_3$–H_2SO_4	0	80	20	79	21

to expect. This agreement may be due to following reason. As intensities of α-methoxyl protons were calculated from peak heights, the errors of the absolute value in each intensities may not be small; especially the intensity at 6.30 τ was overestimated because of overlapping of the absorptions at 6.26 and 6.34 τ. However, the intensity at 6.30 τ was halved for those at 6.26 and 6.34 τ in the calculated intensities from α-methoxyl protons, and the absolute errors of these intensities may cancel out.

Therefore, the signals at 6.26, 6.30, and 6.34 τ were assigned to erythro-di-isotactic, di-syndiotactic and threo-di-isotactic diads, respectively. The proof of these assignments is shown in Appendices I and II.

As the signal corresponding to the di-syndiotactic diad was not found in β-methyl spectrum, the configuration of the polymer should be exclusively isotactic with respect to α-carbons in all polymers. On the other hand, a syndiotactic structure does exist with respect to β-carbons. The crystalline polymers reported in this paper consisted mainly of threo-di-isotactic structure and were stereoregular with respect to α-carbons and β-carbons. On the other hand, the amorphous polymers consisted of isotactic structure with respect to α-carbons, but of atactic structure with respect to β-carbons. Thus, it was found that the tacticities of α-carbon and β-carbon were different. This is the same phenomenon as in the case of poly(isopropyl acrylate-β-d_1) obtained by n-butylmagnesium bromide in toluene at −78°C, which was isotactic with respect to the α-carbon, but atactic with respect to the β-carbon.[4] Such behavior in PMPE is very interesting, because MPE has a bulky group on its β-position.

The regularity of β-carbon in PMPE does not coincide with that of α-carbon as described above. This suggests that either the type of opening of a monomeric double bond is complicated or that the carbon–carbon bond in the polymer chain end[5] or in the incoming monomer[10] rotates in the transition state in the propagation step.

Probabilistic Considerations

Introducing a probability σ_T for having a threo-di-isotactic structure between the α-methoxyl of a cation and the β-methyl of the succeeding monomer, we have relations between molar fractions, F_T F_{DS}, and F_E of α-methoxyl group and σ_T as follows:

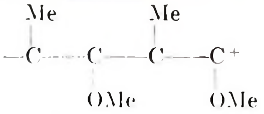
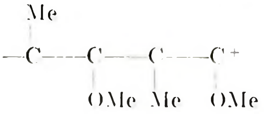
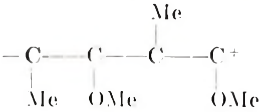
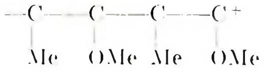
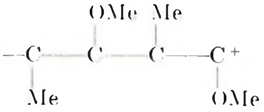
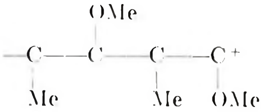
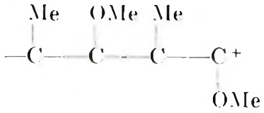
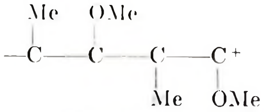
$$\begin{aligned} F_T{}^\alpha &= \sigma_T{}^2 \\ F_{DS}{}^\alpha &= 2\sigma_T(1 - \sigma_T) \qquad (2) \\ F_E{}^\alpha &= (1 - \sigma_T)^2 \end{aligned}$$

in so far as the complete isotacticity of α carbons, where the superscript α of F denotes molar fraction of α-methoxyl group, and the subscripts, T, DS, and E denote threo-di-isotactic, di-syndiotactic, and erythro-di-isotactic diads, respectively. Then, the $F\alpha$ can be plotted against σ_T as shown in Figure 3 in a way similar to Bovey plot.[11] There are systematic discrepancies between experimental and calculated values of molar fractions.

Based on the facts of the above mentioned systematic discrepancies and the disappearance of di-syndiotactic β-methyl resonance, a possible model may be proposed as follows: (*1*) at first, a tacticity is decided between the α-carbon in a growing ion and that in an attacking monomer, (*2*) then, the *cis* or *trans* structure of the β-methyl lying between the two carbons is decided, and (*3*) there is some interaction between succeeding two β-methyl's to decide the *cis* or *trans* structure. (This does not imply no contribution of the penultimate group in the decision of the tacticity of α-methoxyl. Such contribution is ignored.)

In order to describe the tacticity of PMPE based on the proposed model, three parameters, σ, σ_T, and a are introduced. σ is the probability of having an isotactic diad between succeeding two α-methoxyl groups, σ_T is the above mentioned probability, and a is a parameter describing the interaction between two succeeding β-methyl groups. If we set $a = 1$, eight

TABLE III
Description of the Growing End Structure by Probability Parameters

Probability	α	β	Structure
$\sigma\sigma_T^2$	T	T	
$\sigma\sigma_T(1 - \sigma_T)$	DS	E	
$\sigma(1 - \sigma_T)\sigma_T$	DS	T	
$\sigma(1 - \sigma_T)^2$	E	E	
$(1 - \sigma)\sigma_T^2$	DS	DS	
$(1 - \sigma)\sigma_T(1 - \sigma_T)$	T	DS	
$(1 - \sigma)(1 - \sigma_T)\sigma_T$	E	DS	
$(1 - \sigma)(1 - \sigma_T)^2$	DS	DS	

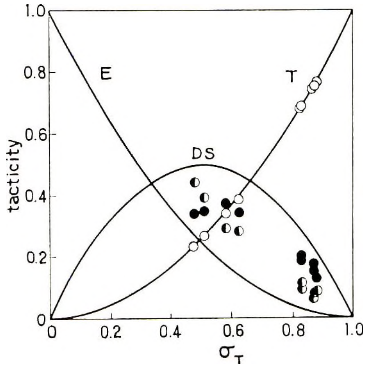


Fig. 3. Relationship between probability parameter (σ_T) and diad tacticity of PMPE: (○) threo-di-isotactic diad fraction (T); (◐) erythro-di-isotactic diad fraction (E); (●) di-syndiotactic diad fraction (DS).

possible structures composed of succeeding pairs of monomer units, corresponding probabilities, and the kinds of ditactic structure seen by intermediate α- and β-carbons can be compiled in Table III.

Then, we can describe molar fractions by σ and σ_T as shown in eqs. (3)–(4):

$$F_T^{\alpha} = \sigma\sigma_T^2 + (1-\sigma)\sigma_T(1-\sigma_T) \tag{3a}$$

$$F_E^{\alpha} = \sigma(1-\sigma_T)^2 + (1-\sigma)\sigma_T(1-\sigma_T) \tag{3b}$$

$$F_{DS}^{\alpha} = 2\sigma\sigma_T(1-\sigma_T) + (1-\sigma)(1-2\sigma_T+2\sigma_T^2) \tag{3c}$$

$$F_T^{\beta} = \sigma\sigma_T \tag{4a}$$

$$F_E^{\beta} = \sigma(1-\sigma_T) \tag{4b}$$

$$F_{DS}^{\beta} = 1 - \sigma \tag{4c}$$

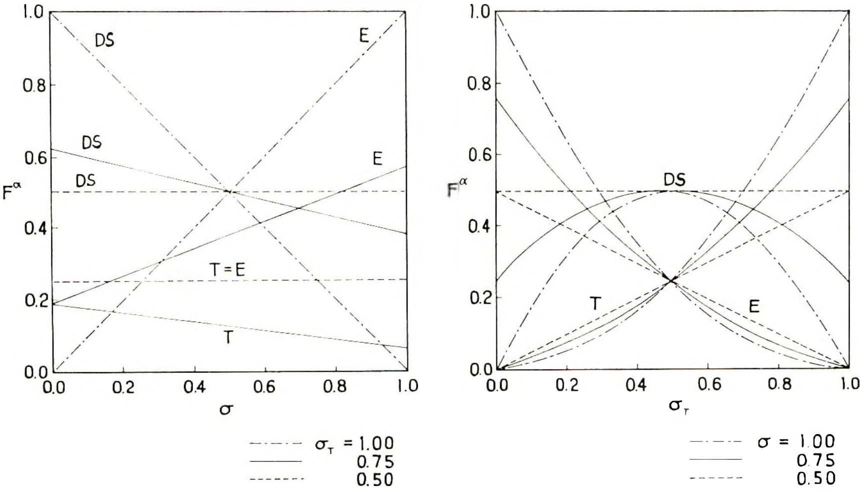


Fig. 4. Dependence of intensity of NMR spectrum of α-methoxyl protons (F^{α}) on probability parameters (σ and σ_T).

TABLE IV
Numerical Values for Parameters Comparison of the Calculated Values of NMR Fractions with the Observed Ones

Monomer	No.	Temperature, °K	F_T^α (exp)	F_E^α (exp)	σ_T	a	F_E^β (calc)	F_E^β (exp)
trans-rich	1	195	0.76	0.08	0.76	1.17	0.15	0.14
	2	233	0.78	0.09	0.75	1.20	0.14	0.17
	3	273	0.69	0.11	0.71	1.14	0.23	0.24
cis-rich	5	195	0.26	0.39	0.45	1.13	0.57	0.56
	6	233	0.34	0.29	0.52	1.13	0.48	0.48
	7	273	0.38	0.28	0.54	1.15	0.45	0.46

where F^{β} denotes the molar fraction of a given ditactic structure (E, DS, or T) seen from the β carbon. The dependence of the F^{α} on σ and σ_T is shown in Figure 4.

There are two ways to introduce an interaction parameter a. One is the replacement of σ_T^2 and $(1 - \sigma_T)^2$, which correspond to the opening of the double bonds in the succeeding two monomers to the same side, by $a^2\sigma_T^2$ and $a^2(1 - \sigma_T)^2$, respectively. This is so-called asymmetric polymerization. The other is the replacement of $\sigma\sigma_T^2$, $\sigma(1 - \sigma_T)^2$, and $(1 - \sigma)\sigma_T(1 - \sigma_T)$ by $\sigma a^2\sigma_T^2$, $\sigma a^2(1 - \sigma_T)^2$, and $(1 - \sigma)a^2\sigma_T(1 - \sigma_T)$, respectively, which corresponds to symmetric polymerization. Unfortunately, our experiment is limited to the case of $\sigma = 1$, in which the above two ways lead to the same formulas. So, it cannot be concluded whether our experiment corresponds to symmetric or asymmetric polymerization. Only the same equations:

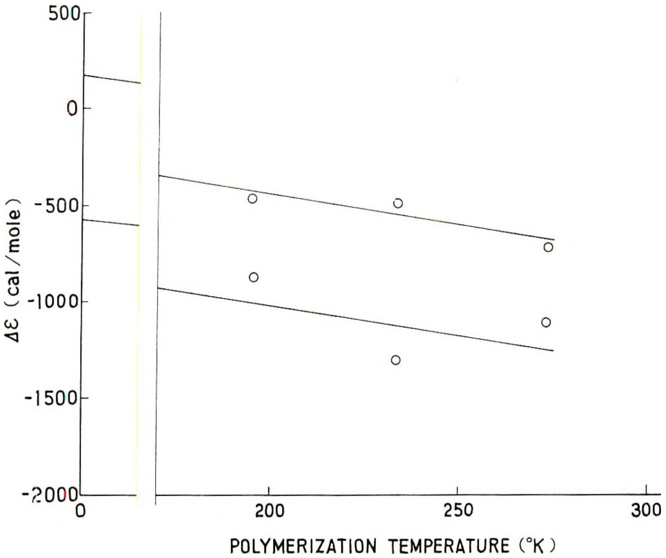


Fig. 5. Plot of Δε in PMPE against polymerization temperature.

$$F_T^{\alpha} = a^2\sigma_T^2 \tag{5a}$$

$$F_E^{\alpha} = a^2(1 - \sigma_T)^2 \tag{5b}$$

$$F_{DS}^{\alpha} = 1 - a^2(1 - 2\sigma_T + 2\sigma_T^2) \tag{5c}$$

$$F_T^{\beta} = {}^1/_2\{1 - a^2(1 - 2\sigma_T)\} \tag{6a}$$

$$F_E^{\beta} = {}^1/_2\{1 + a^2(1 - 2\sigma_T)\} \tag{6b}$$

$$F_{DS}^{\beta} = 0 \tag{6c}$$

can be obtained from the above two ways. The two parameters σ_T and a can be expressed by the molar fraction of α-carbons as follows:

$$\sigma_T = \sqrt{F_T^\alpha/F_E^\alpha}\left(1 + \sqrt{F_T^\alpha/F_E^\alpha}\right) \tag{7}$$

$$a = \sqrt{F_E^\alpha}\left(1 + \sqrt{F_T^\alpha/F_E^\alpha}\right) \tag{8}$$

These values and the value of F_E^β calculated from these values are compiled in Table IV with the observed values of F_E^β. The calculated and observed values of F_E^β show good agreement, so that the consideration of the interaction a may be justified.

A method similar to that of previous papers[12,13] can be used to check whether such interaction really exists or not. If the quantity

$$\Delta\epsilon = -kT \log \{4F_E^\alpha F_T^\alpha/(F_{DS}^\alpha)^2\} \tag{9}$$

is plotted against the polymerization temperature T, Figure 5 is obtained, where k is the Boltzmann constant. It cannot be concluded whether the points for polymers prepared under the same conditions except for polymerization temperature lie on a straight line. If these points are permitted to lie on a straight line, the relations between $\Delta\epsilon$ and T may be written as

$$\Delta\epsilon = -2.2T - 570 \qquad \text{For } \textit{trans}\text{-rich monomer} \tag{10a}$$

$$\Delta\epsilon = -3.1T + 180 \qquad \text{For } \textit{cis}\text{-rich monomer} \tag{10b}$$

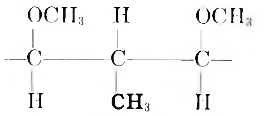
Then, it may be concluded that an interaction between succeeding two β-carbons really exists on the occasion of the opening of double bond.

APPENDIX I

When the relationship in eqs. (1) is established, there are two possibilities for an assignment of the signals of methoxyl and methyl protons.

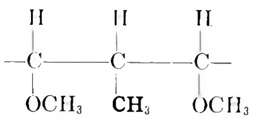
In case 1, the shifts of the both protons are ascribed to differences in chain configuration for most adjacent carbons. Two signals of β-methyl group are due to threo- (t) and erythro-di-isotactic (e) diads and three signals of α-methoxyl group are due to threo- (T), erythro-di-isotactic (E), and di-syndiotactic (DS) diads.

Two signals of β-methyl group:



$$-\overset{OCH_3}{\underset{H}{C}}-\overset{H}{\underset{\mathbf{CH_3}}{C}}-\overset{OCH_3}{\underset{H}{C}}-$$

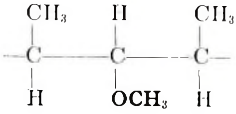
threo-di-isotactic (t)



$$-\overset{H}{\underset{OCH_3}{C}}-\overset{H}{\underset{\mathbf{CH_3}}{C}}-\overset{H}{\underset{OCH_3}{C}}-$$

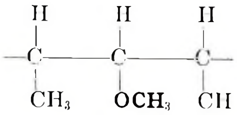
erythro-di-isotactic (e)

Three signals of α-methoxyl group:



$$-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{\mathbf{OCH_3}}{C}}-\overset{CH_3}{\underset{H}{C}}-$$

threo-di-
isotactic (T)



$$-\overset{H}{\underset{CH_3}{C}}-\overset{H}{\underset{\mathbf{OCH_3}}{C}}-\overset{H}{\underset{CH}{C}}-$$

erythro-di-
isotactic (E)

$-\underset{H}{\overset{CH_3}{C}}-\underset{OCH_3}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}- \qquad -\underset{CH_3}{\overset{H}{C}}-\underset{OCH_3}{\overset{H}{C}}-\underset{H}{\overset{CH_3}{C}}-$

di-syndiotactic (DS)

In the above nomenclature for the short sequence length in polymer, the meaning of di is different from that of the Natta's definition.[2] According to the other system of nomenclature,[5] t and e are called threo-meso and erythro-meso methyl protons and T, E, and DS are called threo-meso, erythro-meso, and racemic methoxyl protons, respectively.

In case 2, the two signals of the β-methyl group are due to diad tacticity corresponding to isotactic (i) and syndiotactic (s) diads and the three signals of α-methoxyl group are due to triad tacticity corresponding to isotactic (I), syndiotactic (S), and heterotactic (H) triads as observed in some vinyl polymers.

Two signals of β-methyl group:

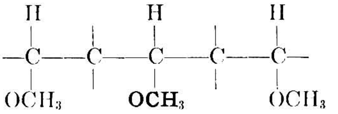
$-\underset{OCH_3}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-\underset{OCH_3}{\overset{H}{C}}- \qquad -\underset{H}{\overset{OCH_3}{C}}-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{OCH_3}{C}}-$

isotactic (i)

$-\underset{H}{\overset{OCH_3}{C}}-\underset{CH_3}{\overset{H}{C}}-\underset{OCH_3}{\overset{H}{C}}- \qquad -\underset{OCH_3}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{OCH_3}{C}}-$

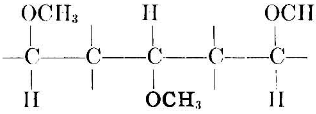
syndiotactic (s)

Three signals of α-methoxyl group:



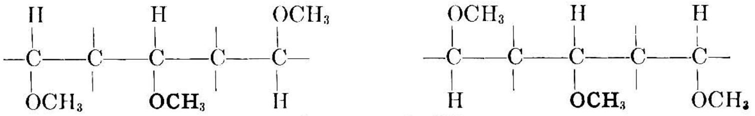
$-\underset{OCH_3}{\overset{H}{C}}-C-\underset{OCH_3}{\overset{H}{C}}-C-\underset{OCH_3}{\overset{H}{C}}-$

isotactic (I)



$-\underset{H}{\overset{OCH_3}{C}}-C-\underset{OCH_3}{\overset{H}{C}}-C-\underset{H}{\overset{OCH_3}{C}}-$

syndiotactic (S)



$-\underset{OCH_3}{\overset{H}{C}}-C-\underset{OCH_3}{\overset{H}{C}}-C-\underset{H}{\overset{OCH_3}{C}}- \qquad -\underset{H}{\overset{OCH_3}{C}}-C-\underset{OCH_3}{\overset{H}{C}}-C-\underset{OCH_3}{\overset{H}{C}}-$

heterotactic (H)

In other cases, e.g., where signals of the β-methyl group show e and t structures and those of α-methoxyl group show I, S, and H structures, eq. (1) is not given.

In case 2, the two signals of the β-methyl spectra must be ascribed to i and s as described above. As i consists of threo and erythro diads and s only of a di-syndiotactic diad when the polymer has a substituent on the β-position, the chemical shifts of threo and erythro diads must be indentical. Erythro-methyl and threo-methyl groups are oriented *trans* and *gauche* with respect to the adjacent methoxyl groups, respectively, for the hypothetical planar zigzag conformation. A di-syndiotactic methyl group is oriented in an intermediate conformation between the erythro-methyl and threo-methyl groups, that is, it is oriented *trans* to one of the adjacent methoxyl groups and *gauche* to the other. In the β-methylene spectrum of poly-(methyl vinyl ether), the isotactic protons are nonequivalent, and the signal of syndiotactic protons appears in the center of the isotactic signals.[8] That isotactic protons are nonequivalent is ascribed[14] to differences in conformation of β-protons to the adjacent methoxyl groups. Therefore, in PMPE, case 2 in which erythro- and threo-methyl protons do not exhibit different chemical shifts is unlikely. Case 1, in which two methyl protons exhibit different chemical shifts, is more reasonable than case 2.

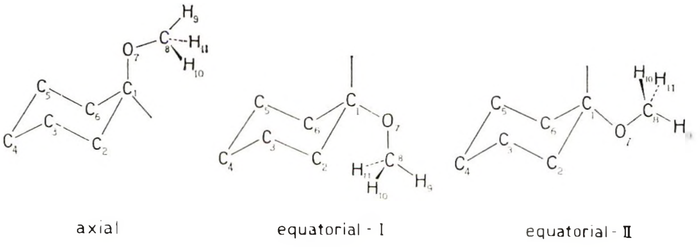
Moreover, the three signals of the α-methoxyl spectrum must be ascribed to I, H, and S in case 2, and the anisotropy of the most adjacent C—CH_3 bonds is completely neglected. The anisotropic effect of the C—CH_3 bond is not so slight that it can be neglected, because the methylene protons of isotactic polypropylene have been shown to be non-equivalent.[15] Jackman[16] has suggested that the anisotropy of the C—C bond is similar to that of the C-O bond. Therefore, it is reasonable that methoxyl signals show the diad tacticity based on the anisotropic effect of the C—C bonds (case 2).

APPENDIX II

In our previous paper,[6] on the basis of the experimental results of Natta et al. the signals at 8.78 and 8.89 τ of methyl protons were assigned to threo (t) and erythro (e) di-isotactic diads, respectively. Therefore, from eq. (1) three methoxyl signals, at 6.26, 6.30, and 6.34 τ, were assigned to erythro-di-isotactic (E), di-syndiotactic (DS), and threo-di-isotactic (T) diads, respectively.

To confirm the above mentioned assignments, the difference in chemcial shifts between erythro- and threo-methoxyl protons was calculated in the same way as in isotactic methylene protons of polypropylene.[10]

Methoxycyclohexane was employed as a model compound for isotactic PMPE. In this model the equatorial and axial methoxyl groups correspond to erythro- and threo-methoxyl groups, respectively. The models shown in Figure 6 were assumed to be the stable conformation of methoxycyclohexane for calculation of the shielding contribution.



axial equatorial - I equatorial - II

Fig. 6. Model conformation of methoxycyclohexane for a calculation of the shielding contribution.

The distances and acute angles of methoxyl protons with respect to the electrical center of anisotropic C—C bonds (2-3 and 5-6 bonds) symmetrical axes were estimated as done for cyclohexane[15] and isotactic polypropylene.[9]

By using the McConnell equation and the value for $(\chi_L - \chi_T)$ of 5.5×10^{-30} cm^3, the shielding contributions at the C—C bonds for the methoxyl protons were calculated. As shown in Table V, the equatorial methoxyl protons are less shielded than the axial ones. The difference in chemical shifts between threo- and erythro-di-isotactic diads on the above assignment was observed to be 0.08 ppm in *o*-dichlorobenzene solution, and the erythro diad was less shielded than the threo diad. This result agreed with the calculated values in Table V. A similar value in the difference of chemical shift was also observed in tetrachloroethylene solution. Therefore, it is reasonable that 6.26 and 6.34 τ of methoxyl protons are assigned to erythro- and threo-di-isotactic diads.

TABLE V

Shielding Contributions $[\sigma_{av}(G)]$ of the Average Induced Field by C—C Bonds on the Methoxyl Protons

Type	No. of H atom	$\sigma_{av}(G) \times 10^6$
Equatorial I	9	−0.070
	10	−0.137
	11	−0.137
Equatorial II	9	−0.040
	10	−0.023
	11	−0.023
Axial	9	+0.034
	10	−0.014
	11	−0.014

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Solution Polymerization of Trioxane Catalyzed by Stannic Chloride

T. MIKI, T. HIGASHIMURA, and S. OKAMURA,
Department of Polymer Chemistry, Kyoto University, Kyoto, Japan

Synopsis

The polymerization of trioxane catalyzed by stannic chloride ($SnCl_4$) in ethylene dichloride was studied and compared with the results obtained with boron trifluoride etherate, $BF_3 \cdot O(C_2H_5)_2$, as catalyst. Under the same conditions, the polymerization rate was larger with $SnCl_4$ than with $BF_3 \cdot O(C_2H_5)_2$, while at a fixed polymer yield the molecular weight of the polymer obtained by $SnCl_4$ was lower than with the $BF_3 \cdot O(C_2H_5)_2$ catalyzed reaction. The overall activation energy of trioxane polymerization with $SnCl_4$ was 11.0 ± 0.8 kcal/mole. The kinetic orders of catalyst and monomer were determined to be close to 2 and 4, respectively. A certain amount of tetraoxane was also produced in an early stage of the polymerization with $SnCl_4$ similar to $BF_3 \cdot O(C_2H_5)_2$-catalyzed reaction. However, the maximum amount of tetraoxane produced at 30°C was larger with $SnCl_4$ than with $BF_3 \cdot O(C_2H_5)_2$. In addition, a ten-membered ring compound (pentoxane) was isolated in the solution polymerization of trioxane catalyzed by both $SnCl_4$ and $BF_3 \cdot O(C_2H_5)_2$. The confirmation of pentoxane formation is strong evidence for the back-biting reaction mechanism.

INTRODUCTION

The authors have studied the solution polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ and found peculiarities that were not observed in the usual cationic polymerization of vinyl monomers; the formation of tetraoxane during the trioxane polymerization,[1] the increase in the molecular weight of polymer with the polymer yield and with the decrease in the catalyst concentration,[2] extraordinary kinetic orders of the catalyst and the monomer,[3,4] etc. In this paper the polymerization of trioxane catalyzed by $SnCl_4$ will be studied and discussed as compared with data obtained with $BF_3 \cdot O(C_2H_5)_2$ as catalyst. In addition, the formation of ten-membered ring compound (pentoxane) was confirmed in the solution polymerization of trioxane catalyzed by both $BF_3 \cdot O(C_2H_5)_2$ and $SnCl_4$.

EXPERIMENTAL

$SnCl_4$ was refined by distilling commercial material.

Purifications of other materials, the procedures of polymerization, and the measurement of viscosity of polymer obtained were the same as described in the previous papers.[2,3] The determinations of the amount of trioxane consumed and of tetraoxane produced according to gas chromatography were the same as described in previous paper.[5]

In the following experiment, ethylene dichloride was used as a solvent and the polymerization temperature was 30°C except in a particular case.

RESULTS AND DISCUSSION

Comparison of Polymerization between $SnCl_4$ and $BF_3{\cdot}O(C_2H_5)_2$ Catalysts

In the polymerization of trioxane catalyzed by $BF_3{\cdot}O(C_2H_5)_2$ in ethylene dichloride, it has been found that the amount of polymer obtained does not coincide with the amount of trioxane consumed, being larger than the former, and that a certain amount of tetraoxane is produced in an early stage of polymerization.[1] These phenomena were also observed in the trioxane polymerization with $SnCl_4$ as catalyst. Figure 1 shows the rate of polymer formation and of monomer consumption under the same conditions, and Figure 2 shows the amount of tetraoxane produced in an early stage of polymerization under the same conditions.

An induction period for the formation of polymer with $SnCl_4$ as catalyst was not observed while the short induction period was observed with $BF_3{\cdot}O(C_2H_5)_2$ as catalyst under the investigated condition. The rate of polymer formation or monomer consumption is larger with $SnCl_4$ catalyst than with $BF_3{\cdot}O(C_2H_5)_2$ catalyst under the studied condition.

The difference between the amount of trioxane accounted for in the polymer formation and in monomer consumption with $SnCl_4$ as catalyst is similar to that with $BF_3{\cdot}O(C_2H_5)_2$ as catalyst and is 7–10 wt-% of the

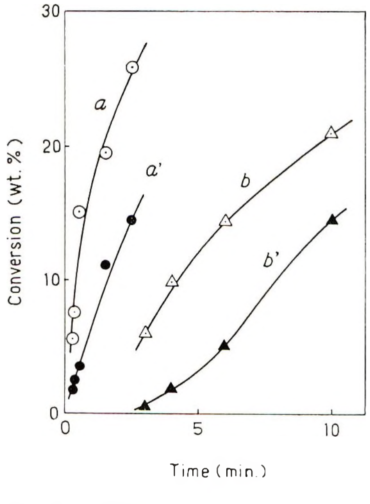

Fig. 1. Comparison between (a,b) monomer consumption and (a',b') polymer yield in the polymerization of trioxane catalyzed by $SnCl_4$ in ethylene dichloride at 30°C; (a) monomer consumption, $SnCl_4$ catalyst; (b) monomer consumption, $BF_3{\cdot}O(C_2H_5)$ catalyst; (a') polymer yield, $SnCl_4$ catalyst; (b') polymer yield, $BF_3{\cdot}O(C_2H_5)_2$ catalyst. [TOX], 3.05 mole/l; [C], 10.0 mmole/l; [H_2O], 5.8 mmole/l.

amount of monomer charged under the investigated condition (Fig. 1). The maximum amount of tetraoxane produced in an early stage of polymerization with $SnCl_4$ as catalyst is about 5 wt-% of the amount of trioxane monomer charged and is slightly larger than that with $BF_3 \cdot O(C_2H_5)_2$ as catalyst. The difference is negligible compared to the amount of monomer charged. Therefore, in the trioxane polymerization with $SnCl_4$ as catalyst, the total amounts of polymer and tetraoxane produced do not either coincide with the amount of tetraoxane consumed at a given period of time, as observed $BF_3 \cdot O(C_2H_5)_2$ as catalyst.[1] This difference between the former and the latter is 3-5 wt-% of the amount of trioxane charged under the condition shown in Figure 1 and is inferred to be due to the formation of solvent- or precipitant-soluble oligomer.

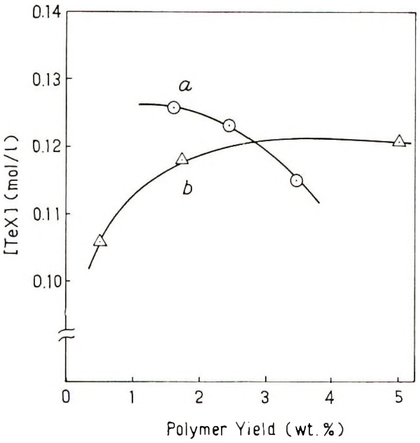

Fig. 2. Relationship between polymer yield and the amount of tetraoxane produced during polymerization: (*a*) $SnCl_4$ catalyst; (*b*) $BF_3 \cdot O(C_2H_5)_2$ catalyst. Polymerization conditions are the same as in Fig. 1.

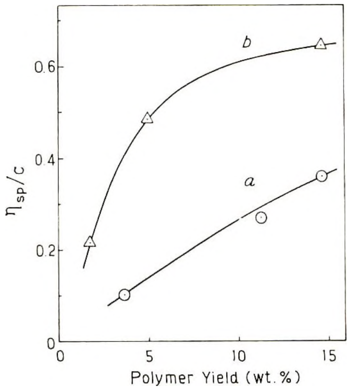

Fig. 3. Effect of the polymer yield on η_{sp}/c of a polymer: (*a*) $SnCl_4$ catalyst; (*b*) $BF_3 \cdot O(C_2H_5)_2$ catalyst. Polymerization conditions are the same as in Fig. 1.

Figure 3 shows the viscosity number of the resulting polymer. As had been reported by Russian researchers in the polymerization of trioxane catalyzed by $SnCl_4$ in methylene chloride at 30°C,[6] the molecular weight of polymer obtained in ethylene dichloride also increases with the polymer yield. While the rate of polymer formation is larger with $SnCl_4$ than with $BF_3 \cdot O(C_2H_5)_2$ as catalyst, the molecular weight of polymer is smaller with $SnCl_4$ than with $BF_3 \cdot O(C_2H_5)_2$ as catalyst at a fixed polymer yield. The latter fact means that the number of polymer molecules is larger with $SnCl_4$ than with $BF_3 \cdot O(C_2H_5)_2$ as catalyst at a fixed polymer yield. Then it is inferred that the concentration of active center during the polymerization is larger with $SnCl_4$ than with $BF_3 \cdot O(C_2H_5)_2$ as catalyst. Therefore, it is concluded that the larger polymerization rate with $SnCl_4$ than with $BF_3 \cdot O(C_2H_5)_2$ as catalyst under the investigated condition is partly due to the larger concentration of active centers with $SnCl_4$ during the polymerization. But it is not clear from our results whether it is also due to the larger propagation rate constant with $SnCl_4$.

As far as the molecular weight of polymer obtained in trioxane polymerization is concerned, Kern et al. concluded that the molecular weight of polymer obtained with more active catalyst is larger.[7] This conclusion does not agree with our result. This discrepancy may be due to the fact that they neglected the increase in the molecular weight of polymer with the polymer yield.

Effect of Polymerization Temperature

Effect of polymerization temperature on the rate of polymer formation and on the amount of tetraoxane produced during the polymerization of trioxane catalyzed by $SnCl_4$ was studied. Figure 4 shows the polymer

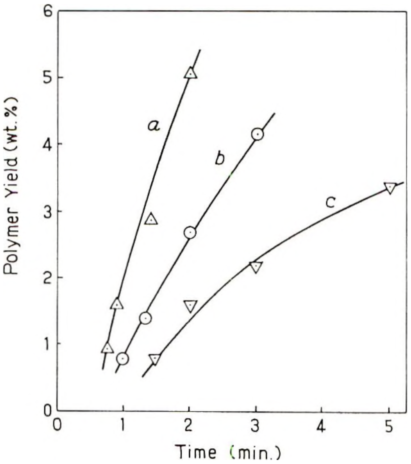

Fig. 4. Effect of polymerization temperature on the polymer yield in ethylene dichloride: (*a*) 40°C; (*b*) 30°C; (*c*) 20°C. [TOX], 3.05 mole/l; [C], 5.0 mmole/l; $[H_2O]$; 5.8 mmole/l.

yield versus time curves at various polymerization temperatures. From Arrhenius' plot of the initial rate determined graphically from Figure 4 against the reciprocal of temperature, the overall activation energy of

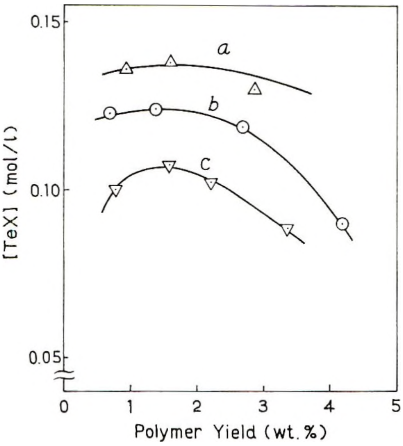

Fig. 5. Effect of polymerization temperature on the amount of tetraoxane produced during polymerization: (*a*) 40°C, (*b*) 30°C; (*c*) 20°C. Polymerization conditions are the same as in Fig. 4.

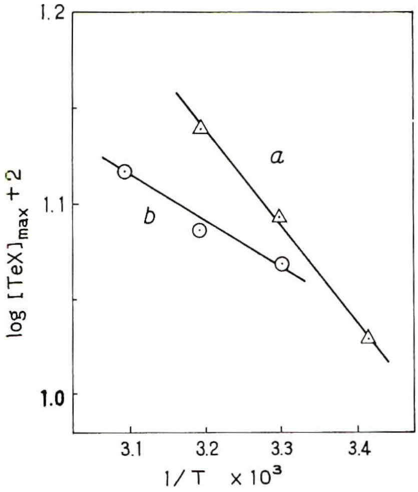

Fig. 6. Arrhenius plot of the maximum amount of tetraoxane produced during polymerization in ethylene dichloride: (*a*) [$SnCl_4$] 5.0 mmole/l, [TOX] 3.05 mole/l [H_2O] 5.8 mmole/l; (*b*) [$BF_3 \cdot O(C_2H_5)_2$] 20.0 mmole/l, [TOX] 3.17 mole/l, [H_2O] 2.5 mmole/l.

polymerization of trioxane catalyzed by $SnCl_4$ was determined to be 11.0 ± 0.8 kcal/mole. This value is smaller than the value in the trioxane polymerization with $BF_3 \cdot O(C_2H_5)_2$ as catalyst, the latter being about 16 kcal/mole.[8]

Figure 5 shows the amount of tetraoxane produced in an early stage of polymerization at various polymerization temperatures, and Figure 6 shows the relationship between the maximum amount of tetraoxane produced and the reciprocal of the polymerization temperature, wherein the same plot in the polymerization with $BF_3 \cdot O(C_2H_5)_2$ as catalyst is represented.[9] The amount of tetraoxane produced in an early stage of trioxane polymerization increased with raising the polymerization temperature. However, the temperature coefficient for the tetraoxane formation during the trioxane polymerization is larger with $SnCl_4$ than with $BF_3 \cdot O(C_2H_5)_2$ as catalyst, as is clearly seen in Figure 6. This may be ascribed to the difference of the counterion in the growing chain end between the two catalysts.

Effects of Concentrations of Reagents

Effects of the concentrations of catalyst and water on the polymer formation rate and on the molecular weight of the polymer are shown in Figure 7 and 8, respectively. It is clearly seen from Figure 7, as previously reported by Kern et al.,[7] that the small amount of water serves as a cocatalyst and accelerates the polymerization rate. It is seen in Figure 8 that the increase in the concentration of $SnCl_4$ decreases the molecular weight of polymer obtained at a fixed polymer yield, and that water serves as a transfer agent to decrease the molecular weight of polymer, as observed in the trioxane polymerization with $BF_3 \cdot O(C_2H_5)_2$ as catalyst.[2]

The kinetic order of $SnCl_4$ catalyst had been found to be one in the polymerization of trioxane catalyzed by $SnCl_4$ in methylene chloride and nitrobenzene at 30°C.[10] However, this result was not observed in ethylene dichloride. The relationship between the concentration of $SnCl_4$ and the

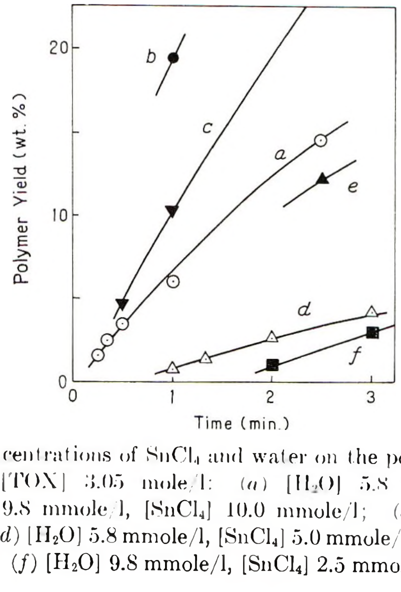

Fig. 7. Effect of concentrations of $SnCl_4$ and water on the polymer yield in ethylene dichloride at 30°C, [TOX] 3.05 mole/l: (*a*) $[H_2O]$ 5.8 mmole/l, $[SnCl_4]$ 10.0 mmole/l; (*b*) $[H_2O]$ 9.8 mmole/l, $[SnCl_4]$ 10.0 mmole/l; (*c*) $[H_2O]$ 9.8 mmole/l, $[SnCl_4]$ 7.5 mmole/l; (*d*) $[H_2O]$ 5.8 mmole/l, $[SnCl_4]$ 5.0 mmole/l; (*e*) $[H_2O]$ 9.8 mmole/l, $[SnCl_4]$ 5.0 mmole/l; (*f*) $[H_2O]$ 9.8 mmole/l, $[SnCl_4]$ 2.5 mmole/l.

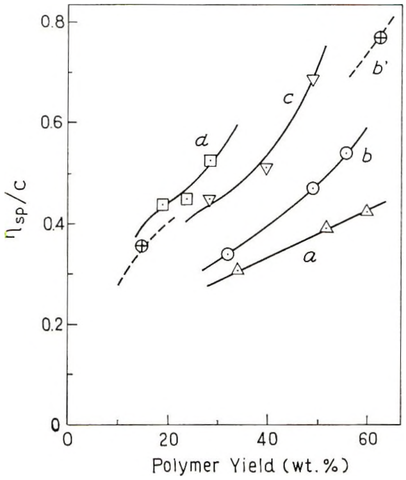

Fig. 8. Relationship between η_{sp}/c of polymer and the polymer yield in various catalyst concentrations in ethylene dichloride, [TOX] 3.05 mole/l, 30°C, [H_2O] 9.8 mmole/l; (*a*) [$SnCl_4$] 20.0 mmole/l; (*b*) [$SnCl_4$] 10.0 mmole/l; (*c*) [$SnCl_4$] 5.0 mmole/l; (*d*) [$SnCl_4$] 2.5 mmole/l; (*b'*) [H_2O] 5.8 mmole/l, [$SnCl_4$] 10.0 mmole/l.

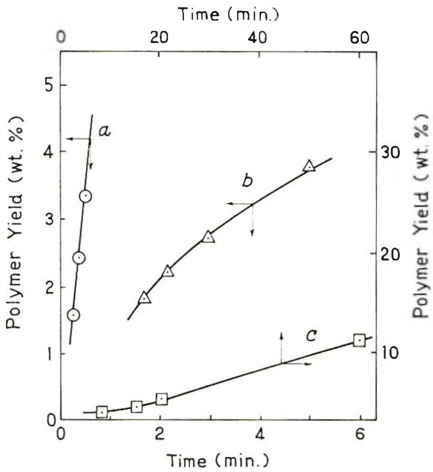

Fig. 9. Effect of the trioxane concentration on the polymer yield in ethylene dichloride at 30°C, [$SnCl_4$] 10 mmole/l; [H_2O] 5.8–6.8 mmole/l: (*a*)[TOX] 3.05 mole/l; (*b*) 1.67 mole/l; (*c*) 1.11 mole/l.

rate of polymer formation was roughly determined from Figure 7 at different water concentrations. The reaction orders at the water concentrations of 9.8 and 5.8 mmole/l are 1.7 and 1.9, respectively, and it is concluded that the kinetic order of $SnCl_4$ catalyst in the trioxane polymerization is larger than unity and is close to 2. In the trioxane polymerization with $BF_3 \cdot O(C_2H_5)_2$ as catalyst the kinetic order of $BF_3 \cdot O(C_2H_5)_2$ is about 0.5.[3] Thus the dependence of the polymerization rate on the concentration of catalyst is quite different between the two catalysts.

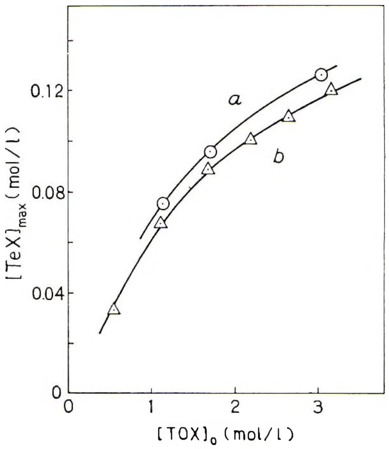

Fig. 10. Effect of the trioxane concentration on the maximum amount of tetraoxane produced during polymerization in ethylene dichloride at 30°C, [C] 10.0 mmole/l: (*a*) $SnCl_4$ catalyst, [H_2O] 5.8–6.8 mmole/l; (*b*) $BF_3 \cdot O(C_2H_5)_2$ catalyst, [H_2O] 1.1–2.5 mmole/l.

The maximum amount of tetraoxane produced in an early stage of polymerization is independent of the initial concentration of $SnCl_4$ within the range from 5.0 to 10 mmole/l, as is observed in the trioxane polymerization with $BF_3 \cdot O(C_2H_5)_2$ as catalyst in ethylene dichloride.[9]

Effect of the initial trioxane concentration on the rate of polymer formation is shown in Figure 9. As is seen in Figure 9, the induction period for the formation of polymer appears at a low initial concentration of trioxane. The kinetic order of trioxane determined from Figure 9 is about 4.1. This value coincides with the value determined in methylene chloride by Enikolopyan et al.[10] However, it is very large and the same order as in the trioxane polymerization with $BF_3 \cdot O(C_2H_5)_2$ as catalyst, wherein the kinetic order of trioxane was about 34.[4]

The amount of tetraoxane produced at an early stage of trioxane polymerization with $SnCl_4$ catalyst also increases with increasing the initial concentration of trioxane, as does in the trioxane polymerization with $BF_3 \cdot O(C_2H_5)_2$ as catalyst.[9] The maximum amount of the tetraoxane produced in the trioxane polymerization was plotted at various initial concentrations of trioxane in Figure 10, in which the same plot was represented with $BF_3 \cdot O(C_2H_5)_2$ as catalyst.[9] As is mentioned above, the maximum amount of tetraoxane produced in the trioxane polymerization at 30°C was larger with $SnCl_4$ than with $BF_3 \cdot O(C_2H_5)_2$ as catalyst over the investigated range of initial trioxane concentration.

Formation of Pentoxane during Polymerization of Trioxane

Reaction products of the trioxane polymerization catalyzed by $BF_3 \cdot O(C_2H_5)_2$ and $SnCl_4$ were examined by gas chromatography under conditions augmenting the sensitivity as much as possible (measurement conditions: column, 25% poly(ethylene glycol)-C22, 1 m, 170°C, H_2, 70 ml/min). A new compound was detected in addition to tetraoxane, trioxane, and other reagents charged in advance. This compound, a white, crystalline material, was isolated by gas chromatography and estimated as pentaoxane through measurement of mass spectroscopy,[11] as suggested earlier.[1] The results of mass spectroscopy of pentoxane are shown in Table I, in which the data with tetraoxane were added as a controlled experiment. The parent ion ($m/e = 150$) of pentoxane was not observed, probably because of the weak intensity obtained with our apparatus. In the case of pentoxane, our data coincided relatively with literature values[11] with respect to m/e values of 91, 119, and 121, while a great discrepancy between our data and literature values[11] with respect to m/e values of 60 and 89 was observed. However, in the case of tetraoxane, the same tendency was observed. This discrepancy observed between our and literature[11] data may be due to the differences in the apparatus and the measurement conditions. Therefore, it is not unreasonable from Table I to identify the new compound isolated as pentoxane.

TABLE I
Relative Intensities for the Mass Spectra of Pentoxane and Tetraoxane

	Pentoxane		Tetraoxane	
m/e	Our data	Literature[11]	Our data	Literature[11]
121	1.3	0.9	0.04	0.01
120	0	0.2	0.5	0.22
119	0.5	0.4	0.02	0.04
91	18.5	20.0	9.2	9.1
90	10.3	7.6	1.0	0.9
89	3.7	9.1	11.9	2.2
61	100	100	100	100
60	7.4	2.6	0	2.6
59	0	0.01	0.8	0.02

The amount of pentoxane produced during the trioxane polymerization was determined by gas chromatography. It was very small, as compared with the amount of tetraoxane produced during the trioxane polymerization. In the polymerization conditions shown in Figure 1, the amount of pentoxane produced in an early stage of polymerization was about 3 mmole/l with $SnCl_4$ as catalyst and about 2 mmole/l with $BF_3{\cdot}O(C_2H_5)_2$ as catalyst. This tendency in the formation amount of pentoxane between the two catalysts is similar to the formation of tetraoxane during the trioxane polymerization by the two catalysts. The amount of pentoxane produced in the early stage of trioxane polymerization increased with increasing polymerization temperature. Pentoxane produced in the early stage of trioxane polymerization disappeared in the later stages of the polymerization. These facts are also similar to the behavior of tetraoxane produced during the trioxane polymerization. The confirmation of pentoxane formation is strong evidence for the existence of the back-biting reaction of the growing chain end which was proposed earlier.[1]

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Mechanism of Three-Dimensional Polymerization of the System Methyl Methacrylate–Glycol Dimethacrylate. I. Determination of the Structure of the Three-Dimensional Product

J. JOKL, J. KOPEČEK, and D. LÍM,
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

Synopsis

A method has been developed for determination of structure of a three-dimensional methyl methacrylate–glycol dimethacrylate copolymer by using NIR absorption spectrometry. The results show that it is possible to determine the content of pendant vinyl groups in the range of approximately 0.5 – 18% of the crosslinking agent in the monomer.

In the preceding paper we studied the problem of the kinetics and formation of three-dimensional polymers in the entire conversion range.[1] The systems glycol monomethacrylate–glycol dimethacrylate–water were suitable for this purpose. The principle of the method used consisted in the parallel study of the dilatometric course of the polymerization process and of the changes of three-dimensional structure obtained. The resulting polymer was characterized by determining the total conversion, the amount of pendant vinyl groups, and the density of the three-dimensional network from deformation behavior and equilibrium swelling. The dependence of the density of the three-dimensional network on the solvent content led to the conclusion concerning the consumption of the crosslinking agent for cyclization.

The pendant vinyl groups were determined by ultraviolet spectrophotometry in an aqueous system. Because of the strong overlapping of the conjugated system of pendant vinyl groups (C=C—C=O) and of the band of carbonyl groups of the polymeric substance, which are present in amounts many times greater, the vinyl group content could be determined only relatively. Another difficulty was the very high absorbance coefficient of both groupings, which made it impossible to determine the absorbance value from the height of the peak. Another uncertain factor was the value of the dilatation factor $\langle \alpha \rangle$ in the Flory relation[2] determining the relation between the network density and equilibrium swelling.

Nevertheless the results obtained in independent experiments made it possible to characterize the three-dimensional polymerization not only from the view-point of the final product, but also in its entire course.

The attempt to determine the absolute amount of pendant vinyl groups in the system mentioned by means of ultraviolet spectrophotometry was unsuccessful. Even slices only 5–10 μ thick did not have the required transparency and therefore, with the use of only a spectrophotometer with a simple monochromator it was impossible to make measurements in the region of true absorption peaks. It should be emphasized that studies of kinetic and structural relationships are especially significant in the region of low contents of crosslinking agent in the monomer. Therefore, the determination concerns only the very small fraction of this amount, bound in the form of unreacted pendant groups in the polymer. In the region of higher contents of crosslinking agent the course of all relationships is too abrupt, so that sufficient accuracy is not achieved.

Other possibilities of spectral analysis have therefore been studied intensively, but only NIR spectrophotometry has been found suitable.

In the present paper a method for the determination of pendant vinyl groups in three-dimensional gels is proposed which permits a more general study of three-dimensional polymers and definition of the products prepared. The monomer system studied was methyl methacrylate–glycol dimethacrylate–solvent (butyl acetate).

Derivation of Relationships for the Spectrophotometry of the Analyzed System

The frequency 6205 cm^{-1} was found to be typical for the vinyl group. Since it can be determined as the combination frequency of the C—H bond of the vinyl group, it could be expected that the position and absorbance coefficient of this band will be very stable and independent of the structure of the remaining part of the molecule or of the arrangement of the polymer. Recently a similar absorption region for vinyl monomer analysis has been described by Willis.[3]

Since, however, the highest possible sensitivity of the method is required, extremely thick layers of samples composed of 20–35 sheets had to be used, which could be freed of unreacted monomer and crosslinking agent residues by extraction within a reasonable period of time.

For evaluation of the vinyl group contents (expressed, for the sake of simplicity, by the equivalent amount of methyl methacrylate), it was necessary to know the overall amount of polymer in the sample, especially in the path of the beam of the spectrophotometer. This determination, however, is subject to great difficulties in the case of swollen materials in connection with drying, weighing, and thickness measurement of all sheets used and complicated by brittleness, irregular thickness, and distortion after drying of the samples. This value, therefore, has also been defined spectrophotometrically by measuring the absorption at a frequency typical for the polymer. For this purpose the frequency $\nu_1 = 7508$ cm^{-1} was selected, corresponding to the combination frequency of C—H bonds in the polymer. To eliminate the influence of light scattering, the imperfect optical quality of the samples, etc., a second auxiliary frequency at $\nu_2 = 7140$ cm^{-1} was chosen. The total amount of the polymer analyzed was determined from the difference of absorbances determined at these frequencies.

In normal spectrophotometry the cell content is homogeneous. In the case of a heterogeneous system the percentage composition of the components in the cell does not correspond to the composition of the components, passed by the analytical beam of the spectrophotometer. The experimental determination of this relation would be very difficult and subject to substantial error. For this reason, equivalent optical layer thicknesses of the individual components were used in derivations instead of concentrations. The relationships of eqs. (1)–(5) may thus be derived. Here we denote by BAC, butyl acetate; M, monomer, methyl methacrylate; P, polymer, poly(methyl methacrylate); VG denotes vinyl groups in the three-dimensional polymer, expressed as monomer with a specific gravity equal to the specific gravity of the polymer; GDMA is crosslinking agent (glycol dimethacrylate).

$$d_{\mathrm{BAC}} + d_{\mathrm{M}} + d_{\mathrm{P}} + d_{\mathrm{VG}} = 40 \text{ mm} \tag{1}$$

The absorbance $A_{\nu_i}{}^{j}$ of the substance j (j = BAC, M, P, VG) present in the 40-mm cell at the analytical frequency ν_i ($i = 1, 2, 3, 4, 5$) is for j = M

$$A_{\nu_3}{}^{\mathrm{M}} = k_1 c_{\mathrm{M}} \tag{2}$$

where we define k_i as a proportionality constant (i = 1, 2, 3, 4) and c_j is the percentage by weight of the substance j in the BAC solution. The difference of absorbances at the frequencies ν_1 and ν_2 (40-mm cell) is

$$\Delta A_{\nu_1 - \nu_2} = k_2(d_{\mathrm{P}} + d_{\mathrm{VG}}) \tag{3}$$

Therefore the total absorbance at $\nu_{1,2}$ is

$$A_{\nu_{1,2}} = d_{\mathrm{BAC}} a_{\nu_{1,2}}{}^{\mathrm{BAC}} + d_{\mathrm{P}} a_{\nu_{1,2}}{}^{\mathrm{P}} + d_{\mathrm{VG}} a_{\nu_{1,2}}{}^{\mathrm{VG}} + \delta A - 40 a_{\nu_{1,2}}{}^{\mathrm{BAC}}$$

(where $a_{\nu_i}{}^{j}$ is the absorbance coefficient of the substance j at the frequency ν_i with an optical layer thickness of 1 mm and δA is the nonspecific absorbance caused by optical imperfections of the samples) and

$$a_{\nu_1}{}^{\mathrm{P}} - a_{\nu_2}{}^{\mathrm{P}} = a_{\nu_1}{}^{\mathrm{VG}} - a_{\nu_2}{}^{\mathrm{VG}}$$

We define also G_j as the mass of substance j in the cell passed by the analytical beam and s_j as the specific gravity of the pure substance j. Then

$$\begin{aligned} c_{\mathrm{M}} = A_{\nu_3}{}^{\mathrm{M}}/k_1 &= 100G_{\mathrm{M}}/(G_{\mathrm{M}} + G_{\mathrm{BAC}}) \\ &= 100 d_{\mathrm{M}} s_{\mathrm{M}}/(d_{\mathrm{M}} s_{\mathrm{M}} + 40 s_{\mathrm{BAC}} - d_{\mathrm{M}} s_{\mathrm{BAC}}) \\ &= 2.5 d_{\mathrm{M}} s_{\mathrm{M}}/s_{\mathrm{BAC}} \end{aligned} \tag{4}$$

because

$$40 s_{\mathrm{BAC}} \gg d_{\mathrm{M}}(s_{\mathrm{M}} - s_{\mathrm{BAC}})$$

and therefore

$$a_{\nu_3}{}^{\mathrm{M}} - a_{\nu_3}{}^{\mathrm{BAC}} = 2.5k_1s_{\mathrm{M}}/s_{\mathrm{BAC}} = 1/k_3$$

For measurement in BAC compared to 40 mm BAC,

$$d_{\mathrm{M}} = A_{\nu_3}{}^{\mathrm{M}}\, s_{\mathrm{BAC}}/(2.5k_1s_{\mathrm{M}}) = k_3A_{\nu_3}{}^{\mathrm{M}} \tag{5}$$

Assuming $s_{\mathrm{VG}} = s_{\mathrm{P}}$ the following holds for the measurement of samples in comparison to BAC:

$$A_{\nu} = d_{\mathrm{P}}a_{\nu_3}{}^{\mathrm{P}} + d_{\mathrm{VG}}a_{\nu_3}{}^{\mathrm{VG}} - (d_{\mathrm{P}} + d_{\mathrm{VG}})a_{\nu_3}{}^{\mathrm{BAC}} \tag{6}$$

and, because [as in eq. (4)]

$$a_{\nu_3}{}^{\mathrm{VG}} = a_{\nu_3}{}^{\mathrm{M}}s_{\mathrm{VG}}/s_{\mathrm{M}} = a_{\nu_3}{}^{\mathrm{M}}\, s_{\mathrm{P}}/s_{\mathrm{M}}$$

the consideration is valid for irradiated prism 40 mm thick with constant cross section. After rearranging, and assuming that

$$a_{\nu}{}^{\mathrm{P}} = a_{\nu_3}{}^{\mathrm{BAC}}$$

and

$$a_{\nu_3}{}^{\mathrm{BAC}} \ll a_{\nu_3}{}^{\mathrm{VG}}$$

we obtain

$$A_{\nu_3} = d_{\mathrm{P}}(a_{\nu_3}{}^{\mathrm{P}} - a_{\nu_3}{}^{\mathrm{BAC}}) + d_{\mathrm{VG}}(a_{\nu_3}{}^{\mathrm{VG}} - a_{\nu_3}{}^{\mathrm{BAC}}) \tag{7}$$

$$A_{\nu_3} = d_{\mathrm{VG}}s_{\mathrm{VG}}/k_3s_{\mathrm{M}} = d_{\mathrm{VG}}2.5k_1s_{\mathrm{P}}/s_{\mathrm{BAC}} \tag{8}$$

For the content x_0 of VG in P (expressed in weight per cent from direct measurement compared with BAC), it may then be stated that

$$\begin{aligned} x_0 &= 100d_{\mathrm{VG}}/(d_{\mathrm{P}} + d_{\mathrm{VG}}) \\ &= 100k_2s_{\mathrm{BAC}}\,A_{\nu_3}/(2.5k_1s_{\mathrm{P}}\Delta A_{\nu_1-\nu_2}) \\ &= k_4A_{\nu_3}/A_{\nu_1-\nu_2} \end{aligned} \tag{9}$$

For differential measurement it follows, for perfectly compensated samples, after quite identical considerations, that the percentage by weight x_m of VG in P is given by

$$x_m = k_4\Delta^m A_{\nu_3}/A_{\nu_1-\nu_2} \tag{10}$$

where the denominator of the fraction contains the value from the measurement of the sample compared to BAC. Equation (10) however, also holds for the case, that $a_{\nu_3}{}^{\mathrm{BAC}} \neq a_{\nu_3}{}^{\mathrm{P}}$. For reference samples prepared with regular, stepwise increase of the crosslinking agent in the monomer mixture, it may be considered, that

$$x_0 = 2x_m - x_n \qquad (11$$

The verification of this relationship confirms the assumption $a^{\mathrm{BAC}}{}_{\nu_3} = a^{\mathrm{P}}{}_{\nu_3}$. For imperfectly compensated samples we may write the equation

$$(x_m)_{\mathrm{theor}} = (x_m)_{\mathrm{meas}} + x_0{}^m(A_{\nu_1-\nu_2}{}^m/A_{\nu_1-\nu_2}{}^x - 1) \tag{12}$$

Experimental

Methyl methacrylate was purified by double distillation on a 40-plate column in inert atmosphere at reduced pressure. Before the experiment the monomer was freshly distilled. Glycol dimethacrylate was prepared from glycol and methyl methacrylate. The raw product was repeatedly distilled with the addition of CuCl as inhibitor, bp 84°C/1 mm Hg, $n_D^{20} = 1.4549$. Butyl acetate was dried and fractionated. The purity of the monomers and of the solvent was checked by gas chromatography.

Methyl azobisisobutyrate was prepared according to Thiele and Heuser.[4] The melting point of the product used was 30.5°C.

The polymerization experiments were carried out between plane-parallel plates sealed with washed silicone rubber tube. After filling the space between the plates with a mixture of monomer, initiator, and solvent, the oxygen was removed from the liquid by passing a stream of nitrogen by means of a hypodermic needle. The plates with the monomers were then heated in a thermostat to 60°C. Parallel dilatometric polymerization experiments were carried out to determine the reproducibility of the polymerization process. The solvent used was butyl acetate. This solvent is easy to purify and its chain transfer constant is of the order of 10^{-5}, so that it has very little influence on the chain length. Its content in the monomer was as low as possible (about 20%) to secure polymerization conditions above the second-order transition point at 60°C, and thus to achieve practically 100% conversion. Data on the polymerization conditions are presented in Table I. The initiator concentration was low enough to keep polymerization under isothermal conditions. For complete polymerization heating for about 6 hr was found to be necessary.

The plates prepared, approximately 1 mm thick, were washed for a period of time necessary to remove the free monomer residue. The degree

TABLE I
Content of Pendant Vinyl Groups in Copolymers of Methyl Methacrylate with Glycol Dimethacrylate[a]

	Composition of the Monomer Mixture			
			GDMA	
Sample	[MMA], mole/l	[GDMA], mole/l × 10^2	(GDMA + MMA), wt-%	x_0, wt-%
1	7.03	2.27	0.64	0.20
2	6.99	4.55	1.27	0.27
3	6.91	9.35	2.61	0.30
4	6.79	15.79	4.40	0.35
5	6.75	18.03	5.02	0.42
6	6.59	26.85	7.46	0.49
7	6.35	40.34	11.17	0.83
8	6.10	54.17	14.95	1.18
9	5.85	68.25	18.77	1.39

[a] [BAC] = 1.54 mole/l; [methyl azobisisobutyrate] = 2.90×10^{-3} mole/l.

of conversion was determined by drying the samples *in vacuo* at 40°C to constant weight (approximately 3 weeks).

The content of pendant vinyl groups was measured by means of a double-beam instrument CF 4 NI (Optica, Milan). The samples (20–35 plates) were placed in silica cells 40 mm thick. The immersion medium used was also butyl acetate. This solvent was found to be a suitable immersion liquid for elimination of high scattering of light on 40–70 boundary surfaces. It has a refractive index close to that of the polymer, good swelling properties for polymer, and spectral transmission in the region of the analytical frequency of the vinyl group. The measurements were carried out against pure butyl acetate and against polymer samples prepared with 0.64% (*m*) and 1.27% (*n*) of the crosslinking agent.

The analytical frequencies, in the range of which the NIR spectra were recorded, were $\nu_1 = 7508\ \text{cm}^{-1}$; $\nu_2 = 7140\ \text{cm}^{-1}$; $\nu_3 = 6205\ \text{cm}^{-1}$; $\nu_4 = 6341\ \text{cm}^{-1}$, and $\nu_5 = 6168\ \text{cm}^{-1}$. $\Delta A_{\nu_1 - \nu_2}$ were read (in the case of samples measured against BAC) as the difference of directly determined absorbances at ν_1 and ν_2.

A_{ν_3} values were evaluated by means of the artificial baseline method (the line being taken from ν_4 to ν_5). The samples measured by the differential procedure were evaluated by the natural baseline method (tangent line to the spectral function at the point ν_5).

The constant k_1 was determined by means of calibration with a number of substances containing the vinyl group (Table II). The most probable value of $k_1 = 0.133$ was taken for the calculation.

The constant k_2 was determined by measurements on poly(methyl methacrylate) sheets 2–25 mm thick in butyl acetate immersion. Due to swelling the optically perfect surface of the calibration sheets is covered with fine cracks after a certain period of time, which do not influence the measured value. This elimination of nonspecific extinction δ_A caused by the optical imperfection of the sample was moreover verified by means of several repetitions of the calibration measurements with increasing amounts of cracks on the surface, and thus also increasing values of δA. The k_2 value was determined from the slope of the calibration plot as 0.0184, therefore $d_P + d_{VG} = \Delta A_{\nu_1 - \nu_2} 54.4$ mm. The calibrations of the constants k_1 and k_2 also verified the validity of the Lambert-Beer law for the analytical system in question.

TABLE II

Determination of the Constant k_1 for Various Methacrylates

	k_1
Methyl methacrylate	0.139
n-Butyl methacrylate	0.135
Isobutyl methacrylate	0.136
Lauryl methacrylate	0.127
Cetyl methacrylate	0.129
Glycol dimethacrylate	0.134

The fact that $a_{\nu_3}^{\mathrm{BAC}} = a_{\nu_3}^{\mathrm{P}}$ was verified directly by measuring a 100-mm layer of a 15% solution of soluble poly(methyl methacrylate) in BAC against 100 mm BAC and indirectly from the agreement of the determined x_0 values with the values calculated according to eqs. (10) and (11) with respect to reference samples x_m and x_n.

The constant k_4 was calculated from eq. (9); its value is 4.01.

Results and Discussion

The values obtained by the described procedure are illustrated in Figure 1 and presented in Table I.

The data obtained confirmed the validity of the Lambert-Beer law for this system and also the stability of the absorbance coefficient of the vinyl group. By comparing the absolute and differential results, reproducibility and tests with poly(methyl methacrylate) sheets measured in presence of various amounts of mononer in butyl acetate it is possible to estimate the error as ±0.03% absolute. The relative error, of course, increases with decreasing content of vinyl group. By repeated measurement it is possible to approach the correct value. The observed relationship between the amount of pendant vinyl groups and the content of the crosslinking agent in the monomer has an exponential character. The curve does not go through the origin. The reason for this should be the subject of further experiments.

It is evident that the lower limit of sensitivity of the method corresponds approximately to the amount of pendant vinyl groups resulting by polymerization of monomer containing 0.5% crosslinking agent in monomer. For lower content of crosslinking agent it is possible to assume, in agreement with small differences in kinetic course of polymerization, that the

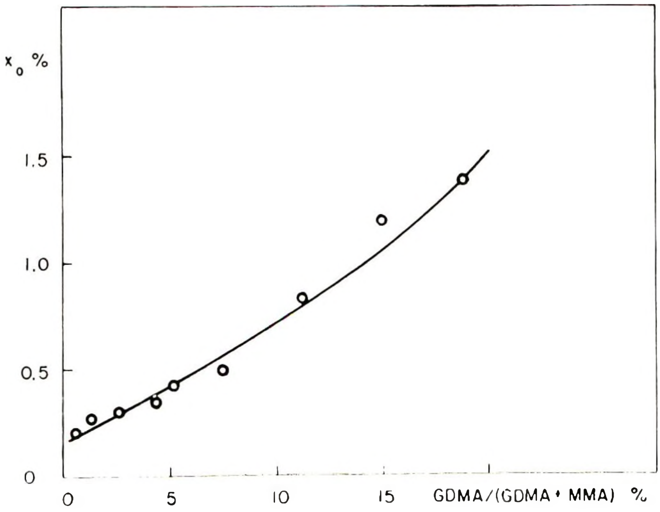

Fig. 1. Dependence of the amount of pendant vinyl groups on the composition of monomer mixture.

content of pendant vinyl groups is not very different from relations corresponding to the measured limit. The results may be substantiated by determination of the course of crosslink density in the range from the lowest spectrometrically evaluated contents of pendant vinyl groups to lower content of crosslinking agent in monomer.

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Studies on the Polymerization of Bifunctional Monomers. XVI. Cyclopolymerization of *o*-Divinylbenzene with Triphenylmethyl Fluoroborate and Presumption of the Presence of the Free Growing Cation in This System*

CHUJI ASO, TOYOKI KUNITAKE, YOSHIHIKO MATSUGUMA, and YOJI IMAIZUMI, *Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka, Japan*

Synopsis

Cyclopolymerization of *o*-divinylbenzene was studied by using triphenylmethyl fluoroborate as initiator. The cyclization constant r_c (ratio of the rate constant for intramolecular cyclization to that for intermolecular propagation) decreased with increase in polarity of the solvent. This solvent effect as well as the effect of catalysts reported previously could be accounted for by a revised model of the propagating species, where both the counter anion and the *o*-vinyl group were coordinated to the carbonium ion. The difference in activation energy between intramolecular cyclization and intermolecular propagation was 6.2 kcal/mole. This value was close to that obtained previously with $BF_3 \cdot OEt_2$ catalyst but greater than those for anionic and radical polymerizations. When tetraalkylammonium fluoroborates were added to the polymerization system in methylene chloride, r_c and the molecular weight of the polymer decreased. These results were ascribed to the decrease in the amount of the free propagating cation by the common ion effect.

INTRODUCTION

According to previous studies on the cationic cyclopolymerization of *o*-divinylbenzene,[1,2] the cyclization constant r_c as defined below varied with polymerization conditions such as catalyst, solvent, and temperature. The variation of r_c with the catalyst was interpreted in terms of the tightness of the growing ion pair, a tighter ion pair being considered to give a smaller r_c.[2] A somewhat similar observation was made in the anionic cyclopolymerization of this monomer.[3] With alkali metal–naphthalene catalysts, a greater r_c value was obtained with a less highly interacting countercation, and the free anion was found to give a higher r_c than an ion pair by studying the common ion effect.

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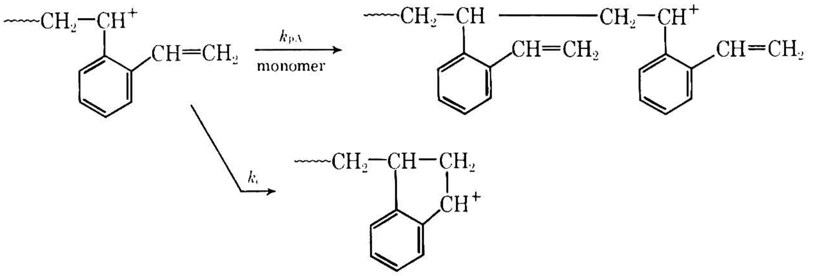
In cationic polymerizations of vinyl monomers with Friedel-Crafts catalysts, the structure of the counterion is usually not clearly defined, unlike the case of the anionic polymerization with alkali metal–naphthalenes. Triphenylcarbonium salts have been utilized as initiators of cationic polymerization of vinyl compounds.[4–9] The initiation is believed to be addition of the triphenylmethyl group to the double bond and, therefore, the counteranion of the growing ion pair is the same as that of the triphenylcarbonium salt. Thus triphenylmethyl fluoroborate was selected as initiator in the present study, in order to study the cationic propagation of *o*-divinylbenzene with a counteranion of the known structure.

The propagation of *o*-divinylbenzene involves two competing steps: intermolecular propagation [eq. (1)] and intramolecular cyclization [eq. (2)].



(1)

(2)

The cyclization constant r_c, is defined as

$$r_c = k_c/k_{pA}$$

and can be calculated from eq. (3) or from eq. (4):[2,10]

$$-\frac{d[\mathrm{m}]}{d[\mathrm{M}]} = \frac{2[\mathrm{M}]}{2[\mathrm{M}] + r_c} \tag{3}$$

$$\frac{[\mathrm{m}]}{[\mathrm{M}]_0\, x} = 1 - \frac{r_c}{2[\mathrm{M}]_0\, x}\left(\ln \frac{2[\mathrm{M}]_0 + r_c}{2[\mathrm{M}]_0\,(1 - x) + r_c}\right) \tag{4}$$

where [m], [M], and x denote concentration of the pendant double bond in the system, monomer concentration, and the fractional conversion of monomer into polymer, respectively.

EXPERIMENTAL

Materials

o-Divinylbenzene was prepared according to the procedure described by Halford and Weissmann,[11] and the purity was confirmed by infrared spectroscopy and by gas chromatography (>99.5% pure). Triphenylmethyl fluoroborate was prepared from triphenylmethyl alcohol and fluoroboric acid in propionic anhydride.[12] The orange yellow precipitate was washed with dry ether, dried *in vacuo*, and kept under nitrogen; mp 179–180°C.

ANAL. Calcd. for $C_{19}H_{15}BF_4$: C, 69.11%; H, 4.58%. Found: C, 68.45%; H, 4.64%.

Ultraviolet spectrum (70% aqueous H_2SO_4): λ_{max} 433 mμ, ϵ_{max} 38 000–39 500 (lit.:[13,14] λ_{max} 432 mμ, ϵ_{max} 38 000–38 600).

Tetraethylammonium fluoroborate was prepared from tetraethylammonium bromide and fluoroboric acid and recrystallized from acetone.[15]

ANAL. Calcd. for $C_8H_{20}NBF_4$: C, 44.25%; H, 9.29%; N, 6.45%. Found: C, 44.27%; H, 9.24%; N, 6.64%.

Tetrabutylammonium fluoroborate was similarly prepared and recrystallized from 50 vol-% aqueous methanol; mp 162.0–162.8°C (lit.:[16] mp 161.8°C).

ANAL. Calcd. for $C_{16}H_{36}NBF_4$: C, 58.36%; H, 11.03%; N, 4.39%. Found: C, 58.19%; H, 11.04%; N, 4.42%.

Polymerization solvents were purified by the usual procedure.

Polymerization Procedures

The polymerization was carried out in Schlenk-type ampules. Given amounts of a catalyst solution and solvent were placed in a vessel kept at the polymerization temperature under nitrogen, and the monomer was added. After given periods, polymerization was stopped by methanol, and the polymer was precipitated by pouring the reaction mixture into excess methanol, separated by centrifugation, and dried *in vacuo.* The polymer recovered was separated into toluene-soluble and toluene-insoluble fractions.

Determination of Residual Unsaturation and Measurements

The quantity of the pendant double bond in polymer was determined, as already described,[2,10] by comparing the infrared peak of the sample at 1630 cm^{-1} ($\nu_{C=C}$ vinyl) in CCl_4 solutions with the same peak of the monomer. Viscosities were measured with a modified Ubbelohde viscometer in benzene at 30°C.

RESULTS AND DISCUSSION

Effect of Solvent on r_c

Table I gives polymerization data of *o*-divinylbenzene at 0°C in various solvents. In polar solvents, polymerization was fast, and the red-orange color of the catalyst solution deepened on addition of monomer. The catalyst was not soluble in toluene and partly insoluble in chlorobenzene, and the red-orange color of the catalyst developed very slowly in the toluene solution.

The r_c value decreased with increase in the dielectric constant of the solvent, except in nitrobenzene solvent. In the last column of Table I are given r_c values obtained with $BF_3 \cdot OEt_2$ catalyst.[2] The closeness of

TABLE I

Polymerization of *o*-Divinylbenzene with Triphenylmethyl Fluoroborate in Several Solvents at 0°C

No.	Solvent	Dielectric constant of solvent	Catalyst concn × 10^{-2}, mole/l	Monomer concn, mole/l	Time, min	Conversion, %[a]	PDB, %[b]	r_c, mole/l	r_c mole/l[c]
C-4	$C_6H_5CH_3$	2.4	4.9[d]	1.01	1 month	45.8 (18.3)	58.5	1.10	1.0
C-5	$CHCl_3$	4.6	5.0	1.01	67	99.0 (72.5)	42.6	1.15	0.97
C-6	C_6H_5Cl	5.6	5.5	1.01	310	41.5	69.0	0.82	0.74
I-1	CH_2Cl_2	15	1.05	0.72	72	56.5	67.7	0.47	
C-2	$C_2H_5NO_2$	30	4.8	1.01	11	30.5	80.7	0.41	0.30
D-4	"	30	0.46	0.86	90	7.1	82.8	0.36	
C-8	$C_6H_5NO_2$	34	5.0	1.01	7	32.7	69.8	0.76	
C-9	CH_3CN	39	5.3	1.01	34	22.3	86.7	0.27	

[a] Percentage conversion of the insoluble fraction is indicated in parenthesis. If not indicated, only the soluble polymer was obtained.

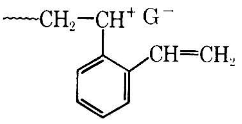
[b] Content of the pendant double bond in polymer. This value is taken as 100% when polymerization proceeds without the intramolecular cyclization.

[c] Obtained with BF_3OEt_2 catalyst.[2]

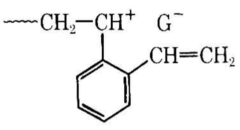
[d] Catalyst not soluble in this solvent.

the two sets of r_c values is remarkable. Since the variation of r_c with several Friedel-Crafts catalysts is large (i.e., variation of 0.1 to 5 mole/l in toluene), this agreement apparently indicates that the chemical nature of the counteranion derived from $BF_3 \cdot OEt_2$ is almost the same as that of BF_4^-. The small but consistent difference in r_c (higher by about 0.1 mole/l. with BF_4^- anion), however, suggests that the fluoroborate anion gives a somewhat looser ion pair than the anion derived from $BF_3 \cdot OEt_2$ (see below).

In the previous study, the variation of r_c with catalyst was explained in terms of the tightness of the growing ion pair. A tight ion pair was represented by I and a loose ion pair by II or III.[2] (G^-: counteranion).



I



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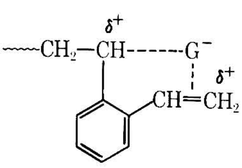
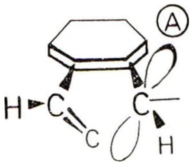


III

Since a high r_c value was obtained with a loose ion pair presumably derived from a strong Friedel-Crafts catalysts and since the intramolecular cyclization [eq. (2)] had a higher activation energy than the intermolecular propagation [eq. (1)], a tight ion pair (I), which gave a smaller r_c, was considered to be less reactive. On the other hand, the weaker coulombic interaction in a loose ion pair was considered to result in either a more reactive cation (II) or increased participation of the neighboring vinyl group as in III. However, the solvent effect on r_c given in Table I cannot be explained simply in terms of the tightness of the growing ion pair, since polar solvents should render an ion pair looser and accordingly give a higher r_c. There was no such inconsistency in the anionic cyclopolymerization of *o*-divinylbenzene.[3] In this case the reaction condition (countercation, solvent) which gave greater rates of propagation in the styrene polymerization, gave higher r_c values, and r_c was concluded to increase simply with the reactivity of the growing anion. The activation parameter obtained and the common ion effect also supported this conclusion.

One possibility worthy of consideration for explaining the unusual solvent effect in the cationic cyclopolymerization is the different extent of participation of the neighboring vinyl group, which depends upon the solvent polarity. In the previous model, the interaction of the positive neighboring vinyl group with the counteranion was considered possible in a loose ion pair (III). However, the *p*-orbital of the benzyl cation and the π-orbital of the vinyl group cannot be simultaneously coplanar with the π-orbital of the benzene ring because of steric hindrance. As the carbonium ion is stabilized by resonance with the benzene ring, the vinyl group will be correspondingly pushed out of the plane. Therefore, the delocalization of the positive charge to the neighboring vinyl group via the benzene ring may be small, even with a loose ion pair. That the two vinyl groups in *o*-divinylbenzene cannot be simultaneously coplanar with the benzene ring was inferred from the NMR spectrum.[17] On the other hand, the molecular model indicates that the direct p, π-interaction of the benzyl carbonium ion and the neighboring vinyl group is possible. For this interaction to occur, both the p-orbital of the benzyl carbon and the vinyl π-orbital have to be tilted toward each other, as shown in IV. The counteranion may be assumed to be at the other side of the vinyl group, so that the positive p-orbital can interact both with the counteranion and with the neighboring vinyl group.



IV

IV

By use of this model for the growing ion pair of o-divinylbenzene, the r_c data can be interpreted fairly reasonably. In a loose ion pair derived from a strong catalyst, the reactivity of the carbonium ion will be greater and the interaction of the neighboring vinyl group with the carbonium ion could be greater in a given solvent, because the positive charge is less shielded by the counteranion. Thus higher r_c values obtained with stronger catalysts may be due to the increased reactivity of the growing cation and/or to the increased interaction of the vinyl group.

The interaction of the neighboring vinyl group with the positive carbon will depend on the solvent used. In a polar (or highly solvating) medium, the carbonium ion becomes solvated and forms a loose ion pair. At the same time, interaction with the vinyl group may be replaced by that with polar solvent molecules. Then, for a given ion pair, the vinyl interaction decreases with polarity of the solvent, making the intramolecular cyclization less favorable. Although increased reactivity of an ion pair in polar solvents should favor the cyclization, this factor seems to be overshadowed by the decreased interaction of the vinyl group, and, therefore, r_c will decrease with polarity of the solvent.

Effect of Temperature on r_c

The variation of r_c with temperature was studied in methylene chloride. The r_c value increased with temperature, being 0.22 mole/l at $-20°C$ and 1.2 mole/l at 20°C. Arrhenius plots of r_c are shown in Figure 1. The corresponding plots with $BF_3 \cdot OEt_2$ catalyst in toluene are given for comparison. The difference in activation energies ($E_c - E_{pA}$) between the intramolecular cyclization and the intermolecular propagation in the $(C_6H_5)_3CBF_4$–methylene chloride system was 6.2 kcal/mole, which is close to 5.3 kcal/mole obtained in the $BF_3 \cdot OEt_2$–toluene system. The pre-exponential terms were also very close. Since the chemical natures of

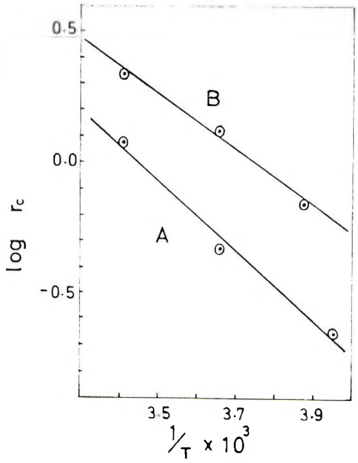


Fig. 1. Arrhenius plots of cyclization constants: (A) $(C_6H_5)_3CBF_4$–methylene chloride system; (B) $BF_3 \cdot OEt_2$–toluene system.

the counterions in these two catalyst systems are considered quite similar, as is apparent from Table I, the difference in the activation parameters does not seem to be affected very much by the solvent.

Table II compares the activation parameters of r_c in several systems.

TABLE II
Activation Parameters for Several Systems of Cyclopolymerization of *o*-Divinylbenzene.

Catalyst	Solvent	A_c/A_{pA}[a]	$E_c - E_{pA}$, kcal/mole[a]	Reference
$BF_3 \cdot OEt_2$	Toluene	2.2×10^4	5.3	Aso et al.[1]
$(C_6H_5)_3CBF_4$	Methylene chloride	5×10^4	6.2	This study
Sodium naphthalene (ion-pair)	Tetrahydrofuran	15	2.2	Aso et al.[3]
Free radical	Benzene	50	1.9	Aso et al.[10]

[a] Calculated from the following equation:

$$r_c = k_c/k_{pA} = (A_c/A_{pA}) \exp \{(-E_c + E_{pA})/RT\}.$$

It is noted that the activation parameters in anionic and radical cyclopolymerizations are quite alike, but they are rather different from those in cationic polymerization. Although even the qualitative discussion on the activation parameter is still difficult, this contrast may imply that the nature of the propagating species can be described by its reactivity (or tightness if it is an ion pair) alone in the anionic and radical systems but that the nature of the propagating species in cationic polymerization is influenced by its tightness as well as geometrical factors such as conformation of the growing chain end, the position of the counteranion and the solvent organization.

TABLE III

Common-Ion Effect in Cyclopolymerization of *o*-Divinylbenzene with Triphenylmethyl Fluoroborate[a]

No.	Catalyst concn × 10^{-2}, mole/l	Additive concn × 10^{-2}, mole/l[b]	$\frac{[\text{Additive}]}{[\text{Catalyst}]}$ molar ratio	Time, min	Conversion, %[c]	PDB, %	r_c, mole/l	[η]	$\bar{M}_n$[d]
I-1	1.05	0	0	72	56.5	67.7	0.47	0.09	4200
F-2	0.93	2.61(A)	2.8	80	9.2	80.1	0.36	0.05	1750
I-2	1.05	3.19(A)	3.0	72	16.9	80.3	0.32	0.04	1350
F-3	0.93	4.81(A)	5.2	120	11.5	80.2	0.35	0.06	2250
D-7	1.01	9.05(A)	9.0	88	26.4	76.2	0.38	0.04	1350
I-3	1.05	3.11(B)	2.9	72	13.9	78.0	0.37	0.05	1750
I-4	1.09	3.28(B)	3.0	120	24.4	79.6	0.32		—

[a] Solvent, methylene chloride; polymerization temperature, 0°C; monomer concentration, 0.718 mole/l.

[b] A = tetraethylammonium fluoroborate added; B = tetrabutylammonium fluoroborate added.

[c] Insoluble polymer not obtained.

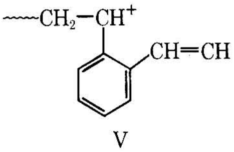
[d] Calculated by using the following relationship:[1] $[\eta] = 2.33 \times 10^{-4} \cdot \bar{M}_n^{0.72}$.

Common Ion Effect

The existence of the free propagating carbanion was established in the "living" polymerization system.[18,19] However, few studies have been made of the presence of the free propagating ion in the cationic polymerization. Biddulph and co-workers[20] discussed the possibility of the free-ion propagation in polymerization of isobutene with $TiCl_4$. However, their data can be explained equally well by assuming the presence of contact and solvent-separated ion pairs.[21] Polymerization results by Sakurada et al. strongly indicated that the rate acceleration in several cationic polymerizations under electric field was due to the dissociation of the propagating ion pair.[22–24]

Since the free-growing anion was shown to be present by studying the effect of $NaBPh_4$ addition in the anionic polymerization of *o*-divinylbenzene,[3] the common-ion effect was similarly investigated in the cationic system.

Table III shows the effect of addition of tetraalkylammonium fluoroborates on r_c. Addition of either of the salts resulted in the decrease in r_c from 0.47 mole/l to 0.35 ± 0.03 mole/l. Neither the increase in the additive concentration nor the difference in the alkyl group affected r_c beyond the experimental uncertainty. These results lead to the interpretation that the propagation by the free cation V cannot be ignored with the catalyst concentration of 0.01 mole/l, and that addition of 0.03 mole/l of Et_4NBF_4 or Bu_4NBF_4 is sufficient to suppress the free ion propagation by the common ion effect. Also noteworthy in Table III is the decrease in the polymerization rate by addition of the common ion. As the free propagating ion is known to be more reactive than the ion pair,[18,19] this difference in rates may be ascribed to the faster rate of initiation and/or propagation with the free ion V.



V

The common-ion effect is also apparent in the molecular weight of the polymer obtained. Addition of Et_4NBF_4 or Bu_4NBF_4 decreased the molecular weight appreciably. Sakurada et al.[22–24] observed the increase in molecular weight under electric field in some cationic polymerizations and ascribed it to the increased free-ion propagation. The present results similarly suggest that the free-ion propagation gave rise to a higher molecular weight than the ion-pair propagation.

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1,2-Dinitrile Polymers. I. Homopolymers and Copolymers of Fumaronitrile, Maleonitrile, and Succinonitrile

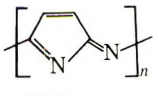
R. LIEPINS, D. CAMPBELL, and C. WALKER, *Camille Dreyfus Laboratory, Research Triangle Institute, Research Triangle Park, North Carolina 27709*

Synopsis

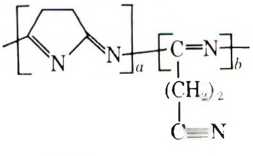
Homopolymers and copolymers of fumaronitrile, maleonitrile, and succinonitrile have been prepared by using medium high temperature free-radical initiators. Black, nonfusible but soluble polymers were obtained. The spectroscopic and chemical evidence indicated a structure containing α-pyrrolenine rings and no free nitrile groups in the fumaronitrile and maleonitrile polymers and 1-pyrroline rings and free nitrile groups in the succinonitrile polymers. The polymers possessed good thermal stability, free spin concentration of 10^{17}–10^{18} spins/g, and an ac conductivity at room temperature in nitrogen of 10^{-6} to 10^{-8} ohm^{-1} cm^{-1}.

INTRODUCTION

From thermodynamic considerations it has been predicted that free-radical polymerization of the nitrile bond, of the type so typical of vinyl or acetylenic compounds, will be highly unlikely.[1] Sosin et al.[2] have been able to affect free-radical polymerization of the nitrile bond in addition to the position alpha to it only by using the high temperature polyrecombination technique. We wish to report polymerization of the nitrile groups in fumaronitrile (FN), maleonitrile (MN), and succinonitrile (SN) in the presence of two peroxides and two hydroperoxides into new polymeric structures:



FN, MN Homopolymers



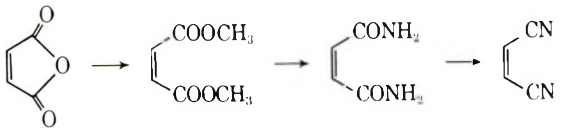
SN Homopolymer

The only other polymer of similar structure reported in the literature is the anionically initiated poly(succinonitrile).[3,4]

RESULTS AND DISCUSSION

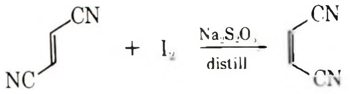
Monomers

Most of the FN and SN work was done with materials as received. Maleonitrile was prepared initially according to the procedure of Linstead and Whalley [eq. (1)].



(1)

Later a simpler and higher yield preparation was found[6] [eq. (2)].



(2)

In this preparation a 38% yield was realized. The product is a light yellow oil, bp 92°C/5 mm, mp 29–30°C, (lit.[6] 31.3–31.8°C). The infrared spectrum of it agreed completely with that reported by Miller et al.[7]

Homopolymerization

The polymerizations were conducted in bulk in either sealed glass ampules or capped glass pressure tubes at temperatures from 110°C to 190°C with the use of benzoyl peroxide, di-*tert*-butyl peroxide, *tert*-butyl hydroperoxide, or cumene hydroperoxide as initiators. Most of the work was done at 160°C with di-*tert*-butyl peroxide as initiator because it gave the best conversions. Some of the experimental data and results are summarized in Table I. At lower temperatures benzoyl peroxide was the better, and at higher temperatures *tert*-butyl hydroperoxide and cumene hydroperoxide were the better initiators. Polymerization in the absence of a free-radical initiator, for example, at 150°C for 69 hr, gave only a 3% yield of polymer of η_{inh} 0.07 (0.303 g/100 ml of methanesulfonic acid at 30.0°C). The polymerization rate appeared to be oxygen-dependent when the polymerizations were conducted in sealed glass ampules, evacuated to 10 μ before sealing. Under these conditions only a few per cent of the polymer after 48 hr at 150°C was obtained. On the other hand, polymerizations of materials charged under nitrogen, probably containing traces of oxygen, gave polymers in good yield (up to 40%) at the same conditions. Typically, the initially colorless solution turned brown and finally black within about fifteen minutes after the tube was placed in the constant temperature bath. The conversion and molecular weight were found to be strongly dependent upon the length of time of polymerization (Table II). The polymerization rate was also temperature-dependent. For example, while at 110°C only trace amounts of the polymer were formed, at 190°C the rate was very fast, and a 90% conversion was realized in 4 hr.

TABLE I
Polymers From 1,2-Dinitriles[a]

Monomers, wt-%			Polymerization temp, °C	Polymerization time, hr	Conversion, %	η_{inh}[b]	Analytical								
							Calcd				Found				
FN	MN	SN					C, %	H, %	N, %	O, %	C, %	H, %	N, %	O, %[c]	Total, %
100	—	—	160	43	72	0.35	61.53	2.59	35.89	—	59.54	3.02	33.03	3.69[d]	99.28
—	100	—	150	48	17[e]	0.31	61.53	2.59	35.89	—	59.07	3.64	34.35	2.79[f]	99.85
—	—	100	150	24	15	1.28	60.00	5.30	34.99	—	59.18	5.06	32.57	2.86	99.67
50	50	—	160	47	45	0.18	59.31	3.33	33.69	—	61.10	3.60	31.49	2.67	98.86
—	50	50	160	23	90	0.67	59.13	4.35	33.46	—	60.69	4.48	33.46	4.80	103.43
50	—	50	160	23	68	0.41	59.36	4.04	32.80	—	57.67	4.10	33.26	5.52	100.55
67	—	33	160	23	84	0.48	59.42	3.69	32.87	—	57.38	4.23	33.25	6.66	101.52
33	—	67	160	23	88[g]	0.45	59.29	4.39	32.71	—	59.41	4.65	32.72	4.98	101.76

[a] All polymerizations were conducted in glass pressure tubes placed in a constant temperature silicone bath and using about 4% of di-*tert*-butyl peroxide as initiator.

[b] Determined on solutions from 0.330 to 0.481 g/100 m lof methanesulfonic acid at 30.0°C.

[c] Determined independently.

[d] About 7% residual methanol indicated.

[e] The rest of the material was a viscous tan colored oil; infrared spectra indicated the presence of free nitrile groups.

[f] About 6% residual methanol indicated.

[g] About 5% of the material was not soluble in hot methanesulfonic acid.

TABLE II
Conversion and Inherent Viscosity of Polyfumaronitrile versus Polymerization Time at 160°C[a]

Time, hr	Conversion, %	η_{inh}
4	6	0.10
9	29	0.17
43	70	0.35
80	83[b]	0.40

[a] About 4% of di-*tert*-butyl peroxide used as initiator.

[b] Only about 30% of the material was soluble in hot methanesulfonic acid.

The FN and MN homopolymers were obtained as black powders. Although the MN homopolymer appeared to be identical to FN homopolymer in every respect, the homopolymerization results of MN were quite different from those of FN. In the homopolymerizatian of FN no products other than the black polymer and unpolymerized FN were recovered. Furthermore, the polymer yield was polymerization time-dependent. In the homopolymerization of MN, in addition to the black polymer, a viscous yellow oil was produced. No unreacted MN or FN could be recovered. The oily material contained free nitrile groups according to the infrared spectrum. Furthermore, under the conditions used, only about a 17% conversion of the monomer to polymer could be realized. These results suggest that the *cis* isomer undergoes some preferential reaction other than polymerization, possibly formation of porphin precursors. That MN can form tetrazaporphin under ionic conditions has been demonstrated by Linstead and Whalley.[5] Furthermore, FN under similar conditions shows no tendency to pigment formation.[8] The SN homopolymer was obtained as an olive-brown powder. Only the low conversion material was completely soluble in acidic solvents. As the conversion increased above 15%, an increasing amount of insoluble polymer was produced.

Copolymerization

Copolymerizations of the three monomers were conducted in bulk at 150°C and 160°C with di-*tert*-butyl peroxide as initiator. In general, higher conversion rates and higher molecular weights were obtained than in corresponding homopolymerizations. All of the copolymers (including SN) were obtained as black powders. Of the three FN/SN copolymers: 67/33, 50/50, and 33/67 (in per cent by weight), only the highest SN content copolymer contained some insoluble material. The 50/50 FN/MN copolymer was identical to both of the homopolymers. The 50/50 FN/SN and MN/SN copolymers had identical infrared spectra and appeared to be similar in other respects.

None of the homopolymers and copolymers had a melting point below 530°C and none seemed to melt in an open flame. However, all FN and MN polymers were soluble in different solvents depending upon their inherent viscosity: η_{inh} up to about 0.20 soluble in dimethylformamide, dimethyl sulfoxide, hexamethylphosphoramide; η_{inh} 0.20–0.40 soluble in sulfuric, phosphoric, formic, and methanesulfonic acids; η_{inh} above 0.40 soluble in fuming sulfuric acid. Low conversion but high molecular weight (e.g., $\eta_{inh} = 1.3$) SN homopolymers were easily soluble in acidic solvents.

Since the polymers were prepared under bulk conditions the only other material introduced in the polymer was methanol during the extraction. The analytical data confirmed this. No residue or other impurities were found in these polymers.

Structure Characterization

Spectroscopic. Infrared spectra of these polymers were determined on KBr pellets. The more characteristic absorptions are listed in Table III.

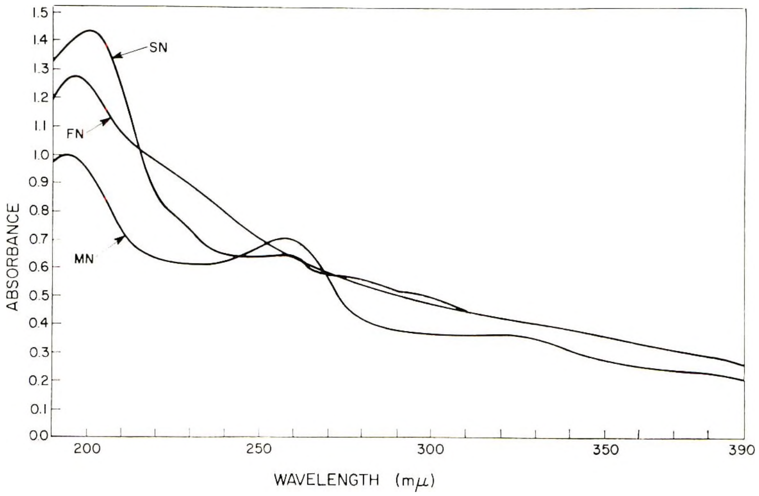


Fig. 1. Ultraviolet spectra.

Of the three homopolymers only the SN homopolymer contained an infrared absorption characteristic of a nitrile group. Furthermore, both the 2250 and 2190 cm^{-1} absorptions were of equal intensity. The strongest absorptions in all cases were those of C=C and C=N. The 2195–2190 cm^{-1} absorption was strong and sharp in the case of FN and MN polymers. The OH absorption was introduced during the extraction of the polymers with methanol. It is very difficult to remove the last traces of methanol from these polymers.

Difficulties were experienced in obtaining good NMR spectrum on a higher molecular weight material because of solubility problems. A spectrum was obtained on a lower molecular weight FN polymer (η_{inh} 0.121) in hot deuterated dimethyl sulfoxide. In the 0–1000 cps region four major peaks at 7.04, 7.90, 8.24, and 8.74 ppm (against a TMS standard in a capillary) were observed. The signals are characteristic of vinyl protons. Fumaronitrile itself gives only one peak at 7.30 ppm.

TABLE III

Infrared Data on 1,2-Dinitrile Polymers

	Wavelength, cm^{-1}						
Polymer	OH and/or NH	C≡N	Characteristic[a]	C═O	C═C and C═N	N → O	*cis* CH═CH
FN	3400–3100	—	2195–2190	—	1660–1500	—	705–690
MN	3500–3100	—	2190	—	1640–1500	—	700–690
SN	3500–3200	2250	2190	—	1670–1490	1290 980	—
SN, base-treated	3500–3100	—	2195–2190	1725	1670–1350	1290 980	—
50/50 FN/SN	3500–3000	—	2195–2175	—	1670–1480	—	705–690

[a] Characteristic of these polymers, apparently due to a conjugated C═N system.[9] Except for absorptions due to C≡N (at 2210 cm^{-1} and longer wavelengths) and central C≡C (at 2260–2190 cm^{-1}) no other groups have been reported to absorb in this region. The only well documented example having a broadened absorption at 2195–2175 cm^{-1} appears to be the triethylammonium salt of tetracyanoquinodimethane.[10]

TABLE IV
Ultraviolet Data on 1,2-Dinitrile Polymers

Polymer	Inherent viscosity	Max. absorption, mμ	ε	End of absorption, mμ
FN	0.35	196	8329	550
	0.14	196	4592	—
MN	0.31	193	4906	550
SN	1.28	201	5134	460
FN/MN	0.28	197	6248	750
Fumaronitrile monomer	—	229	20132	—

The ultraviolet light absorption spectra of FN, SN, and MN polymers in sulfuric acid are given in Figure 1. The copolymer spectra were similar to that of FN homopolymer. The extremely broad absorption would seem to indicate a considerable polydispersity in the molecular weight. The FN absorption curve is practically identical to those for polyphenylacetylenes,[11] except for the position of the maximum absorption which is shifted from about 260 mμ for the polyphenylacetylenes to about 200 mμ for the FN, MN and SN homopolymers and copolymers. The replacement of ethylenic linkage $\{C{=}C\}$ by an azomethine linkage $\{C{=}N\}$ will result in a displacement of the ultraviolet light absorption maxima towards shorter wavelengths.[12] The molecular extinction coefficients were calculated by using the molecular weight of the postulated repeat units (Table IV). The FN homopolymer data indicated that the intensity of the absorption band increased with increasing molecular weight or with increasing length of the conjugated system.

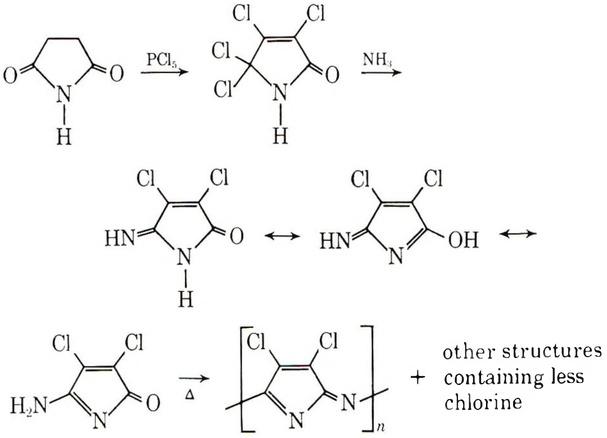
Basic Hydrolysis. Use of 25% methanolic potassium hydroxide in a sealed glass tube at 90°C degraded the polymer as judged by a decrease in the inherent viscosity; however, the 2195–2190 cm^{-1} absorption band was not markedly affected. This demonstrates the absence of nitrile groups. Corresponding treatment on the SN homopolymer completely eliminated the 2250 cm^{-1} absorption while leaving the 2190 cm^{-1} absorption and thus confirming the presence of free nitrile groups in the SN homopolymer.

Na_2SO_3 Reduction. Chiang and Friedlander[13] used Critchfield and Johnson's[14] procedure in reducing α,β-unsaturated nitriles in their polyacrylonitriles. Application of this procedure to FN homopolymer had no effect upon the 2195–2190 cm^{-1} absorption band. This constitutes a further evidence for the absence of α,β-unsaturated nitriles in FN and MN polymers.

On the basis of the physical appearance of the polymers, their solubility characteristics, analytical data, basic hydrolysis, and sodium sulfite reduction results as well as the spectroscopic evidence the completely conjugated structures are proposed.

In the case of FN, a slow *trans* to *cis* isomerization step precedes the fast cyclopolymerization step. Thus, the intermediate (*cis* isomer) is never present in sufficient concentration to give detectable amounts of any other products in this polymerization.

Independent Synthesis. To obtain a further proof for the postulated structure independent synthesis of a compound representing the repeating unit in the FN and MN homopolymers was undertaken. Subsequently the compound was converted into a polymeric material by a condensation reaction. The synthetic sequence used is shown in eq. (3).



(3)

The tetrachloromaleimide derivative was prepared according to the procedure of Anschutz and Schroeter.[15]

The product was isolated as a light green liquid with sharp odor. The NMR spectrum showed only one type of hydrogen at 8.24 ppm (TMS internal standard), characteristic of —CO—NH—CCl_2—.

The chlorine atoms alpha to the heteroatom are very reactive,[16] and the ammonolysis reaction was performed at -79°C. The product was isolated as a light-green solid and it can exist in three tautomeric forms. The infrared evidence, no characteristic imide N—H absorption at 1820 cm^{-1}, and NMR, only one broad signal centered at 3.88 ppm (TMS standard in a capillary), amine hydrogens, indicated that the amino isomer (dichloroaminoisopyrrolone) was the predominant tautomer. Furthermore, the material contained a strong and sharp absorption at 2190 cm^{-1}, characteristic of the FN, MN, and SN polymers, and thus constitutes a further proof for the type of the repeating unit containing a conjugated C═N system postulated. Although the model compound synthesized here contains two chlorine groups that were not in the polymers, this would not affect the conclusions because all of the C—Cl absorptions occur at 800–600 cm^{-1} and the chlorine groups would not affect the other absorptions listed.

The dichloroaminoisopyrrolone is not very stable, as judged from the change in color to dark brown in a short time when exposed to atmosphere. It appeared to be stable under nitrogen and when kept at -20°C.

The light-green solid was then heated under vacuum to progressively higher temperatures giving increasingly darker colored and less soluble product. The infrared spectrum on the material heated to 130°C was similar to those of FN and MN homopolymers, including the 2190 cm^{-1} absorption band.

Chemical Properties

The various chemical properties were investigated only with the fumaronitrile homopolymer. The x-ray powder diffraction diagrams indicated the material to be amorphous.

Catalytic Hydrogenation. The diagnostic conditions[4] for carbon–carbon double bond hydrogenation in the presence of carbon–nitrogen double bond were used. Hydrogen uptake was observed, and the infrared absorption spectrum on the hydrogenated material did not show the 690–705 cm^{-1} absorption (*cis*-CH=CH—) which was present in the original material. Only qualitative observations were made, as the polymer was not completely soluble in dimethylformamide.

Halogenation. Attempted brominations of the polymer in water or carbon tetrachloride suspensions at room temperature led to very little if any bromine uptake. However, the use of iodine monobromide in carbon tetrachloride at room temperature did lead to halogen uptake. Analytical data showed 20% halogen in the polymer, and the infrared absorption spectrum showed decreased absorption at 2190 cm^{-1} a large decrease in the 1500–1550 cm^{-1} absorption, and a very strong increase in the 1400 cm^{-1} absorption. The great decrease in the 1500–1550 cm^{-1} absorption along with the decrease in the 2190 cm^{-1} absorption would indicate halogen addition across the carbon–nitrogen double bond; however, the possibility of salt formation with the nitrogens cannot be eliminated.

Oxidation. Oxidative degradation of the polymer was attempted with the use of chromium trioxide in sulfuric acid[17] and also 30% hydrogen peroxide in sulfuric acid.[18] These reagents were chosen because of their successful application in tetrazaporphine degradations. In both cases a light yellow, extremely viscous oil was obtained. However, despite several attempts no monomeric materials could be isolated. A typical infrared absorption spectrum of the hydrogen peroxide oxidation product indicates the presence of alkyl ether (1060–1150 cm^{-1}) and epoxy (near 1250 cm^{-1}, 890 cm^{-1}, *trans*, 830 cm^{-1}, *cis*)[8] groups.

Diels-Alder Reaction. The repeating unit of FN and MN homopolymers contains two conjugated double bonds in a *cis* configuration. It was of interest, therefore, to attempt the Diels-Alder reaction on the polymer with maleic anhydride. The reaction took place only with difficulty above 170°C. The infrared absorption spectrum showed the following changes: broad absorption at 2900–3550 cm^{-1}, reduction in the intensity of the 2190 cm^{-1} absorption, introduction of strong absorptions at 1770 and 1700 cm^{-1} (carboxyl carbonyl), and weak absorptions at 1200–1300, 1050–1075, 900–950 cm^{-1} which are typical of polymeric anhydrides.[19,20] On the other hand, the typical anhydride carbonyl absorption at 1860 cm^{-1} was absent. Apparently, hydrolysis of the anhydride group to the carboxylic acid had occurred under the experimental conditions. Analysis of the product showed 19% oxygen indicating that about 30% of maleic acid was incorporated in the polymer.

Thermal Properties

Heating of low molecular weight (η_{inh} below 0.20) fumaronitrile polymers in a vacuum oven at 140°C and progressively higher temperature (up to 190°C) increased their inherent viscosity by as much as a factor of two. The increase in viscosity was not accompanied by changes in the infrared absorption spectrum or by insoluble material formation. This is indicative of a coupling reaction taking place between the lower molecular weight chains.

Thermogravimetric analysis was performed on samples of η_{inh} 0.30–0.40 in air and nitrogen at a heating rate of 5°C/min. The nitrogen data (Table V) showed that the three homopolymers are similar in their thermal stability and that the SN homopolymer is somewhat poorer of the three. This is understandable because the SN polymer contains —CH$_2$—CH$_2$— segment in the repeating unit as compared to all conjugated systems in the FN and MN polymers. The FN and MN homopolymers compare in thermal stability to some of the polybenzimidazoles.[21] The 50/50 copolymers of FN and MN and SN possessed poorer thermal stability than corresponding homopolymers.

TABLE V
TGA Data on 1,2-Dinitrile Polymers

Polymer	Temperature of 10% wt loss in nitrogen, °C	Temperature of 50% wt loss in nitrogen, °C
FN	342	795
MN	370	785
SN	358	710
50/50 FN/MN	352	675
50/50 FN/SN	346	704

Heating of a sample of FN homopolymer in a vacuum system (2μ pressure) at 500–550°C for 2$^1/_4$ hr produced a lower nitrogen content material (25% versus 33% in the original polymer) with much improved heat stability in air, i.e., less than 10% weight loss at 500°C.

ESR Properties

As the isolated polymers possessed the rather high spin concentrations of 10^{17}–10^{18} spins/g, it was of interest to follow the polymerization by ESR and perhaps note the time period at which the high spin concentration devel-

TABLE VI
ESR Data with Time of Polymerization

Total polymerization time, min	Color of material	Radical concn, per cm of sample	ΔH_{MSL}, G
4	Light tan	Faint signal	—
13	Brown	$\sim 10^{14}$	3
20	Dark brown	9.6×10^{14}	2.8
210	Black	5×10^{15}	4.1
2535	Black	9.3×10^{16}	3.9
4170	Black	3.6×10^{17}	5

oped. The procedure that we used consisted of charging 0.40 g of fumaronitrile and 0.016 g of di-*tert*-butyl peroxide under nitrogen into an ESR tube, capping it with a cork stopper, and then polymerizing in a silicone bath at 160°C. For the ESR measurements the tube was removed from the bath and cooled in running water before taking the measurements. The ESR data are given in Table VI.

As can be seen from the data, the spin concentration increases with polymerization time from the beginning. Furthermore, as the half-life for di-*tert*-butyl peroxide at 160°C is only 20 min and, considering the spin concentrations as well as the type of signal observed, it can be concluded that we are not measuring any large concentrations of *tert*-butoxy radicals but rather some other free-radical species that is characteristic of the polymer. Furthermore, the narrow line width is in agreement with the ESR data on highly conjugated polymers in general. For example, polyphenylacetylene of molecular weight 1100 had a free spin concentration of 5×10^{17} spins/g and a line width of 4 G.[22] The spins in our polymer were found to be oxygen insensitive and they were also present in solution (methanesulfonic acid). No fine structure could be detected despite considerable efforts to observe it.

Heating of the polymer in vacuum at 500–550°C produced two distinct types of electronic structures as judged from the ESR signal. The total spin concentration increased by at least two orders of magnitude (10^{19} spins/g) and the signal consisted of two components: (*1*) a narrow one, 1.5 G, and (*2*) a broader one, about 10 G. When the tube was open to air, a slow decrease in the total spin concentration, to the level before heating, was observed. However, after the tube was open to air for 24 hr the concentration of the spins again started to increase, and after 60 hr (the only other measurement made) it was considerably above the 24-hr level. This is best accounted for by assuming a charge-transfer complex formation between the diffusing oxygen and the conjugated chain segments. A study of the interaction of polyphenylacetylene with such electron acceptor molecules as oxygen and iodine had led to the same conclusions.[23]

Electrical Properties

Dielectric Constant. The dielectric constant of the fumaronitrile polymer was determined on a pellet of the compacted powder. Details for the preparation of the pellet are given in the next section. Sample preparation and measuring technique were identical to those of Peterlin and Elwell.[24] The dielectric constant ϵ at 26°C and 1000 cps was found to be 8.5.

Ac Conductivity Measurements. Meaningful conductivity measurements on compacted powders of polymers are difficult to obtain. The various pitfalls associated with these measurements as well as the precautions to be taken have been amply described.[25-27] Some of the details of our experimental procedure are described first. All of the polymer samples investigated were soluble materials. No impurities other than small amounts of methanol, which were extremely difficult to remove, were present in these polymers. The pellets were prepared by placing about 100 mg of the powder into a KBr pellet press (Perkin-Elmer), applying 10 000 lb/in.^{2} pressure at room temperature, heating to 130–135°C in an oven, and then applying 30 000 lb/in.^{2} for about 1 hr. The electrodes were painted with E-kote 40 silver conductive spray paint. The lead wires (gold) were attached with E-kote 3042 silver epoxy paint. The assembly was then allowed to dry at room temperature in an evacuated desiccator for at least 16 hr. The sample was mounted in a shielded cell and attached to the gold leads by means of the E-kote 3042 silver epoxy paint. The cell was purged with dry nitrogen for about four hours before the measurements were made.

The conductivity measurements were conducted by using the Boonton 260-A Q-meter over a frequency range of 1–10 Mcps. The conductivity usually increased with increase in frequency and then leveled off between 6 and 10 Mcps. An average value of the level part was reported. Spurious surface or photoconduction effects were eliminated by using a painted guard ring. Some of the conductivity data are listed in Table VII.

The room temperature conductivity data in a nitrogen atmosphere for the FN and MN polymers was in the 10^{-6} to 10^{-7} ohm^{-1} cm^{-1} range and for the SN polymer at least one order of magnitude lower. In the case of MN polymer a much smaller sample size was used without the guard ring, and hence the value may be open to question. In the case of FN polymers

TABLE VII
Ac Conductivity of 1,2-Dinitrile Polymers

Sample	Electrode radius, cm	Sample thickness, cm	Conductivity $\times 10^{-7}$, ohm^{-1} cm^{-1}
FN (483-7)	0.45	0.025	9.2
MN (434-57)	0.15	0.017	17.3
SN (483-19)	0.46	0.051	0.8
50/50 FN/MN (434-56)	0.44	0.034	15.9
50/50 FN/SN (483-50)	0.45	0.056	0.2

variation of the pellet thickness from 0.025 to 0.066 cm had no effect upon the conductivity value. More detailed conductivity studies, including the effects of temperature, pressure, and ambient atmosphere are planned.

In summary, our work shows that by using medium high temperature free-radical initiators in the polymerization of certain 1,2-dinitriles, infusible but soluble, highly conjugated, black polymers can be obtained. The spectroscopic and chemical evidence indicated that these polymers contained conjugated $C{=}C$, $C{=}N$, $CH{=}CH$, and no $C{\equiv}N$. The polymers possessed good thermal stability, had a high concentration of free spins and a conductivity in the semiconducting range. The significance of the technique described here may be in the simplicity with which completely conjugated, soluble, polymers can be obtained.

EXPERIMENTAL

Preparation of Maleonitrile

Fumaronitrile (8.5 g) and iodine (0.5 g) were combined under nitrogen in a glass pressure tube. The tube was capped and placed in a silicone bath at 175–180°C for 7 hr. The product was dissolved in reagent-grade chloroform (100 ml) to which was added 5.0 g of reagent grade anhydrous sodium thiosulfate. The mixture was allowed to stand overnight, the solid was filtered off, and the chloroform stripped in a Rotovac. The residue was distilled under reduced pressure in a Claisen flask yielding the following materials: first fraction 3.2 g, bp up to 120°C/30 mm, fumaronitrile; second fraction, 3.8 g, bp 122–130°C/30 mm, maleonitrile; and a black residue. The second fraction was refractionated through a small (0.5 × 7 in.) fractionating column yielding 3.18 g (38%) of maleonitrile, bp 92°C/5 mm, mp 29–30°C. The infrared spectrum of the product was identical to that reported by Miller et al.[6]

Typical Homopolymerization

FN (1.0 g) and di-*tert*-butyl peroxide (0.04 g) were charged under nitrogen in a glass pressure tube (1 × 7 in.) and then were placed in a silicone bath at 160 ± 1°C for 43 hr. The black solid was suspended in 40 ml of methanol and heated to refluxing for about 5 min. The solid was then filtered and the extraction repeated. The material was dried in a vacuum oven at about 113°C for 20 hr. Isolated was 0.70 g (70%) of black shiny powder, η_{inh} 0.35 (0.425 g/100 ml methanesulfonic acid at 30.0°C).

Typical Copolymerization

FN (0.33 g), SN (0.67 g), and di-*tert*-butyl peroxide (0.04 g) were all combined under nitrogen in a pressure tube (1 × 7 in.), and then polymerized in a silicone bath at 160 ± 1°C for 23 hr. The procedure for isolating the copolymer was the same as for homopolymers. Isolated was 0.88 g (88%) of black powder, η_{inh} 0.45 (0.411 g/100 ml of methanesulfonic acid at 30.0°C).

Preparation of 2,2,3,4-Tetrachloro-3-pyrrolinone

Succinimide (7.0 g, 0.071 mole) was combined with phosphorus pentachloride (59.2 g, 0.284 mole) in a 100 ml round-bottomed flask fitted with a reflux condenser. The contents was then heated in a silicone bath to 162°C and refluxed at 162–167°C for 2.5 hr. The flask was then fitted with a small fractionating column (0.5 × 9 in.) and the contents distilled under reduced pressure. The forerun consisted of phosphorus oxychloride and two fractions were collected: (*1*) 70–80°C/5 mm, (*2*) 80–90°C/5 mm. Refractionation yielded two main fractions: (*1*) 94–97°C/21 mm, n^{23} 1.5305, 6.0 g; (*2*) 100–106°C/21 mm, n^{24} 1.5391, 2.0 g. The total yield was 8.0 g (51%).

ANAL. Calcd for C_4HNOCl_4: C, 21.74%; H, 0.45%; Cl, 64.22%. Found: C, 22.08%; H, 0.36%; Cl, 65.84%.

Preparation of 3,4-Dichloro-5-aminoisopyrrolone

Tetrachloropyrrolinone (3.3 g) was added at a slow drop rate to liquid ammonia (15 g) cooled to −78°C. The mixture was kept in a Dry Ice–acetone bath for 3 hr, then allowed to warm up to room temperature, and the excess ammonia was allowed to evaporate. The residue was extracted with anhydrous ether (five times each 100 ml); the ether solution was filtered and the solvent evaporated in a Rotovac at room temperature, leaving behind a light green-colored solid, 0.5 g (20%). The material was dried in a vacuum oven at room temperature for several hours. It did not have a noticeable melting point, instead, it changed into a black solid upon heating.

ANAL. Calcd for $C_4H_2ON_2Cl_2$: C, 29.10%; H, 1.21%; N, 16.98%; Cl, 42.99%. Found: C, 28.96%; H, 2.81%; N, 18.25%; Cl, 42.88%.

Oxidative Degradation

Fumaronitrile polymer (0.145 g) was dissolved in conc. sulfuric acid (6 ml) and the solution was cooled in an ice bath. To the cooled solution added 30% H_2O_2 (1 ml) at a slow drop rate. The reaction mixture was then allowed to warm up to room temperature and was kept there for 40 min. About 20 g of crushed ice was next added followed by ferrous sulfate (1.0 g) after 4 min. The mixture was then diluted with 50 ml of water and extracted with ether for 26 hr. Evaporation of the ether gave a light yellow extremely viscous residue. No monomeric materials could be isolated.

Diels-Alder Reaction

Fumaronitrile polymer (0.05 g) was combined under nitrogen with maleic anhydride (0.40 g, 6 molar excess) in a 100-ml round-bottomed flask equipped with a reflux condenser. The flask was heated in a potassium thiocyanate bath to 265–275°C and kept there for 2 hr. The reaction product was extracted with boiling acetone twice and dried in a vacuum oven at 80°C for 6 hr. Isolated was 0.065 g of black product. Analysis showed 19% oxygen in the product, indicating about 30% maleic acid incorporation.

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Metal-Containing Initiator Systems. IV. Polymerization of Methyl Methacrylate by Systems of Some Activated Metals and Organic Halides

TAKAYUKI OTSU and MASAMI YAMAGUCHI, *Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimotocho, Sumiyoshi-ku, Osaka, Japan*

Synopsis

A study of the polymerization of methyl methacrylate initiated by the binary systems of some activated metals and organic halides has been made. It was found that the initiator activities of these systems were greatly dependent on the kind and the preparation or activation method of the metals (i.e., oxidation potential, surface area, and purity), and also on the kind of organic halides (i.e., bond-dissociation energy of their carbon–halogen bonds). From the kinetic studies of the polymerization at 60°C with the system reduced nickel–carbon tetrachloride, the rate of polymerization was found to be proportional to the monomer concentration and to the square root of concentration of both nickel and carbon tetrachloride at the lower concentration range of carbon tetrachloride, indicating that the system induced the radical polymerization. A similar conclusion was also obtained from the copolymerization with styrene with this system at 60°C, i.e., the resulting copolymer composition curve was in agreement with that obtained with azobisisobutyronitrile (AIBN). The apparent overall activation energy for the methyl methacrylate polymerization with this system was estimated to be 7.5 kcal/mole, which was considerably lower than that with AIBN. On the basis of the results obtained, an initiation mechanism for the polymerization with these initiator systems is presented and discussed.

INTRODUCTION

Recently, it has been reported that some metal-containing initiator systems consisting of metal peroxides,[1] metal alkyls,[2] metal carbonyls,[3] metal chelates,[4,5] and transition metal halides[6] can serve as effective radical initiators of vinyl monomers. These studies are connected with an investigation of induced selective and stereospecific radical polymerizations of vinyl monomers.

In the previous papers[7–9] we have found that the systems of some activated metals and organic halides can induce the radical polymerization of vinyl monomers. Some of these systems had been known as Ullmann, Gomberg, and Wurz-Fittig reactions in which metallic copper, silver, and alkali metals can react with some organic halides to produce an intermediate alkyl radical which readily dimerizes to give a product. However, no available information on these systems as radical initiators has appeared, except for the paper of Furukawa and co-workers[10] who used metallic copper and benzyl chloride as an initiator system.

Recently Olivé et al.[11] reported that the systems of some transition metal colloids and organohalogen compounds can induce the radical polymerization of methyl methacrylate. More recently, Iwatsuki et al.[12] also reported the polymerization of methyl methacrylate initiated by hydrogenation catalysts in the presence of carbon tetrachloride.

The present paper describes the results on the polymerization of methyl methacrylate with systems of various metals and organic halides, and on the kinetic studies of the polymerization with the system of reduced nickel and carbon tetrachloride at 60°C.

EXPERIMENTAL

Materials

Raney metals were prepared from their commercial aluminum alloys according to the Adkins W-5 method,[13] followed by successive washing with water, methanol, and then benzene.

Urushibara metals were obtained by adding zinc dust to an aqueous solution of metal chloride according to the method described by Taira[14] and used after washing with water, methanol, and finally benzene.

Reduced nickel was commercially available stabilized hydrogenation catalyst (Nikki Chemical Co.) composed of 50% Ni on kieselguhr. Before use, this catalyst was activated by heating at about 200°C in a stream of hydrogen for 1 hr.

The other kinds of hydrogenation catalyst, formate nickel (50% Ni on kieselguhr), platinum (1% Pt on charcoal), palladium (5% Pd on charcoal) and rhodium (5% Rh on charcoal), which were available as commercial products, were used after hydrogen reduction at 200°C for 1 hr. The commercial metal powders were also used without further purification.

Organic halides used in this study were purified by distillation or recrystallization of the commercial reagents.

Methyl methacrylate and styrene were purified by ordinary methods and distilled under a reduced pressure before use. The other reagents were purified by ordinary methods.

Polymerization Procedure

Into a hard glass tube containing a given amount of the metal, the required amount of organic halide, and the monomer were placed, and this tube was connected to a vacuum system. After degassing of its contents by repeated freezing and thawing, the tube was sealed off under vacuum.

Polymerizations and copolymerizations were carried out in the dark with shaking of the tube in a thermostat maintained at a given temperature. After polymerization, the contents of the tube were poured into a large amount of methanol containing concentrated hydrochloric acid to precipitate the polymer and to dissolve the residual metal initiator. The resulting polymer was then purified by reprecipitating two or three times from benzene solution into methanol. The conversion was calculated from the weight of dry polymer obtained.

Analysis of the Polymers

The number-average degree of polymerization ($\bar{P}_n$) of the polymers was calculated from the intrinsic viscosities $[\eta]$ in chloroform at 30°C according to the following equation:[15]

$$[\eta] = 2.50 \times 10^{-3} \bar{P}_n^{0.8}$$

The syndiotacticity of the polymers was determined from the absorbance ratios (D_{1063}/D_{1393}) in the infrared spectra according to the method described in a previous paper.[16]

The composition of the copolymers with styrene was determined by elementary analysis for carbon.

RESULTS

Effects of Metals on the Initiator Activity

The results of the polymerization of methyl methacrylate with various metals in the presence of carbon tetrachloride as organic halide are shown in Table I.

As can be seen from Table I, all the commercial metal powders used showed no activity for methyl methacrylate polymerization in the presence of carbon tetrachloride, but all activated metals available as hydrogenation catalyst were quite effective as initiator. These results indicate that it is necessary for the metals to have a fresh and pure surface. No polymer was obtained by activated metal alone (see Table II).

A comparison of the initiating activities of the metals in the series of Raney and Urushibara types from Table I shows that the activated nickel was the most active initiator. However, a definite relationship between the initiating activities and the kind of metals was not observed.

The degree of polymerization of the resulting polymers decreased with increasing of the rate of polymerization as well as in ordinary radical polymerization. The syndiotacticity of the polymers was almost constant independently of the kinds of metals used in the initiator systems and was also the same as the value obtained by azobisisobutyronitrile (AIBN), indicating that these initiator systems did not induce stereospecific polymerization of methyl methacrylate.

TABLE I

Polymerization of Methyl Methacrylate with the Various Metals–Carbon Tetrachloride Systems at 60°C[a]

Metals	Polymer yield, %	Degree of polymerization	Syndio-tacticity, %
Raney Ni	41.0	700	42
Urushibara Ni	54.4	300	43
Formate Ni	36.5	2000	44
Reduced Ni	97.1	300	45
Reduced Ni	9.1[b]	—	—
Commercial Ni	0	—	—
Raney Co	22.6	2000	45
Urushibara Co	49.5	400	46
Commercial Co	0	—	—
Raney Fe	21.1	1900	42
Urushibara Fe	21.3	700	48
Commercial Fe	0	—	—
Raney Cu	25.2	900	43
Urushibara Cu	22.4	1400	42
Commercial Cu	0	—	—
Pd on charcoal	18.7[b]	2300	48
Rh on charcoal	3.4[b]	—	—
Pt on charcoal	9.2[b]	1700	43
Commercial Zn	0	—	—
Commercial Al	0	—	—
None	0	—	(43)[c]

[a] Time, 3 hr; $[M] = 4.46$ mole/l; $[CCl_4] = 0.49$ mole/l; $[\text{Metal}] = 0.81$ g-atom/l; in benzene.

[b] $[\text{Metal}] = 8.1 \times 10^{-3}$ g-atom/l.

[c] Determined for radical polymer obtained by AIBN.

Effects of Organic Halides

Table II shows the results of polymerization of methyl methacrylate with Raney nickel in the presence of various kinds of halides at 60°C.

As is seen from Table II, the initiating activity of the halides in the presence of Raney nickel markedly increased in the following order: $CH_2Cl_2 < CHCl_3 < CCl_4$; $CHCl_3 < CHBr_3 < CHI_3$; $n\text{-}C_4H_9Cl < tert\text{-}C_4H_9Cl$; $C_6H_5Cl < C_6H_5CH_2Cl$; $CHCl{=}CCl_2 < CH_2{=}CHCH_2Cl$. This order coincides with decreasing bond-dissociation energy of the carbon–halogen bonds involved in the halides.

From Table II, the degree of polymerization of the resulting polymers was observed to decrease in proportion to the increase in initiating activity of the initiator systems. The syndiotacticity of the polymers was not changed by the kinds of halides used.

Kinetic Studies of Polymerization with the Reduced Nickel–Carbon Tetrachloride System

Figure 1 shows the time–conversion relations on the polymerization of methyl methacrylate with the reduced nickel–carbon tetrachloride system

TABLE II
Effect of Halides on the Polymerization of Methyl Methacrylate by Raney Nickel at 60°C[a]

Halide	Polymer yield, %	Degree of polymerization	Syndiotacticity, %
CH_2Cl_2	4.6	4300	42
$CHCl_3$	19.6	1300	41
CCl_4	48.5	700	42
$C_2H_4Cl_2$	1.7	—	—
$C_2H_2Cl_4$	8.5	1900	42
C_2Cl_6	33.5	1300	46
$CHBr_3$	20.0	400	44
CHI_3	41.4	40	—
tert-C_4H_9Cl	10.0	5100	43
n-C_4H_9Cl	1.9	—	—
C_6H_5Cl	0.5	—	—
C_6H_5Br	0.9	—	—
C_6H_5I	0.3	—	—
o-$C_6H_4Cl_2$	0.9	—	—
1,3,5-$C_6H_3Cl_3$	1.4	—	—
$C_6H_5CH_2Cl$	21.8	1400	48
$CHCl=CCl_2$	0.3	—	—
$CH_2=CHCH_2Cl$	16.7	2300	45
$TiCl_3$	0	—	—
$MgCl_2$	0	—	—
None	0	—	(43)[b]

[a] Time, 3 hr; [M] = 4.46 mole/l; [Halide] = 0.38 mole/l; [Ni] = 0.81 g-atom/l; in benzene.

[b] Determined for radical polymer obtained by AIBN.

in the temperature range 30–80°C. The straight-line relationships were obtained at every temperature.

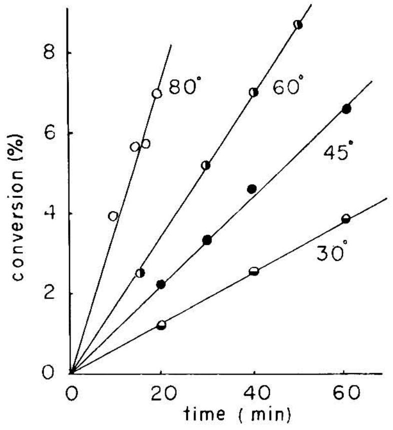

Fig. 1. Time–conversion relations on the polymerization of methyl methacrylate by the reduced nickel–carbon tetrachloride system at 30–80°C. [Ni] = 2.55×10^{-2} g-atom/l; [CCl_4] = 0.104 mole/l; [M] = 5.62 mole/l; in benzene.

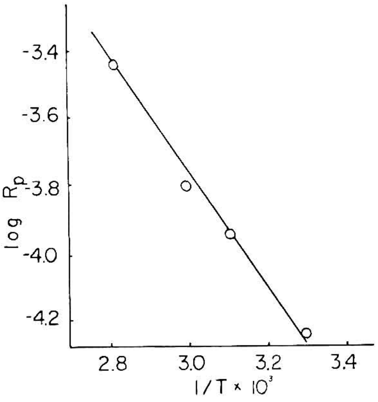

Fig. 2. Arrhenius plot of log R_p vs. $1/T$.

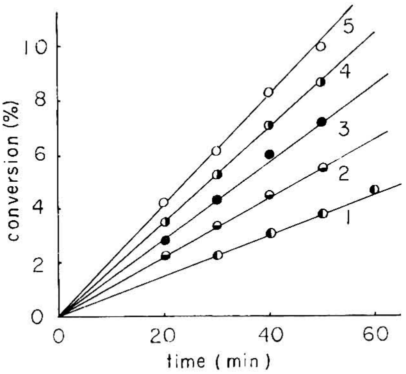

Fig. 3. Time–conversion relations on the polymerization of methyl methacrylate by the different concentration of reduced nickel in the presence of constant concentration of carbon tetrachloride at 60°C: (*1*) 0.64×10^{-2}; (*2*) 1.28×10^{-2}; (*3*) 1.91×10^{-2}; (*4*) 2.55×10^{-2}; (*5*) 3.83×10^{-2} g-atom/l of nickel. $[CCl_4] = 0.104$ mole/l; $[M] = 5.62$ mole/l; in benzene.

The rate of polymerization R_p, determined from the slopes of the straight lines in Figure 1, was plotted with the reciprocal polymerization temperatures as shown in Figure 2. The apparent activation energy for overall polymerization with this system was calculated to be 7.5 kcal/mole. Accordingly, the activation energy for initiation was obtained as 6.2 kcal/mole by using the reported rate constants[17] for propagation and termination. This value was quite small as compared with that with AIBN (30.8 kcal/mole).[18]

Figure 3 shows the time–conversion relations for polymerization carried out by using the different concentration of reduced nickel in the presence of the constant concentration of carbon tetrachloride at 60°C. Although this polymerization system was heterogeneous, straight-line relationships were obtained. The plots of R_p against the concentration of reduced nickel are shown in Figure 4, from which the rate was found to be propor-

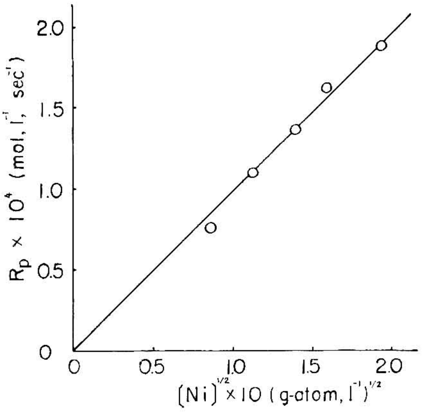

Fig. 4. Relationship between R_p and the concentration of reduced nickel at 60°C. $[\mathrm{CCl_4}] = 0.104$ mole/l; $[\mathrm{M}] = 5.62$ mole/l; in benzene.

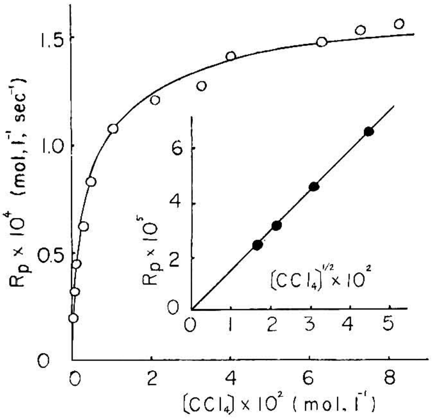

Fig. 5. Relationship between R_p and the concentration of carbon tetrachloride at 60°C. $[\mathrm{Ni}] = 5.55 \times 10^{-2}$ g-atom/l; $[\mathrm{M}] = 5.62$ mole/l; in benzene.

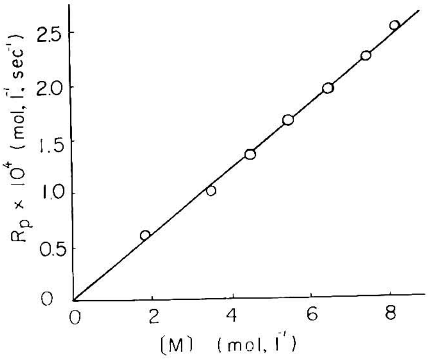

Fig. 6. Relationship between R_p and the monomer concentration at 60°C. $[\mathrm{Ni}] = 2.55 \times 10^{-2}$ g-atom/l; $[\mathrm{CCl_4}] = 0.104$ mole/l; in benzene.

tional to the square root of concentration of reduced nickel. This result also indicates that this initiator system induces radical polymerization.

The relationship between the rate of polymerization and the concentration of carbon tetrachloride is shown in Figure 5. The square-root dependence of the concentration of carbon tetrachloride on the rate was observed only in a CCl_4 concentration range lower than 5×10^2 mole/l. In the range of carbon tetrachloride concentration higher than this, however, the rate remained constant independently of its concentration. This result might suggest that the initiating radical was produced via the complex formation between reduced nickel and carbon tetrachloride, as was pointed out by Iwatsuki et al.[12]

Figure 6 shows the plot of the rate of polymerization against the concentration of methyl methacrylate monomer. It is clear that the rate was directly proportional to the monomer concentration. This result might also indicate that the monomer did not participate in the step of the production of an initiating radical.

When the polymerization of methyl methacrylate with this system was carried out in the presence of air, the rate was observed to decrease markedly from 7.7%/hr. in the absence of air to 2.2%/hr. Accordingly, it was obvious that this polymerization proceeded by a radical mechanism.

Copolymerization with Styrene

In order to clarify further whether the polymerization with these systems proceeds via a radical mechanism, copolymerization of styrene (M_1) with methyl methacrylate (M_2) with the reduced nickel–carbon tetrachloride system was investigated at 60 and 0°C. From the results obtained, the monomer–copolymer composition curves shown in Figure 7 were obtained. The copolymer composition curve obtained by this system at 60°C was in agreement with that by AIBN, but that obtained at 0°C was somewhat

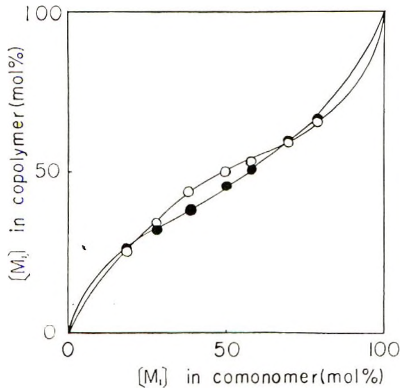

Fig. 7. Copolymer composition curves for the copolymerization of styrene (M_1) and methyl methacrylate (M_2) by the reduced nickel–carbon tetrachloride system: (-●-) at 0°C; (-○-) at 60°C. ($[M_1] + [M_2]$) = 7.2 mole/l; [Ni] = 0.13 g-atom/l; $[CCl_4]$ = 0.125 mole/l; in benzene.

different. The monomer reactivity ratios were calculated as follows: $r_1 = 0.36$, $r_2 = 0.44$ at 60°C (lit.[19] $r_1 = 0.52$, $r_2 = 0.46$); $r_1 = 0.46$, $r_2 = 0.79$ at 0°C.

The result at 60°C is considered to indicate that the copolymerization with this initiator system proceeds via a radical mechanism.

Analysis of Reaction Products

To determine the initiation mechanism with these initiator systems, the reaction of reduced nickel with carbon tetrachloride in the absence of monomer was carried out at 80°C. From gas chromatographic analysis of the reaction products, the formation of hexachloroethane was confirmed. From the aqueous solution which was extracted the reaction mixture with water, nickel and chloride ions were also detected.

DISCUSSION

From the results on the polymerization kinetics and on the copolymerization with styrene, it is clear that the system of Raney or reduced nickel and carbon tetrachloride can induce the radical polymerization of methyl methacrylate. The fact that the syndiotacticity of the resulting polymers is the same as that of ordinary radical polymer, independent the metals and organic halides used (Tables I and II), also suggests that all of these systems can serve as an ordinary radical initiator.

Although metals which can form the effective initiator system with some organic halides must have a fresh surface, as shown in Table I, no definite correlation is observed between the initiating activities and the kind of metals. One reason may be that the metals exist as heterogeneous solids in these polymerizing mixtures. However, it may be suggested that both the oxidation potential of the metals and the preparation and activation methods, which determine their surface area and purity, are the controlling factors for determining the initiating activity of these systems.

From Table II, the initiating activity of the organic halides to Raney nickel was found to increase as the substitution by halogen atom increased and also as the labile halogen atoms were involved in the organic halides. These results strongly suggest that the effectiveness of the halides for initiation increases with decreasing bond-dissociation energy of their carbon–halogen bonds.

As was pointed out by Olivé et al.[11] and Iwatsuki et al.,[12] the initiation by these systems is thought to occur according to the following mechanism: a complex is formed between the metals (Me) and the organic halides (RX), and then one-electron transfer from metal to carbon–halogen bond in the halides occurs to give the initiating radical:

$$\text{R—X} + \text{Me} \rightleftharpoons [\text{Complex}] \rightarrow \text{R}\cdot + \text{Me}^+ + \text{X}^-$$

This reaction scheme is supported by the fact that hexachloroethane, nickel ion, and chloride ion were found in the reaction mixture of reduced nickel and carbon tetrachloride at 80°C.

In this mechanism, if the step of one-electron transfer is rate-determining, the ease of the initiating radical production must be dependent on both the oxidation potential of the metals and the bond-dissociation energy of the carbon–halogen bond in the halides. As is seen from Table I, however, a definite correlation was not observed between the initiator activity and the kind of activated metal used.

Regarding to this point, Olivé et al.[11] have stated that the step of complex formation is important. However, the effect of the halide structures on initiation may suggest that the rate-determining step is one-electron transfer in the complex. Accordingly, this result may be understandable if the surface area and the surface purity of the metals to form the transition state complex with the halides are significant rather than the oxidation potentials. However it must be noted that the reactivity of the initiating radical produced from the halides toward the methyl methacrylate monomer is also important.

A probable structure of the complex in the transition state of the above reaction may be written as follows:

$$\underset{\text{I}}{[\mathrm{R}:\mathrm{X}\ \mathrm{Me}} \leftrightarrow \underset{\text{II}}{\mathrm{R}\cdot\mathrm{X}^{-}:\mathrm{Me}^{+}]}$$

in which I is the structure near the reactant system and II is that after one-electron transfer has occurred. The importance of a similar transition state structure has been discussed by Kochi and Davis[20] for the reduction of alkyl halides with chromium (II) ion.

It is known that some systems, such as transition metal–ethyl bromide[21] and magnesium–alkyl halide[22] can induce anionic polymerization. Recently, we also found that the systems of reduced nickel and some organic halides initiate the cationic polymerization of monomers such as styrene,[23] isobutyl vinyl ether,[23] and butadiene.[24] Accordingly, the contribution of transition state structures other than I and II mentioned above must be considered in these cases. Such a selective initiation for monomers with the systems of metals and halides will be described in the next paper.

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On the Blue-Colored Species, Possibly Assignable to a Radical Cation, Formed by the Aromatic Hydrocarbon–Sulfur Dioxide–Oxygen System: The Polymerization of Olefins Initiated by Aromatic Hydrocarbons–Oxygen in Liquid Sulfur Dioxide

TOSHIKAZU NAGAI, TETSUO MIYAZAKI, YUZO SONOYAMA,
and NIICHIRO TOKURA, *Department of Applied Chemistry,
Faculty of Engineering, Osaka University, Suita,
Osaka, Japan*

Synopsis

It was found that styrene in liquid sulfur dioxide polymerizes, giving polystyrene readily and quantitatively by addition of such aromatic hydrocarbons as anthracene and *trans*- or *cis*-stilbene in the presence of oxygen, and the polymerization proceeds via a cationic process. The observations on the electronic spectra and kinetics in the system suggested that the polymerization was initiated by an electron transfer from the aromatic hydrocarbon to oxygen, followed by the formation of styrene radical cation. Supporting evidence of the radical cation is that 1,1-diphenylethylene in liquid sulfur dioxide in the presence of oxygen shows a peak at $\lambda_{max} = 605$ mμ and reacts to give benzophenone and 1,1,3,3-tetraphenyl-butene-1, which are eliminated by addition of a radical or cation inhibitor.

INTRODUCTION

Comprehensive studies of the anionic polymerizations, represented by a "living polymer" and initiated by radical anions, have already been made,[1] but quite recently cationic polymerizations initiated by a radical cation produced in a direct electron-transfer reaction between some electron-donating monomers and various characteristic electron acceptors also were reported.[2]

In a previous communication[3] we reported the fact that anthracene is an effective initiator of a cationic polymerization of styrene in liquid sulfur dioxide only in the presence of oxygen. This paper is concerned with a more detailed and developed description of the reaction, in which the formation of a blue-colored species and the kinetic results under the various conditions are discussed; a possible mechanism also is presented.

EXPERIMENTAL

Materials

Liquid Sulfur Dioxide. A commercial liquid sulfur dioxide of high purity was placed in a 300-ml pressurized glass vessel equipped with a needle bulb; it was dried over P_2O_5 and distilled carefully with a specially designed distiller; see C in Figure 1.

Styrene. Styrene was purified by distillation twice under reduced pressure after several washings with 10% NaOH aqueous solution.

1,1-Diphenylethylene. This was synthesized by dehydration of methyl diphenyl carbinol by the method of Allen and Converse;[4] b.p. 117–118°C at 4.5 mm.

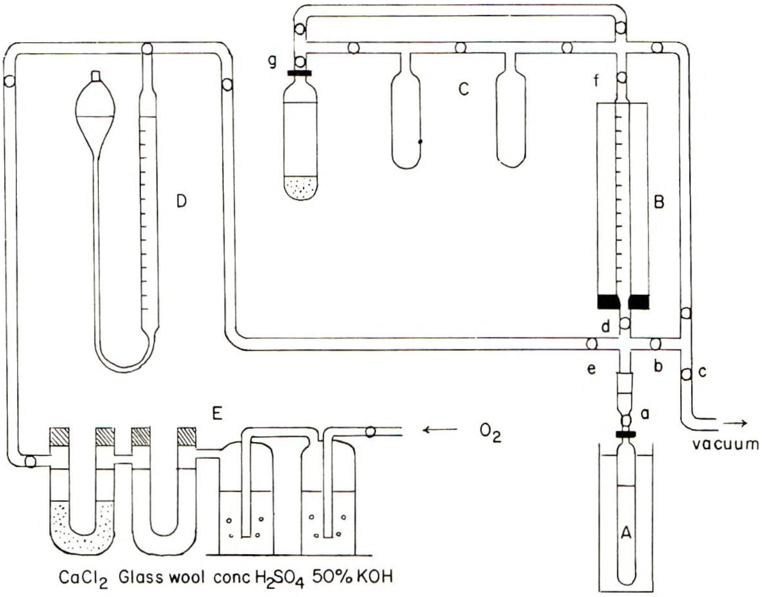


Fig. 1. Polymerization apparatus.

1,1-Di-*p*-chlorophenylethylene. This was synthesized by dehydration of di-*p*-chlorophenyl methyl carbinol, which was obtained from the reaction of *p,p*-dichlorobenzophenone[5] with methyl magnesium iodide; m.p. 89°C.[6a]

1-*p*-Chlorophenyl-1-phenylethylene. This was synthesized by dehydration of *p*-chlorodiphenyl methyl carbinol, which was obtained from the reaction of *p*-chlorobenzophenone[7] with methyl magnesium iodide; b.p. 151–152°C at 6 mm.[6a]

1-*p*-Methoxyphenyl-1-phenylethylene. This was prepared by dehydration of *p*-methoxydiphenyl methyl carbinol, which was obtained from the reaction of *p*-methoxyacetophenone with phenylmagnesium bromide; m.p. 74–75°C.[8]

1,1-Di-*p*-methoxyphenylethylene. This was prepared by the reaction[9] of anisole with acetyl chloride in the presence of $AlCl_3$ in CS_2; m.p. 142–143°C.

Triphenylethylene. Triphenylethylene was synthesized[10] by dehydration of benzyldiphenyl carbinol, which was obtained from the reaction of benzophenone with benzylmagnesium chloride; m.p. 67.5–68.5°C.

Tetraphenylethylene. This was synthesized[11] in the coupling reaction of diphenyldichloromethane, given by the reaction of benzophenone with PCl_5 and recrystallized from a mixture of 1:1 ethanol–benzene; m.p. 219.5–220.5°C.

1,1,4,4-Tetraphenyl-1,3-butadiene. This was synthesized[6b] by dehydration of 1,1,4,4-tetraphenyl-1,4-butandiol, which was obtained from the reaction of diethyl succinate with phenylmagnesium bromide; m.p. 201°C.

Aromatic Hydrocarbon. The commercial or synthesized compound was recrystallized from a suitable solvent:

naphthalene	m.p. 81.0°C
anthracene	m.p. 215.0°C
perylene	m.p. 272–273°C
diphenyl	m.p. 70–71°C
trans-stilbene	m.p. 123.0°C
cis-stilbene	b.p. 145°C at 13 mm
acenaphthylene	m.p. 91 ∼92°C
picric acid	m.p. 122°C
sym-1,3,5-trinitrobenzene	m.p. 122.5°C

Anthracene–*sym*-1,3,5-Trinitrobenzene Complex. Each hot solution of equivalent moles of anthracene and trinitrobenzene in chloroform was mixed, allowed to stand at room temperature for several hours to give an orange-yellow needle crystal, and recrystallized from ethanol; m.p. 161.5°C.

Anthracene Picrate. Anthracene picrate was prepared by the method described above, to give a dark-red needle crystal and was recrystallized from chloroform; m.p. 139°C.

Oxygen. A commercial oxygen of high grade was washed with 50% KOH and concentrated H_2SO_4, passed through glass tubes filled with glass wool and $CaCl_2$, to avoid completely any contamination of the H_2SO_4, and introduced into the reaction vessel; see Figure 1.

The other solvents used were purified by the usual methods.

Polymerization Apparatus and Procedure

Figure 1 shows the polymerization apparatus constructed from three parts: an oxygen refiner E, an oxygen flowmeter D, and a liquid sulfur dioxide distiller C. First definite amounts of monomer and initiator were placed in the reaction vessel A. After cock "a" was closed, the temperature of the vessel was kept at −78°C. When the vessel had been attached to the apparatus, the cocks "a," "b," and "c" were opened, and the vessel was evacuated; then cock "b" was closed. When cocks "f" and "g" were opened, liquid sulfur dioxide was distilled into jar B, which was cooled with methanol and solid carbon dioxide; then cock "f" was closed. The temperature of the jar being kept at 5–15°C and cock "d" being opened, a definite volume of the liquid sulfur dioxide was added to the reaction vessel A. Next, cocks "a" and "d" were closed, and the system was evacuated again. Then cock "b" was closed and cock "c" opened. Then, after a check of the flowmeter D, cock "a" was opened carefully, and a definite amount of oxygen was let into the reaction vessel A. Finally, the reaction vessel A was taken off and vigorously stirred, and then the polymerization was carried out at a given temperature. The polymer obtained was precipitated by being added to a large amount of methanol and was then purified by reprecipitation from its benzene solution with methanol. The intrinsic viscosity of the polystyrene was measured in benzene solution at 25°C with an Ubbelohde viscosity meter.

Electronic Spectra

The electronic spectra were obtained with a Hitachi Model EPS-3 recording spectrophotometer with a pressure cell; the width of the cell could be adjusted by insertion of a spacer when necessary.

Infrared Spectra

The infrared spectra were run on a Hitachi Model EPI-S2. The spectra were measured from the polymer as film.

RESULTS AND DISCUSSION

Polymerization of Styrene Initiated by Anthracene–Oxygen

Polymerization Results. The polymerization results are shown in Tables I and II.

Evidence of Cationic Polymerization. The fact that the present polymerization proceeds cationically was shown by the following experimental results. (*1*) The infrared spectrum of the polymer was quite identical

TABLE I
Results of Polymerization at 0°C: Effect of Anthracene Concentration

Expt. no.	Styrene,[a] mol/l	Anthracene,[a] mol/l ($\times 10^3$)	Yield,[b] %	$[\eta]$, ml/g	M.W.,[c] ($\times 10^{-4}$)
1	1.54	3.01	92.9	0.622	12.4
2	1.54	4.40	93.1	0.588	11.4
3	1.54	8.28	93.0	0.531	9.8
4	1.54	16.3	95.1	0.502	9.0
5	1.54	33.0	96.1	0.416	6.8

[a] Liquid SO_2, 14.3 ml, and O_2, 10^{-3} mol, were used.

[b] Reaction time was 6 hr.

[c] Pepper's equation, $[\eta] = 2.7 \times 10^{-4} M^{0.66}$ in benzene at 25°C, was used.

TABLE II
Results of Polymerization at 0°C: Effect of Amount of Oxygen Added

Expt. no.	Styrene,[a] mol/l	Anthracene, mol ($\times 10^4$)	O_2, mol ($\times 10^5$)	Yield,[b] %	[η], ml/g
1	1.54	4.49	0.416	23.9	0.217
2	1.54	4.49	2.08	91.3	0.303
3	1.54	4.49	9.16	91.5	0.322
4	1.54	4.49	44.5	92.8	0.309
5	1.54	4.49	109.	93.5	0.301

[a] Liquid SO_2, 14.2 ml, was used.
[b] Reaction time was 4 hr.

with that of an authentic polystyrene, indicating that the polymer contained none of the styrene–polysulfone given by a radical polymerization. (*2*) The elementary analysis corresponded to polystyrene and showed an absence of sulfur [for $(C_8H_8)_n$ (%), C 92.26 and H 7.74 were calculated, and C 91.88 and H 7.45 were observed]. (*3*) The addition of dimethyl sulfoxide, which is an inhibitor of cationic polymerization, inhibited this polymerization reaction completely.

Electronic Spectra. At the beginning of the polymerization reaction the yellow-brown color of a charge-transfer complex of anthracene with sulfur dioxide was observed. However, the color gradually became blue as the polymerization proceeded, when an electronic spectrum of the solution gave a λ_{max} at 610 mμ as shown in Figure 2. This spectrum is very similar to that of a diphenylethylene radical cation, reported by Leftin and Hall,[12] which is obtainable from diphenylethylene adsorbed on silica–alumina or dissolved in benzene–trichloroacetic acid.[13] The spectra of anthracene,[14] the carbonium ion $C_6H_5\overset{\oplus}{C}HCH_3$,[15] and the growing polymer carbonium ion[16] in various solvents are all near 400 mμ. Consequently, the spectrum obtained seems to be that of a styrene radical cation, $(C_6H_5\text{-}CH{=}CH_2)^{\dot{+}}$.

$\overline{\text{DP}}$ versus Concentration Ratio of Styrene to Anthracene at 0°C. As shown in Figure 3, line a, a nearly linear relationship between the degree of polymerization, $\overline{DP}$, and the ratio of the concentration of styrene, [M], to that of anthracene, [A], was observed in the presence of oxygen. On the other hand, one of us has reported[17] that cationic polymerizations in liquid sulfur dioxide have approximately living nature and $\overline{DP}$ is linearly dependent upon [M]/[C], being expressed as $\overline{DP} = K_1[M]/[C] + K_2$, where [C] is the concentration of the initiator and K_1 and K_2 are the constants. In the present case, however, anthracene may act as a chain-transfer reagent. Thus, a relationship between the concentration of anthracene and $\overline{DP}$ was examined at a definite concentration of BF_3OEt_2 as initiator and of monomer in the absence of oxygen (Fig. 3, line a′). The slope of line a is much greater than that of line a′, suggesting that anthracene acts somewhat as initiator but very little as chain-transfer reagent. As will be described, the additional evidence of the role of an-

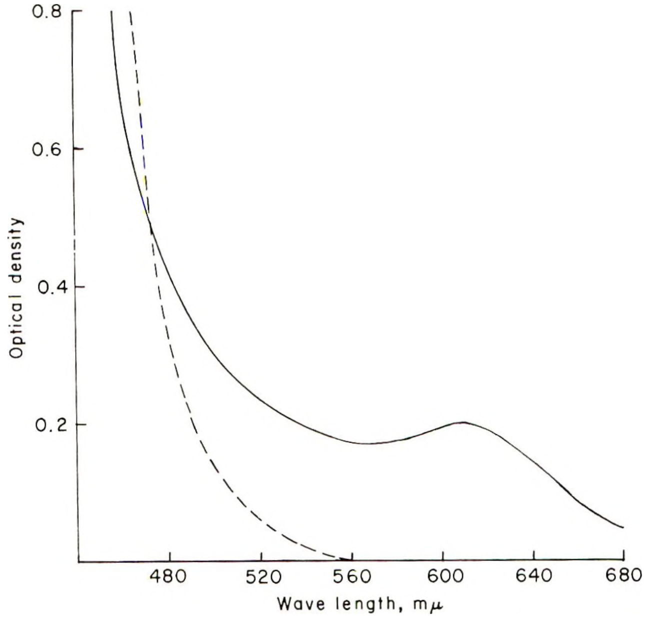


Fig. 2. Absorption spectra. Solvent, liquid SO_2; cell length, 10 mm; (- - -) anthracene, 1.3×10^{-2} mol/l, and styrene, 3.80 mol/l; (——) measured 2.25 hr after addition of oxygen to solution.

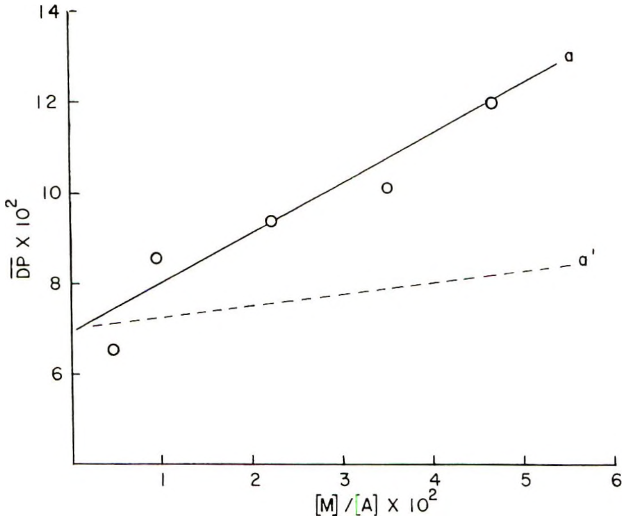


Fig. 3. Degree of polymerization versus ratio of styrene concentration, [M], to anthracene concentration, [A]: (*a*) present system; (a′) BF_3OEt_2 used as initiator in the absence of oxygen.

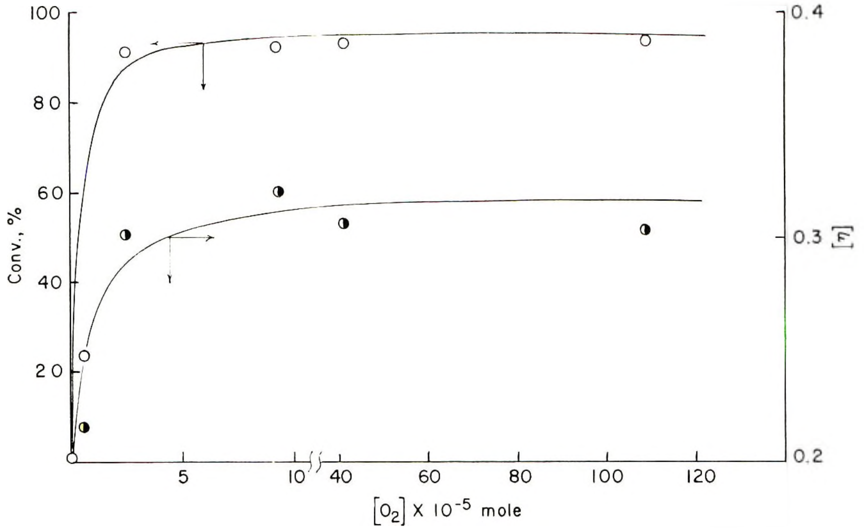


Fig. 4. Effect of oxygen: (○) conversion and (◑) intrinsic viscosity versus oxygen concentration.

thracene as initiator was shown from the fact that the rates of the polymerization decreased as the concentration of anthracene decreased, which was an inverse relationship, if anthracene plays the role only of chain-transfer reagent.

TABLE III

Cationic-Polymerization Initiators Possibly Produced in the System

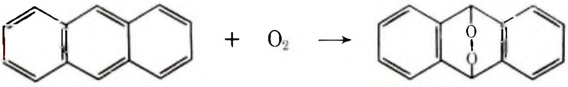
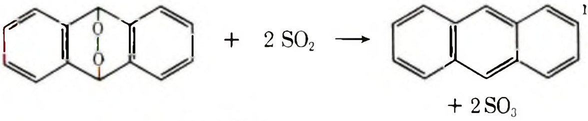
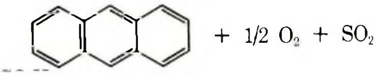
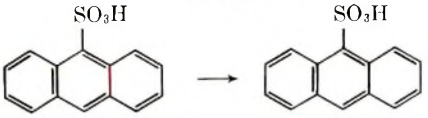
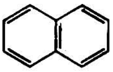
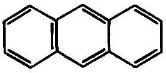
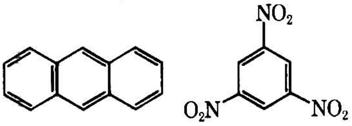
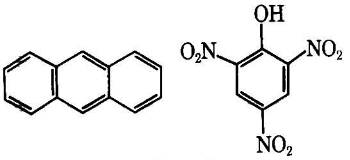
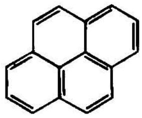
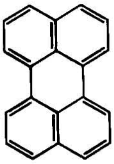
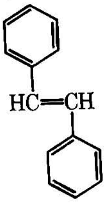
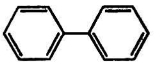
Possible initiator	Reaction	Qualitative test
Sulfur trioxide	$2SO_2 + O_2 \rightarrow 2SO_3$ $SO_3 + H_2O \rightarrow H_2SO_4$	detection of SO_4^{2-} by Ba^{2+}, negative
Anthracene peroxide		KI method
		negative
Anthracene sulfonic acid		alkaline titration
		negative

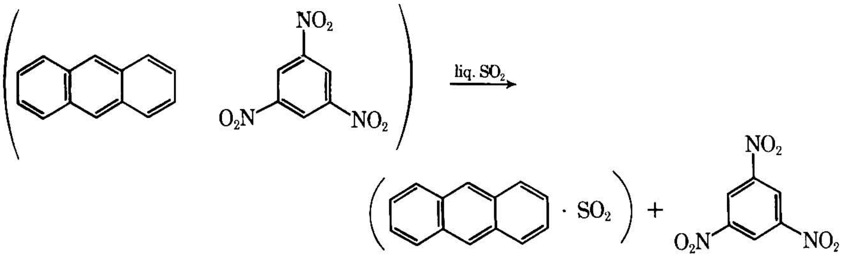
TABLE IV
Ionization Potential and Initiating Ability of Aromatic Hydrocarbons

Aromatic hydrocarbon	Structure	Ionization potential, eV	Initiating ability
Naphthalene		8.30	−
Anthracene		7.74	+
Anthracene–trinitrobenzoate		—	+
Anthracene picrate		—	+
Pyrene		7.82	−
Perylene		—	−
trans-Stilbene		7.99	+
Biphenyl		8.53	—

Effect of Oxygen Concentration. For information on the effect of the concentration of oxygen a relationship between the yield or intrinsic viscosity and the molar concentration of oxygen was plotted from Tables I and II as shown in Figure 4. No change in yield or intrinsic viscosity was observed at 10^{-5} mole of oxygen, indicating that oxygen behaves as an ordinary catalyst.

Possible Initiators of Cationic Polymerization. In the reaction vessels are sulfur dioxide, anthracene, and oxygen, which might have the ability to produce such initiators of a cationic polymerization as sulfur trioxide, anthracene peroxide, and anthracene sulfonic acid; see Table III. We saw from the following experiments, however, that these compounds were not formed. Liquid sulfur dioxide, 11.0 ml (0°C), anthracene, 3.46×10^{-4} mol, and O_2, 10^{-3} mol, were placed in the reaction vessel and allowed to stand for 4 hr at 0°C. Afterwards a qualitative test of the residue obtained after vaporizing of sulfur dioxide showed that none of the presumed compounds were formed at all. Moreover, the residue had no ability to initiate the polymerization of styrene in the absence of oxygen at 0°C.

Initiating Ability of Other Aromatic Hydrocarbons. It was found that the anthracene-*sym*-1,3,5-trinitrobenzene complex, anthracene picrate, 1,1-diphenylethylene, and *cis*- and *trans*-stilbene, as well as anthracene, can initiate the polymerization of styrene in liquid sulfur dioxide only in the presence of oxygen. Anthracene-*sym*-trinitrobenzene may act like anthracene itself, since the acceptor component is replaced with sulfur dioxide as follows:[18]



The same replacement in liquid sulfur dioxide may occur in the case of anthracene picrate. No relationship was found between the initiating ability and the ionization potential of the aromatic compounds; see Table IV.

Polymerization of Styrene in Liquid Sulfur Dioxide at 0°C with *trans*-Stilbene as Initiator in Presence of Oxygen

Polymerization Results. It was found that *trans*-stilbene was as good an initiator of the polymerization of styrene in liquid sulfur dioxide in the presence of oxygen as anthracene, but the induction period of the reaction was longer. The polymerization results are shown in Table V.

TABLE V

Results of the Polymerization at 0°C: Effect of *trans*-Stilbene Concentration

Expt. No.	Styrene,[a] mol/l	*trans*-Stilbene,[a] mol/l ($\times 10^3$)	Yield,[b] %	$[\eta]$, 100 ml/g	M.W.[c] ($\times 10^{-4}$)
1	1.50	3.20	59.4	0.465	7.67
2	1.50	5.01	92.0	0.343	5.04
3	1.50	9.92	94.1	0.265	3.40
4	1.50	20.5	96.4	0.180	1.90
5	1.50	38.8	97.5	0.142	1.32

[a] Liquid SO_2, 14.4 ml, and O_2, 10^{-3} mol, were used.

[b] Reaction time 5 hr.

[c] Pepper's equation, $[\eta] = 2.7 \times 10^{-4} M^{0.66}$ in benzene at 25°C, was used.

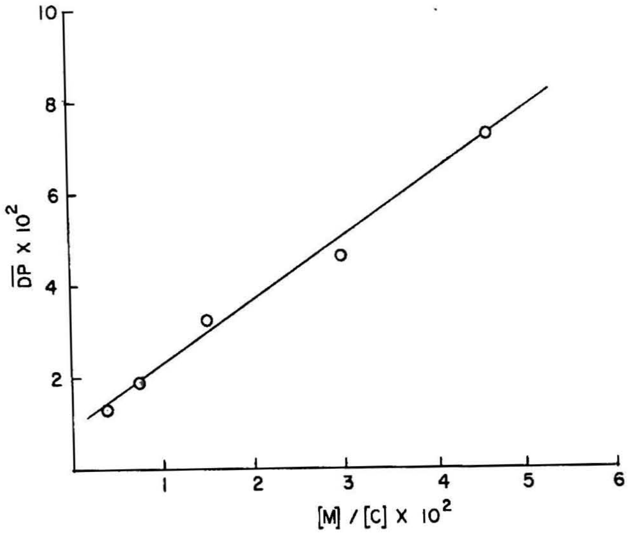


Fig. 5. Degree of polymerization versus ratio of concentration of styrene, [M], to concentration of *trans*-stilbene, [C].

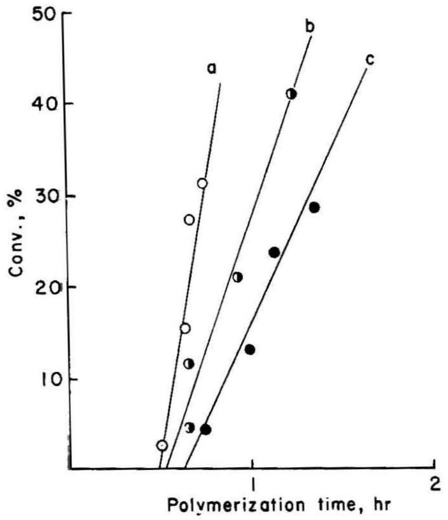


Fig. 6. Rate of polymerization. Temperature, 0°C; styrene, 1.53 mol/l; O_2, 10^{-3} mol; liquid SO_2, 14.1 ml. Anthracene (mol/l): (*a*) 4.40 × 10^{-3}; (*b*) 1.05 × 10^{-3}; (*c*) 6.89 × 10^{-4}.

Relationship between $\overline{DP}$ versus Concentration Ratio of Styrene to *trans*-Stilbene at 0°C. As shown in Figure 5, a distinctive linear relationship between the degree of polymerization and the ratio of the concentration of styrene to that of *trans*-stilbene was obtained. Its slope K_1 was found to be 7:5, whereas the slope K_1', when $SnCl_4$ was initiator, has been found to be 7:10, and the slope K_1'', when BF_3OEt_2 was initiator,

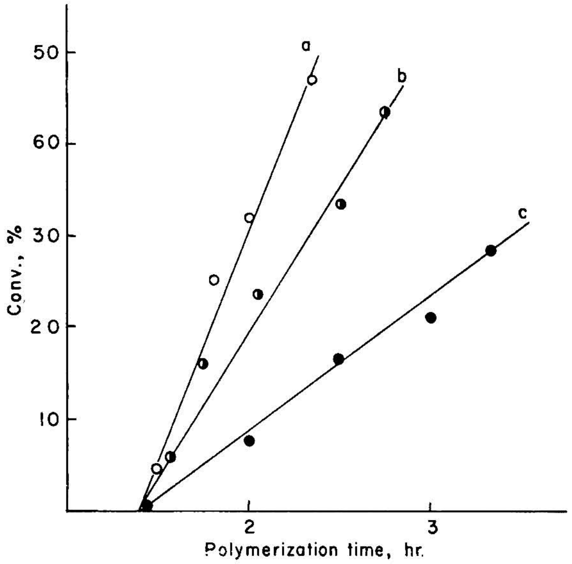


Fig. 7. Rate of polymerization. Temperature, 0°C; styrene, 1.53 mol/l.; O_2, 10^{-3} mol; liquid SO_2, 14.1 ml. *trans*-Stilbene; (mol/l.): (*a*) 8.66 × 10^{-3}; (*b*) 4.25 × 10^{-3}; (*c*) 1.95 × 10^{-3}.

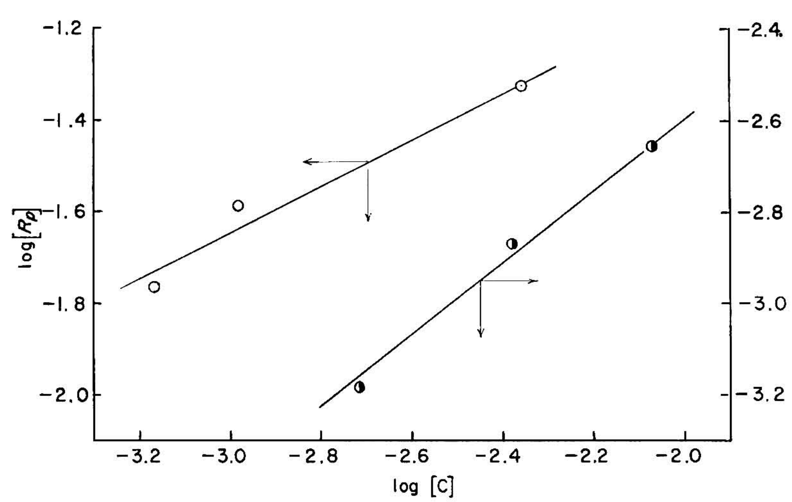


Fig. 8. Order of initiator: (O) anthracene; (◑) *trans*-stilbene; (left or right ordinate) log R_p (rate of polymerization) versus log [C].

2:3.[17] The ratio of K_1 to K_1' or K_1'' is approximately 2, suggesting that the polymerization proceeds by means of the dicarbonium ion rather than the monocarbonium ion.

Orders of Initiators. The overall initiation rates of the polymerizations were dependent upon the concentrations of anthracene and *trans*-stilbene, and the values 0.52 and 0.82 were their respective orders, as shown in

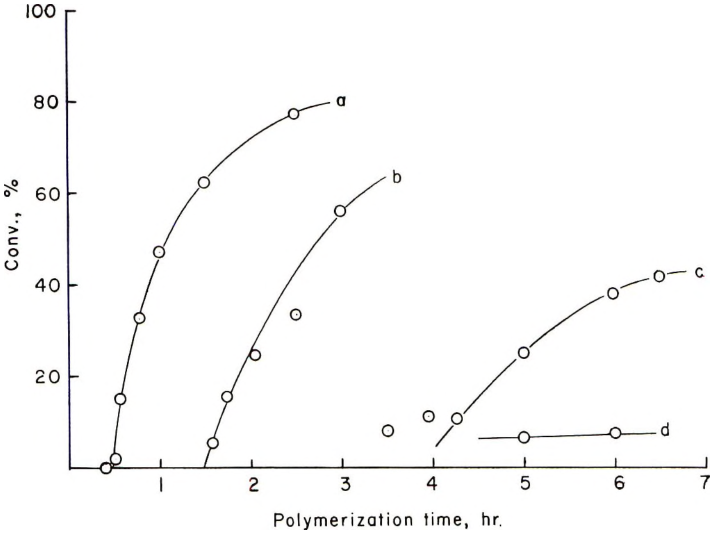


Fig. 9. Induction period. Temperature, 0°C; styrene, 1.53 mol/l; liquid SO_2, 14.1 ml. Concentrations: (*a*) anthracene, 4.40×10^{-3} mol/l, and O_2, 10^{-3} mol; (*b*) *trans*-stilbene, 4.25×10^{-3} mol/l, and O_2, 10^{-3} mol; (*c*) O_2, 10^{-3} mol; (*d*) no oxygen.

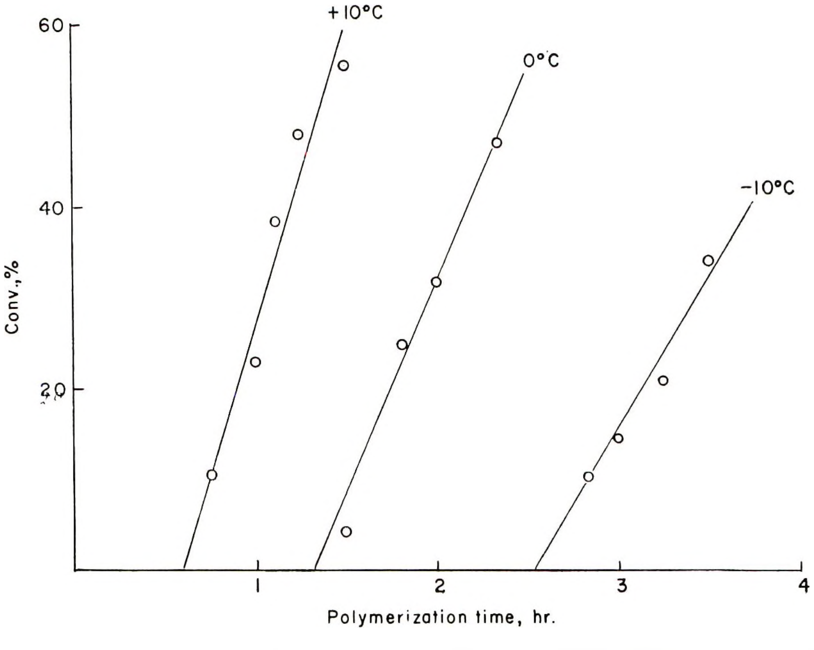


Fig. 10. Induction period at various temperatures. Concentrations: styrene, 1.53 mol/l; liquid SO_2, 14.1 ml; O_2, 10^{-3} mol; *trans*-stilbene, 8.66×10^{-3} mol/l.

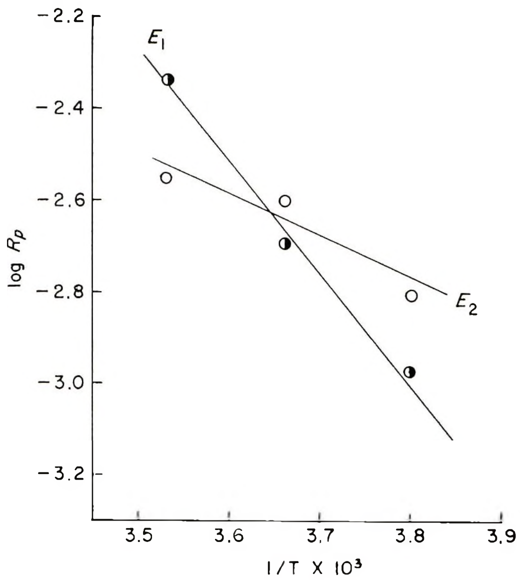


Fig. 11. Activation energies: (E_1) initiation; (E_2) propagation–termination.

Figures 6, 7, and 8; this indicates that the aromatic hydrocarbons play roles as initiators in the present polymerization.

Induction Periods. Figure 9 shows the induction periods of each initiator at 0°C. From this result it was found that oxygen had some ability to polymerize styrene in liquid sulfur dioxide to give polystyrene (not the styrene polysulfone). The polymer was confirmed by the infrared spectrum and elementary analyses; it was found to have a high molecular weight (1.4×10^5), though the induction period was about 4 hr, fairly longer than the induction periods with aromatic hydrocarbons.

Activation Energy. The length of the induction period was closely connected with the kind of initiator and with the polymerization temperature, as shown in Figures 9 and 10. The activation energies were $E_1 = 10.5$ kcal/mol, from the changes in lengths of induction periods, and $E_2 = 4.4$ kcal/mol, from the changes in polymerization rates, as shown in Figure 11, where E_1 was assumed to be the energy needed for initiation and E_2 that for propagation–termination. It is noted that the activation energy of 10.5 kcal/mol for initiation is much greater than the usual value in cationic polymerization.

Possible Reaction Mechanism

From the above-mentioned experimental results the following mechanism via a radical cation is deduced.

O_2 as initiator:

$$C_6H_5CH{=}CH_2 + O_2 \xrightarrow{\text{liq. } SO_2} (C_6H_5CH{=}CH_2)^{\dot{+}} + \dot{\bar{}}O_2(SO_2) \quad (1)$$

$$\dot{\bar{}}O_2(SO_2) \rightleftarrows O_2 + \dot{\bar{}}SO_2 \quad (2)$$

Aromatic hydrocarbon–O_2 as initiator:

$$\mathrm{Ar(SO_2)} \rightleftarrows \mathrm{Ar} + \mathrm{SO_2} \tag{3}$$

$$\mathrm{Ar} + \mathrm{O_2} \xrightarrow{\text{liq. SO}_2} \mathrm{Ar}^{\cdot+} + {}^{\cdot-}\mathrm{O_2(SO_2)} \tag{4}$$

$$\mathrm{Ar}^{\cdot+} + \mathrm{C_6H_5CH{=}CH_2} \rightarrow \mathrm{(C_6H_5CH{=}CH_2)}^{\cdot+} + \mathrm{Ar} \tag{5}$$

$$\mathrm{(C_6H_5CH{=}CH_2)}^{\cdot+} \xrightarrow{\mathrm{C_6H_5CH{=}CH_2}} \text{polymer} \tag{6}$$

where Ar is an aromatic hydrocarbon. Equation (1) is plausible from the fact that styrene polymerizes in liquid sulfur dioxide in the presence of oxygen alone, though the induction period is longer, and that the polymerization proceeds cationically, containing a slightly blue species that may correspond to the styrene radical cation, in spite of no formation of sulfur trioxide from the reaction of sulfur dioxide with oxygen. Perhaps a styrene radical cation is formed because an oxygen radical anion $^{\cdot-}O_2$ is solvated by some sulfur dioxide molecules and is stabilized. Equation (2) was assumed from the fact that oxygen plays the usual role of catalyst, as shown in Figure 3. The addition of aromatic hydrocarbons to the initiation system produces radical cations with the transfer of electrons from the aromatic hydrocarbons to oxygen prior to the formation of styrene radical cations [eq. (4)], which may be followed by the transfer of electrons from styrene to the aromatic hydrocarbon radical cation. The reason for the induction period is not obvious; however, the same induction period as that mentioned above was observed in a different procedure, in which a solution of anthracene in liquid sulfur dioxide in the presence of oxygen was allowed to stand for a long time and then was introduced into the styrene monomer. This observation suggests that such a reaction as that expressed in eq. (5) has something to do with the induction period.

Behavior of DPE and Its Derivatives in Liquid Sulfur Dioxide in Presence of Oxygen

It was assumed that the absorption at 610 mμ may be due to a styrene radical cation. To obtain further information on such spectra the absorptions of 1,1-diphenylethylene (DPE) or its derivatives in liquid sulfur dioxide were examined. Oxygen was introduced into a solution of DPE or one of its derivatives in liquid sulfur dioxide. A deep blue appeared either immediately or gradually, when the electronic spectra gave a strong absorption at a $\lambda_{\max}$ of 605 to 670 mμ, as shown in Figure 12, indicating a typical substituent effect. Leftin and Hall[12] showed conclusively that the absorption at 607 mμ given by an adsorption of DPE on silica alumina could be assigned to a DPE radical cation, and they succeeded in detecting the ESR signal of the 607 mμ species in later studies,[19] though they had failed in their earlier studies.

The absorption at 605 mμ recorded in the present study is very nearly that obtained by Leftin and Hall, but we were still unsuccessful in detecting the ESR signal. A typical plot of D_{605}, the optical density at 605 mμ, versus time is given in Figure 13. The 605 mμ peak develops immediately

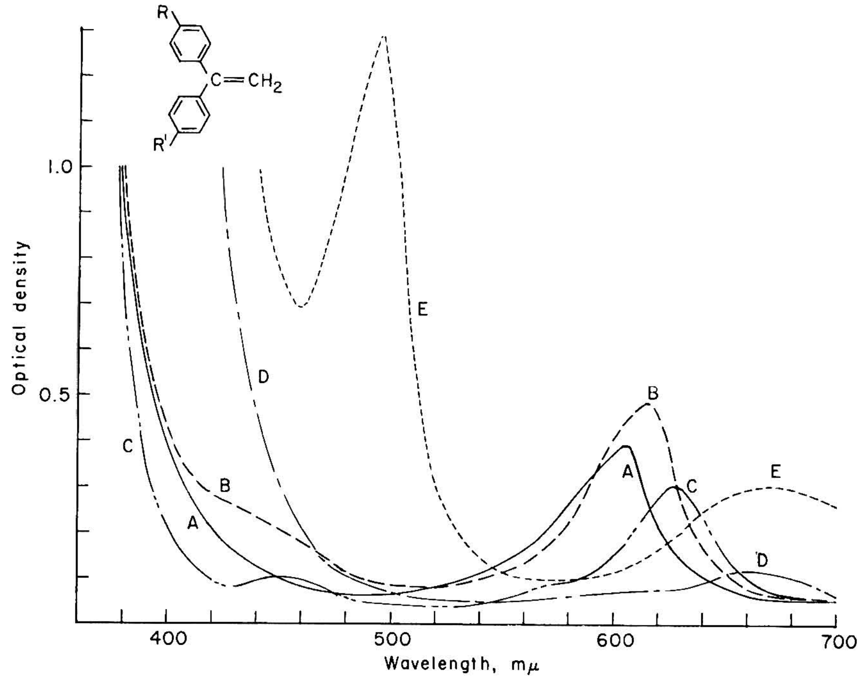


Fig. 12. Absorption spectra. The intensities vary with time and are accelerated by indirect sunlight, especially in the case of curve *E*. (*A*) R = R' = H; (*B*) R = Cl, R' = H; (*C*) R = R' = Cl; (*D*) R = OCH_3, R' = H; (*E*) R = R' = OCH_3. Concentration, 0.0539 mol/l; solvent, SO_2; cell length, 2 mm. All measured 24 hr after addition of oxygen (0.17 mol/l).

and reaches a maximum value during 2 hr; the slow fall of the blue-species peak is followed by the gradual appearance of a red species, indicating a secondary change of the blue species.

It was also observed that the blue species immediately disappears on contact with air or on the evolution of SO_2 from the system. A blue solution of 0.18 mol of DPE per 80 ml of SO_2, and 8×10^{-3} mol of O_2 was allowed to stand for 24 hr at 0°C. A careful examination of the reaction mixture showed a white crystal (1,1,3,3-tetraphenylbutene-1, 34% yield), benzophenone (4%), and a small amount of a water-soluble compound, along with unchanged DPE (60%). Of the water-soluble compound the NMR spectra showed only methylene proton at 7.74 τ, and the IR spectra showed 1040 and 1200 cm^{-1} due to SO_3, 3400 cm^{-1} due to OH, and 1650 cm^{-1} due to C=O. Of the white crystal the IR spectrum showed no absorption at 895 cm^{-1} ($>C=CH_2$), and the NMR spectrum showed peaks at 8.57 τ (CH_3—), 3.22 τ (olefin), and 2.80 τ (phenyl), the areas being in the ratio 3:1:20, indicating that the crystal was 1,1,3,3-tetraphenylbutene-1, which was confirmed by comparison of the infrared spectrum and by a mixed melting-point method with an authentic sample[20] obtained from the reaction of DPE with $SnCl_4$ in benzene. On the other hand, DPE in

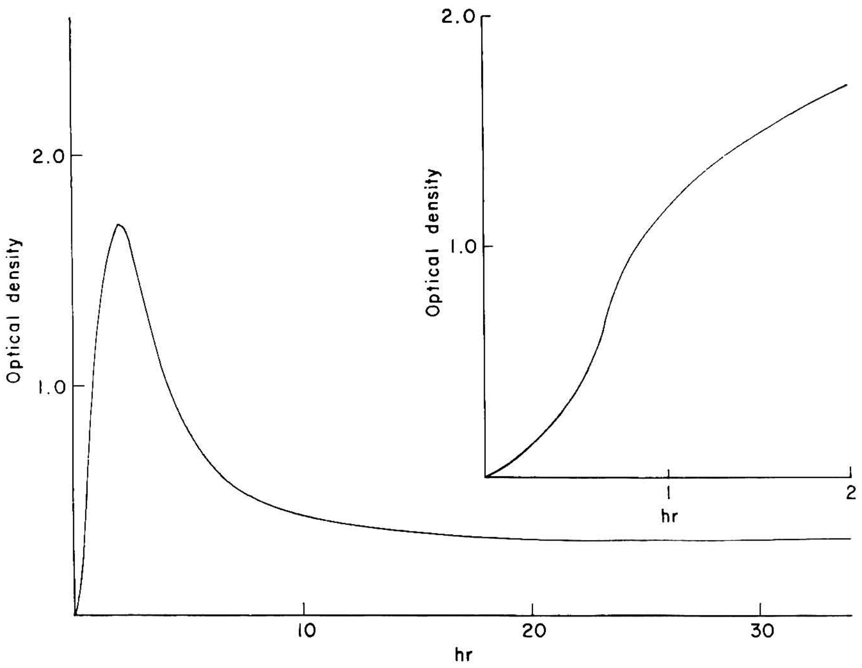


Fig. 13. Typical plot of D_{605} in the system DPE–O_2–SO_2. The position of the peak shifts to a later time and lower intensity with smaller concentration of olefin or oxygen. DPE, 1.91 mol/l; O_2, 0.2 mol/l; cell length, 0.5 mm. (Smaller plot indicates enlarged scale).

liquid SO_2 without oxygen does not alter under the same conditions and shows no coloring. The production of benzophenone and 1,1,3,3-tetraphenylbutene-1 was eliminated by adding a radical or cation inhibitor, as

TABLE VI

Effect of Inhibitor Added to 1,1-Diphenylethylene–O_2–SO_2 System[a]

				Products, %	
DPE, mol	O_2, mol ($\times 10^3$)	Liq. SO_2, ml	Inhibitor, mol ($\times 10^4$)	1,1,3,3-Tetraphenylbutene-1	Benzophenone
0.18	8	80	—	34.0	4.0
0.057	5	25	H_2O, 550	0	3.4
0.057	5	25	DPPH, 2.0	trace	0
0.057	5	25	I_2, 3.9	>99.0[b]	trace
0.057	5	25	CCl_4, 4.3	42.0	3.0
0.057	5	25	galvinoxyl, 4.1	2.0	0
0.18	0	80	—	0	0

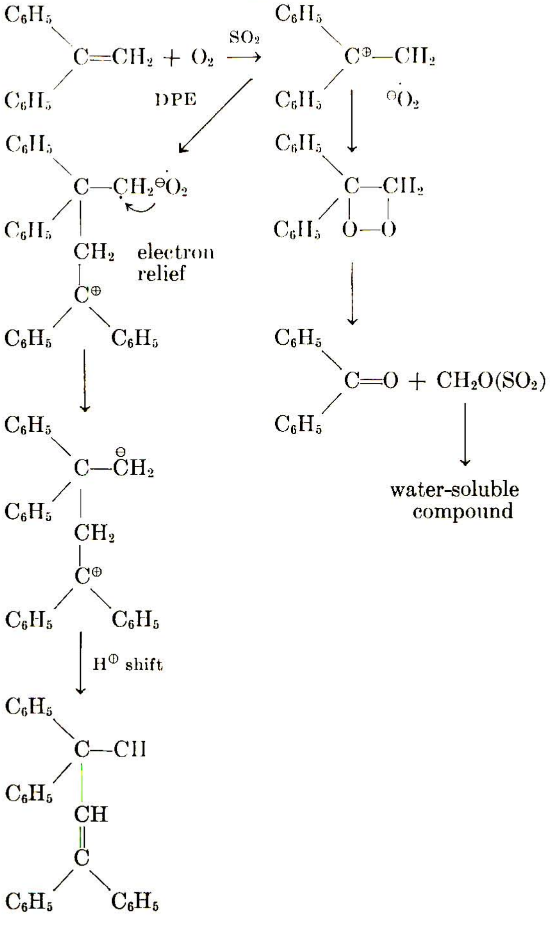
[a] The reactions were carried out at 0°C for 24 hr.

[b] With I_2 as inhibitor the yield is very great, probably because of the action of I_2 as a catalyst of cationic polymerization (cf. Kano et al.[21]).

shown in Table VI, indicating the presence of DPE radical cation as the reaction intermediate.

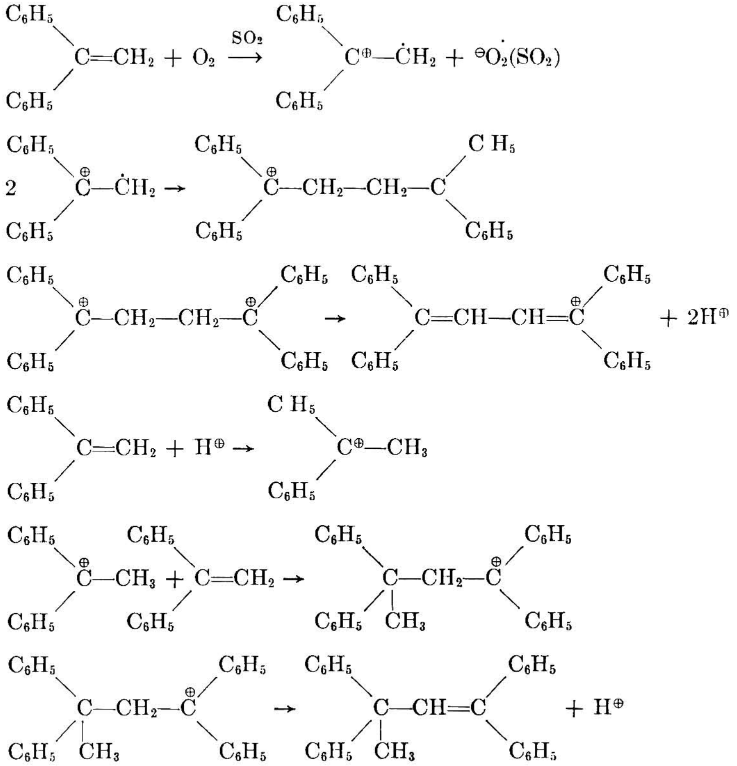
The reaction sequence might be expressed by one of the following; scheme 1 is preferable to scheme 2.

Scheme 1



The supporting evidence for scheme 1 is that tetraphenylbutadiene was not found in the reaction mixture, while tetraphenylbutadiene did not isomerize under the reaction condition; and that the cations derived from tetraphenylbutadiene, or DPE in concentrated H_2SO_4, were all yellow species and not the red species found in the present system. That the radical–radical coupling reaction that could occur in the DPE radical anion does not occur in the DPE radical cation may be explained by the fact that DPE readily undergoes electrophilic attack from a cation but not from an anion.

Scheme 2



Behavior of TPE in Liquid Sulfur Dioxide in Presence of Oxygen

The same experiment as that with DPE was repeated with tetraphenylethylene (TPE) as the olefin; this compound is unable to dimerize because of the steric hindrance due to four phenyl groups. The introduction of oxygen into a solution of TPE in liquid sulfur dioxide gave a blue-green color immediately, and the electronic spectrum showed λ_{max} at 650 $m\mu$, as shown in Figure 14. Evans and Tabner[22] showed λ_{max} at 645 $m\mu$ as the absorption of a TPE radical anion in a reaction of TPE with Na metal in tetrahydrofuran and obtained the strong ESR signal. Thus, the absorption found in the present system may be that of TPE radical cation, considering that the transition energy has been proved same for both radical ions and is due to the symmetry characteristics of the molecular orbitals. That the solution did not change in color (Fig. 15), although it was allowed to stand for two months, suggests that the dimerization did not occur because of the steric hindrance of phenyl groups, as expected, and that the parent TPE was unchanged after removal of the liquid sulfur dioxide suggests that the absorption in a longer-wavelength region is due, not to the perplexing chemical species, but to such a simple one as a radical cation, which may be obtained through a one-electron transfer; however, we failed to detect the ESR signal of this solution, as we did in the case of

DPE, despite the coincidence of its electronic spectrum with that of a TPE radical anion.

The colored species formed from TPE was unable to initiate the polymerization of styrene in liquid sulfur dioxide in the presence of oxygen at 0°C. This fact might be interpreted as the TPE radical cation's inability

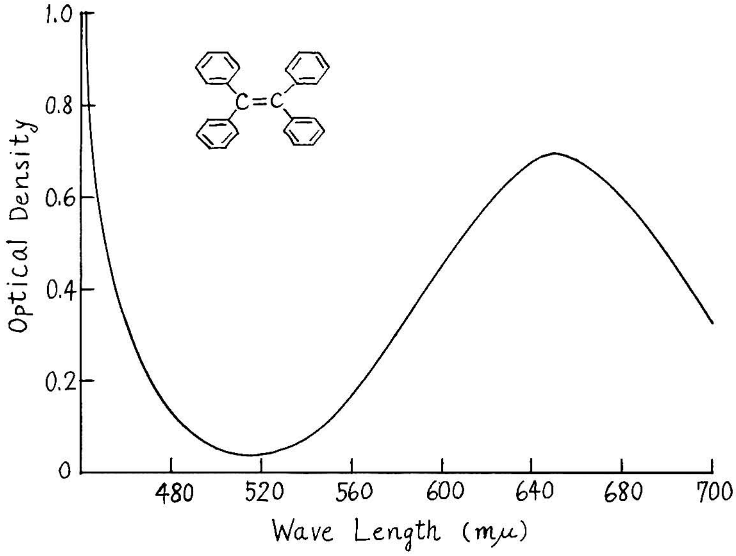


Fig. 14. Absorption spectrum of tetraphenylethylene, 8.3 mmol/l, in liquid SO_2, with added O_2; cell width, 10 mm.

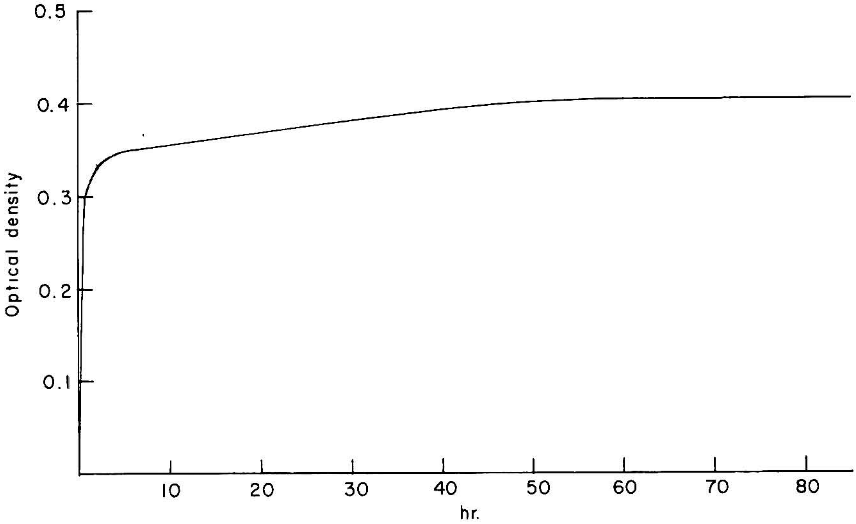


Fig. 15. Typical plot of D_{650} in system TPE–O_2–SO_2; TPE, 8.3 mmol/l; O_2, 5×10^{-3} mol; cell length, 10 mm.

to intercept the electron from styrene because of the steric hindrance due to the four twisted phenyl groups in TPE.

Other Olefin–SO_2–O_2 Systems

The behaviors of such olefins as triphenylethylene, tetraphenylbutadiene, 1,1-diphenyl-2,2-dimethylethylene, 1,1-diphenyl-2-methylethylene, acenaphthylene, and *cis*- and *trans*-stilbene in liquid SO_2–O_2 systems were also examined. Each of the olefins exhibits no color, except for an absorption at 612 mμ in the case of 1,1-diphenyl-2,2-dimethylethylene and a slight absorption at 605 mμ in the case of 1,1,3,3-tetraphenyl-butene 1. Furthermore, none of the olefins except acenaphthylene reacted in the system SO_2–O_2. When acenaphthylene was dissolved in 7 ml of liquid SO_2 in a pressured vessel in 0.47 mol/l concentration and O_2 (5×10^{-3} mol) was introduced, and the solution was allowed to stand for 41 hr at 0°C, the yield was 4.2% polymer (molecular weight about 1200, softening point about 300°C, and results of tests for sulfur, double bond, and peroxide all negative); however, no polymer was detected in the absence of oxygen.

The catalytic behaviors of the olefins toward styrene polymerization in the SO_2–O_2 system are presented in Table VII. The results show that the polymerization relates chiefly to the blue species.

TABLE VII

Polymerization of Styrene in Aromatic Hydrocarbon–O_2–SO_2 Systems[a]

Catalyst (aromatic hydrocarbon)	Polystyrene yield, %	Coloring	
		In presence of styrene	In absence of styrene
None	12.2	pale blue	
1,1-Diphenylethylene	29.1	blue	blue
Triphenylethylene	0	none	none
Tetraphenylethylene	0	green	green
Tetraphenylbutadiene	0	none	none
cis-Stilbene	34.5	blue	none
trans-Stilbene	91.7	blue	none
Acenaphthylene	0	none	none
Anthracene	93.5	blue	none
Anthracene–DPPH[b]	0	none	none

[a] Reaction conditions: styrene, 0.026 mol; aromatic hydrocarbon (catalyst), 4.4×10^{-4} mol; O_2, 5×10^{-3} mol; SO_2, 14 ml; at 0°C; reaction time, 4 hr.

[b] DPPH, 2.0×10^{-4} mol, was used (the addition of CCl_4 instead of DPPH was found to have no inhibiting effect on the polymerization).

The fact that the blue colors and the catalytic effects in the polymerization of styrene are sensitive to the structures of the aromatic hydrocarbons, as is seen in Tables VII and IV, remains to be elucidated. Further work is required to explain fully these interesting observations.

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Polymerization of Methyl Methacrylate in a Tetrahydrofuran–Maleic Anhydride System. Part II

JOZEF BERGER and MILAN LAZÁR, *Polymer Institute of the Slovak Academy of Sciences, Bratislava, Czechoslovakia*

Synopsis

A donor–acceptor complex consisting of tetrahydrofuran and maleic anhydride initiates photochemical and thermal polymerization of methyl methacrylate. The mechanism of the transformation of this complex was investigated by studying changes in its electrical conductivity, its chemiluminescence, and various influences on its initiating capability (water, air, DPPH, substitution of styrene for methyl methacrylate and of 1,4-dioxane for tetrahydrofuran). It has been shown that initiation by radicals cannot be clearly excluded and that ionic radicals form in the system and can initiate the anionic growth of the chain.

INTRODUCTION

The fact that cyclic ethers form with maleic anhydride a donor–acceptor complex has lately been used for the polymerization with these ethers.[2] Bawn et al.[3] established that the complex formed by tetrahydrofuran and maleic anhydride decomposes in visible light ($\lambda > 3100$ Å). The products of the decomposition initiate the polymerization of methyl methacrylate. We have attempted herein to explain the mechanism of this initiation.

EXPERIMENTAL

The methods of purifying methyl methacrylate, paraffin, maleic anhydride, n-heptane, and methyl alcohol, of polymerizing methyl methacrylate in a mixture of tetrahydrofuran and maleic anhydride, and of determining the constitution of a copolymer have been described elsewhere.[1,4] Styrene was purified by the method used for methyl methacrylate. Tetrahydrofuran (chemically pure, $n_D^{20} = 1.407$, product of the firm Carlo Erba, Italy) was dried over sodium and directly before use was distilled in nitrogen atmosphere; the quoted method of purification is sufficient because metallic sodium removes efficiently from tetrahydrofuran, humidity and peroxides.[5] Measurements of chemiluminescence did not prove their presence. 1,4-Dioxane, chemically pure, was purified by the method used for tetrahydrofuran. 1,1′-Diphenyl-2-picrylhydrazyl (DPPH) was prepared by oxidation of 1,1′-diphenyl-2-picrylhydrazine by means of powdery PbO_2.[6] The hydrazine, denoted chemically pure, was a product of the firm Fluka AG, Chemische Fabrik Buchs SG, Schweiz.

For the identification of radicals formed owing to the interaction of light and, eventually, heat with a solution of maleic anhydride the chemiluminescence, which appears upon recombination of two particles (radicals, but also ions) by the emission of photons, was measured. The measurements were made on a PU-SNK-7M instrument constructed by the Institute of Chemical Physics of the Academy of Sciences of the U.S.S.R. in 1965.

The sample of solution, containing various molar amounts of its components in a total volume of 4 ml, was placed in a glass vessel. The vessel was put in a dark chamber of the apparatus, at the focus of the mirrors before the diaphragm at the entrance to the photomultiplier. The emitted light was captured by an FEU-38 photomultiplier (Sb, Na, K, Cs) with sensitivity to wavelengths longer than 3000 Å and up to 4400 Å at −78°C.[7] The relative intensity of the light was measured.

The specific conductivities of solutions of maleic anhydride in tetrahydrofuran were measured with an EPTK smooth platinum electrode welded in the ground cover of a flat-bottomed vessel that could be illuminated. The vessel was put in a constant-temperature bath (±0.3°C). The conductoscope, which has a range of 5×10^{-2} to 2×10^{7} ohms, and the electrode are products of the firm Laboratorní přístroje.

RESULTS

Influences on the Polymerization of Methyl Methacrylate

The influence of DPPH on the polymerization was studied in an endeavor to determine the character of the particles initiating polymerization. Its course is, as may be seen from Figure 1, quite distinctive after a certain

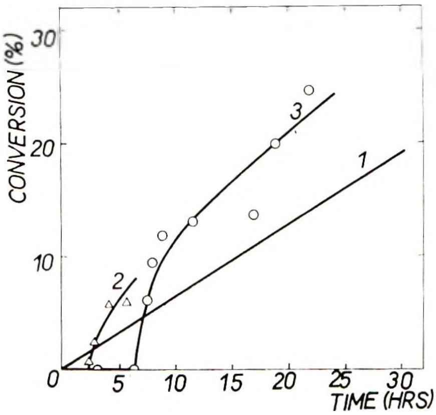

Fig. 1. Conversion–time curves of methyl methacrylate polymerization in tetrahydrofuran–maleic anhydride (30°C, in N_2) with DPPH in concentrations (*1*) zero,[1] (*2*) 2×10^{-3} mol/l, and (*3*) 5×10^{-3} mol/l.

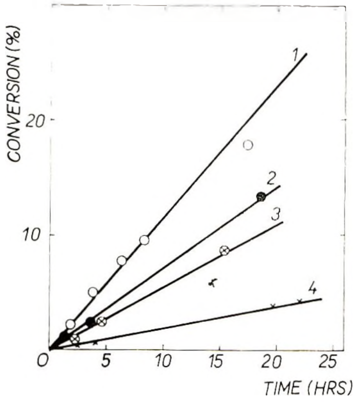

Fig. 2. Conversion–time curves of styrene polymerization tetrahydrofuran–maleic anhydride in N_2: (*1*) 50°C, lighting; (*2*) 50°C, darkness; (*3*) 30°C, lighting; (*4*) 30°C, darkness.

inhibition period, depending on the concentration of DPPH in the system. The beginning of the polymerization reaction is indicated by a change of the violet color of the solution to a red–brown.

It was shown further that the polymerization rate is approximately four times higher in nitrogen atomsphere[1] than in air. In air the dependence of monomer conversion on polymerization time is linear, beginning at $t = 0$. The effect of the presence of water was verified by polymerizations in nitrogen atmosphere at two concentrations, 2 and 4 mol/l. It was proved that the effect is negligible.

The substitution of 1,4-dioxane for tetrahydrofuran, in the same molar concentration, leads to a change in the kinetic properties of the system, above all to a reduction in the overall rate of polymerization; see Table I. This occurs also upon substitution of styrene for methyl methacrylate in a tetrahydrofuran–maleic anhydride system; see Figure 2.

TABLE I
Polymerization of Methyl Methacrylate in 1,4-Dioxane–Maleic Anhydride in Nitrogen Atmosphere under Visible Light at 30°C

Polymerization time, hr	Conversion, calculated as MMA + MA, %
1	—
17	—
19	0.6
43	4.2
47	6.0

However, the proportion of photoinitiated polymer is higher with styrene $P_{vi} = (V_c - V_t)/V_c \times 100\%$, where V_c is the total polymerization rate and V_t is the rate of thermal polymerization); see Table II.

TABLE II
Comparison of Proportions of Photoinitiated Polymerization of Methyl Methacrylate and Styrene

Monomer	P_{vf}, %		Reference
	At 30°C	At 50°C	
Methyl methacrylate	30.8	9.7	previous work[1]
Styrene	66.6	39.1	present work

The influence of "aging" of the tetrahydrofuran-maleic anhydride complex in the presence of methyl methacrylate on the polymerization was investigated. By "aging" is meant keeping the mixture at a constant temperature while no interaction with light is allowed. After the expiration of different periods of blanking the mixture was exposed to light; see Figure 3. From the conversion of the monomer the conversion corresponding to the respective thermal polymerization[1] was subtracted.

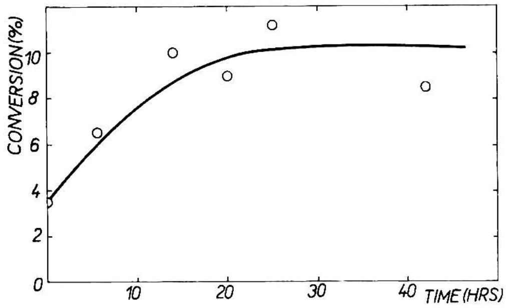

Fig. 3. Dependence of monomer conversion in methyl methacrylate–tetrahydrofuran–maleic anhydride, reached in 4 hr lighting of the sample at 30°C in N_2 on preceding time of thermal "aging" of complex. Molar ratio of components, 9.1:12.1:1.

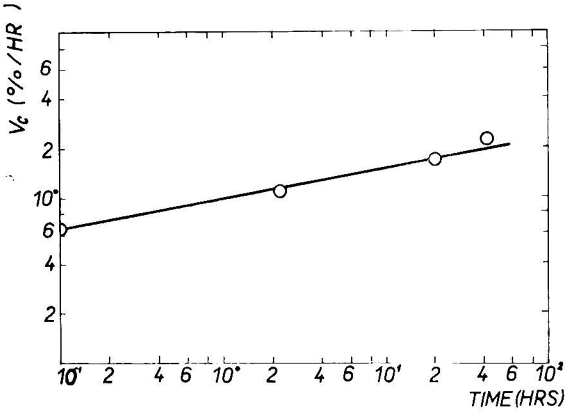

Fig. 4. Dependence of logarithm of polymerization rate, V_c, on logarithm of time of "aging" of complex in irradiated sample. Temperature of "aging" and of polymerization during lighting was 30°C in N_2. Molar ratio of components, 9.1:12.1:1.

The aging of the complex tetrahydrofuran–maleic anhydride as a function of the time of exposure to light also was investigated. Methyl methacrylate was added to the system later. The mixture was exposed to light again for a period of time, and the polymerization rate was determined. The dependence of the polymerization rate on the time of such aging of the complex may be expressed on logarithmic coordinates as a linear relation; see Figure 4.

The change in content of maleic anhydride in a monomer mixture is shown by the change of its content in the copolymer; see Table III.

TABLE III
Dependence of Content of Maleic Anhydride in Its Copolymer with Methyl Methacrylate on Composition of Monomer Mixture[a]

Concn. in monomer mixture, mol-%		Concn. of MA in copolymer, mole-%	
MA	MMA	Found at 30°C	Calculated[b] at 60°C, in radical polymerization
4.5	41.4	1.4	3.0
19.0	35.1	12.3	12.2
24.7	32.7	19.9	14.9
29.7	30.5	21.5	17.7
42.9	24.8	28.0	25.5

[a] Polymerized by irradiation of system MMA–THF–MA for 13 hr at 30°C in N_2.
[b] From Tsuchida et al.[8]

Measurement of Electrical Conductivity and Chemiluminescence

The conductivity of solutions of maleic anhydride and tetrahydrofuran in a molar ratio of 1:12.1 was measured. Various arrangements of the experiment were made: different temperatures (20 or 30°C), atmospheres (nitrogen or air), and lightings of the sample with eventual prevention of its interaction with light.

From Figure 5 the following are apparent.

(1) A marked difference in change of specific conductivity $\varkappa$ between the solutions: an attempt to polymerize methyl methacrylate in a mixture of phthalic anhydride and tetrahydrofuran has shown that no polymerization at all occurs.

TABLE IV
Values of Slope n Determined by Measuring Specific Conductivity $\varkappa$ of Solutions of Maleic Anhydride in Tetrahydrofuran in Different Conditions

Expt. No.	Temp., °C	Atm.	Lighting	n
1	20	N_2	+	0.201
2	30	N_2	+	0.325
3	30	N_2	−	0.205
4	30	air	+	0.250

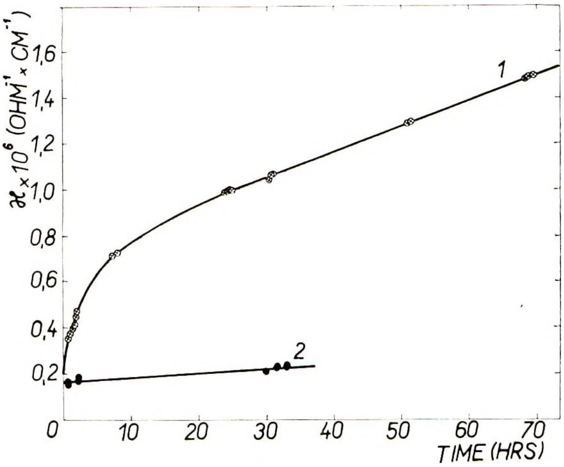

Fig. 5. Dependence of specific conductivity $\mathcal{K}$ of solutions on duration of lighting at 30°C in N_2: (*1*) maleic anhydride in tetrahydrofuran; (*2*) phthalic anhydride in tetrahydrofuran.

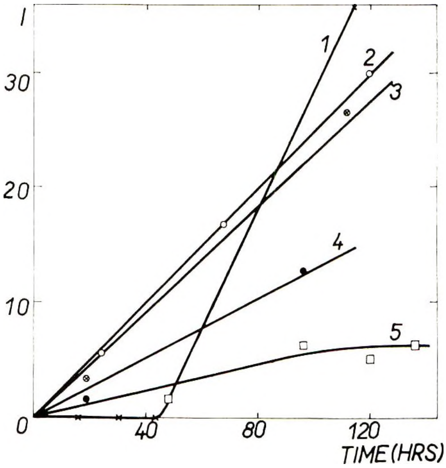

Fig. 6. Dependence of relative intensity of luminescence on the duration of lighting: (*1*) N_2, 43 hr in dark at 50°C, then 72 hr in light at 30°C; (*2*) vacuum, 30°C; (*3*) N_2, 30°C; (*4*) air, 30°C; (*5*) N_2, 30°C. Molar ratio of maleic anhydride to tetrahydrofuran (*1*–*4*): 5:12.1; (*5*) 1:12.1.

(*2*) The exponential pattern of curve 1 which, plotted in logarithmic coordinates, becomes linear: the dependence has the same pattern under other conditions and consequently may be expressed in the form $\log \varkappa = n \log t$, where n is the slope of the straight line and also the constant for the conditions of the experiment; see Table IV.

The measurements of chemiluminescence were carried out in solutions of maleic anhydride in tetrahydrofuran (1:12.1 and 5:12.1) with different arrangements of the experiment (Fig. 6). The intensity was always measured in oxygen at 50°C, since without oxygen there is no luminescence.

Figure 6 shows that the relative intensity of the luminescence depends on the medium in which the sample is lighted (vacuum > nitrogen ≫ air), on the ratio of the components, and on whether the sample has been previously irradiated. The intensity depends on the temperature of the measured sample. A solution of phthalic anhydride in tetrahydrofuran shows no chemiluminescence even after 100 hr of irradiation.

Color of the Solution

Solutions of maleic anhydride in tetrahydrofuran change their color upon longer lighting. The rate of change in color and the final color of the solution depend mainly on the intensity of the lighting and on the atmosphere surrounding the sample. In air the color changes from colorless to yellow to violet to dark brown (in about 1 wk). However, meanwhile the rate of color change slows with the increase of nitrogen concentration, and in vacuum no change occurs at all, the sample remaining colorless if interaction with light is prevented. The change of color intensity depends also on the ratio of the components; it is greater when the molar ratio is 5:12.1 than when it is 1:12.1.

In a maleic anhydride–tetrahydrofuran solution containing methyl methacrylate discoloration does not occur, not even at high monomer conversions. A very low concentration of methyl methacrylate (a molar ratio of methyl methacrylate to tetrahydrofuran to maleic anhydride of 1:16.35:1.35) is sufficient to prevent discoloration.

A solution of phthalic anhydride in tetrahydrofuran (5:12.1) does not discolor in the light.

DISCUSSION

To characterize the particles forming in tetrahydrofuran–maleic anhydride that are also polymerization initiators it is above all necessary to consider the results of the measurements of chemiluminescence and electrical conductivity. The luminescence is the result of recombination of peroxide radicals.[9] That it should be the result of charged ions, often supposed in the identical blue region of the spectrum,[10,11] or to the recombination of carbonic radicals[9] cannot be accepted, since it is not observed either in nitrogen atomosphere or in vacuum, but only in the presence of oxygen.

Between the patterns of the dependence of relative intensity of luminescence on time on the one hand and the dependence of the increase of conductivity on time on the other there is a disproportion, which can be a consequence of the fact that in the two cases the measured magnitudes are not reflecting identical states.

In a system with one type of radical the intensity of luminescence is proportional to the rate of recombination of the radicals. In a stationary state that rate is equal to the rate of initiation. When two types of radical (more and less active) are present, the more active ones are consumed in reaction with the less active ones, and the rate of recombination of peroxide radicals is not equal to the rate of formation of all radicals. The intensity of luminescence, then, characterizes only the concentration of peroxide radicals. The recombination of tetrahydrofuran and maleic anhydride radicals is established, since their adduct has been isolated.[12] Apart from that, even if the more active radicals were not used up, interactions between radicals having different reactivities show different thermal effects, which do not need to be manifested by luminescence in the visible region at the 4400 Å maximum sensitivity of the photomultiplier used.

On the other hand, the dependence of the specific conductivity of maleic anhydride–tetrahydrofuran on duration of illumination (and also the darkening in air and in nitrogen atmosphere) shows a pattern close to that of the dependence of rate of methyl methacrylate polymerization on "aging" during illumination (Fig. 4). Both dependences are linear when expressed on logarithmic coordinates.

When phthalic anhydride replaces maleic anhydride in tetrahydrofuran, the solution does not display, on being lit, an increase in either conductivity or discoloration, nor does it show chemiluminescence, and methyl methacrylate does not polymerize in it.

On the basis of these results and of the fact that in a mixture of the monomer with tetrahydrofuran and maleic anhydride the polymerization rate,[1] the rate of change of conductivity (Table 4), and the relative intensity of luminescence (Fig. 6) equally depend on the medium (nitrogen, vacuum > air, light > air, dark), it appears justifiable to consider ions (ion radicals) the particles responsible for polymerization initiation.

The change in content of maleic anhydride and methyl methacrylate in a monomer mixture is reflected in the composition of the copolymer prepared in the course of illumination. A comparison of the maleic anhydride content found in copolymer with that calculated (in a radical-initiated copolymerization) does not preclude the possibility of a radical-growth reaction (Table III).

The rate of thermal polymerization of methyl methacrylate in the given system is not negligible in comparison with that of irradiation polymerization at temperatures of 20–60°C.[1] The measurements of chemiluminescence indicate that in the dark, in a solution of maleic anhydride–tetrahydrofuran, free radicals do not form (Fig. 6, curve 1); upon irradiation the chemiluminescence develops. On the other hand, the conductivity of the solutions increase in both cases.

The results indicate that thermal decomposition of the complex can lead to ion radicals that are rather strongly bound in couples and that lighting causes dissociation of them and their transformation (or the transformation of the complex itself) to radicals that can more easily diffuse from their place of formation. Polymerization during lighting at temperatures of 20–60°C can then be initiated at any moment by particles generated either thermally or photochemically.

Besides the formation of radical ions and ions that polymerize independently there can arise a polymethyl methacrylate block on the ionic end and a copolymer of methyl methacrylate and maleic anhydride on the radical end. The differences between the polymerization rates of methyl methacrylate[1] and of styrene (Fig. 2) and (Table II), monomers with different reactivities with regard to the type of initiation do not contradict this hypothesis. Nor can the formation of dimeric anion radicals and their transformation to dianions, with the localization of active centers, be excluded.[13] Since the transformation is the limiting state of initiation, it is understandable that the conversion of monomer during irradiation is a function of the duration of the preceding darkness (Fig. 3).

However, even more complicated processes may be considered, in which radicals on the ends of the molecule are able to attach more molecules of the monomer, e.g., maleic anhydride before recombination. If an inhibitor of radical polymerization (DPPH) is present, it is attached preferably and, if it is relatively efficient, the probability of its being attached to the radical end of the dimeric ion radical is much greater than that of the monomer's. On the anionic end of the adduct, DPPH—M_2^-, no growth reaction occurs (conversion not observed during the inhibition period, until the color of the solution changes from violet to orange), probably in consequence of steric barrier. We have no explanation of the higher polymerization rate after the exhaustion of DPPH in the system (Fig. 1). Similar results were observed in the cationic, photoinitiated polymerization of *N*-vinylcarbazole.[14]

It is necessary to mention a further factor that may influence the polymerization of methyl methacrylate in the system: the solvating ability of tetrahydrofuran which, according to Arest-Jakubovic,[13] is not negligible, since it affects the rate constant of the growth reaction. The rate of polymerization for styrene is considerably lower with 1,4-dioxane than with tetrahydrofuran, in full accordance with our results (Table I). The negligible effect of water on polymerization may also be an indication of efficient solvation of the initiating ions by components of the methyl methacrylate–tetrahydrofuran–maleic anhydride system.

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Studies of the Graft Copolymerization of Methyl Methacrylate by Means of the Photochemical Reduction of Ceric Ion Adsorbed on Cellulosic Materials

YOSHITAKA OGIWARA, HITOSHI KUBOTA, and
YUKIE OGIWARA, *Faculty of Engineering, Gunma University, Kiryu, Japan*

Synopsis

It was observed that the rate of reduction of ceric ion adsorbed on cellulose was remarkably accelerated by irradiation with ultraviolet light, and this behavior depended upon the kind of cellulose. When the graft copolymerization of methyl methacrylate on cellulose with adsorbed ceric ion was carried out by irradiation with ultraviolet light, the percent grafting decreased for softwood, bleached sulfite pulp and increased for hardwood semichemical pulp. The average molecular weight of the grafts was observed generally to decrease. If it is assumed that the ceric ions, which are reduced at an accelerated rate in the early stages of reaction with SCP, do not participate in the graft formation, a relation is observed between the modified amount of reduced ceric ion and the number of grafted chains formed, and the molar ratios of these quantities are 12:1 without irradiation and 75:1 to 100:1 with irradiation. Even when the rate of reduction of ceric ion is accelerated, the increase in the number of grafted chains is found to be very small.

INTRODUCTION

In our previous report[1] it was shown that the ceric ion adsorbed on cellulose has a relation to the total amount of carbonyl groups in the cellulose and that the amount of the adsorbed ceric ion is gradually decreased by reduction with cellulose. Further, when vinyl monomer is present in the system, graft copolymer is formed, and the rate of reduction is affected not only by the reaction conditions but also by the kind of cellulose. It is known that ultraviolet light accelerate the reduction of aqueous solutions of ceric salts,[2-5] and it was supposed that the same effect would be observed in a system including cellulose.

In the study reported herein the effect of irradiation with ultraviolet light on ceric ions adsorbed on cellulose and the graft copolymerization in such a system with methyl methacrylate were investigated. The mechanism of graft copolymerization on cellulose with an initiator system consisting of ceric ion is discussed.

EXPERIMENTAL

Cellulose Samples Adsorbing Ceric Ion

Cellulose samples such as absorbent cotton (cotton), softwood, bleached sulfite pulp (SP) and two kinds of hardwood, semichemical pulp (SCP_1, SCP_2) with different degrees of bleaching were immersed in an aqueous solution of 10 to 20 mmol/l of ceric ammonium nitrate at 45°C for 60 min, to give samples with sufficient adsorbed ceric ion. After the ionically bonded ceric ion was removed by treatment with $0.1N$ HCl (ratio of liquid to solid, 150:1), the samples were washed with water and then pressed, to expel the water.

Determination of Adsorbed Ceric Ion

As described in our previous report,[1] cellulose was suspended in water and, after a certain amount of ferrous sulfate was added to it, the ceric ion adsorbed on the cellulose was back-titrated with a known concentration of ceric sulfate solution with *o*-phenanthroline as indicator.

Ultraviolet Irradiation

With the use of a Toshiba high-pressure mercury lamp H-400P the irradiations were conducted in an occasionally agitated glass vessel about 10 cm distant from the light source at 45°C. The temperature of the reaction system did not change during irradiation.

Graft Copolymerization

A 200-ml hard-glass vessel of about 1 mm thickness was used. The total content of 42.5 ml consisted of 0.500 g of cellulose sample with adsorbed ceric ion, 15 ml of $0.1N$ HNO_3, 2.5 ml of methyl methacrylate, and water. After the atmosphere was replaced with nitrogen, the system was irradiated by ultraviolet light at 45°C for a given duration, and the graft copolymerization was carried out. The per cent grafting, average molecular weight of grafts, and number of grafted chains were determined by methods described previously.[6]

RESULTS AND DISCUSSION

Reduction of Adsorbed Ceric Ion under Ultraviolet Light

In our previous work it was shown that the adsorbed ceric ion was highly stable and the amount reduced ranged from 6 to 8% of the initially adsorbed amount for SP and SCP. The present work the reduction of ceric ions under the irradiation of ultraviolet light was examined. The changes of the ceric ion adsorbed on each sample with time are shown in Figure 1 for the graft copolymerization systems without monomer. The ordinate is the logarithm of the amount of ceric ion, and when this is plotted against time, the concentrations of adsorbed ceric ion are shown to decrease as straight

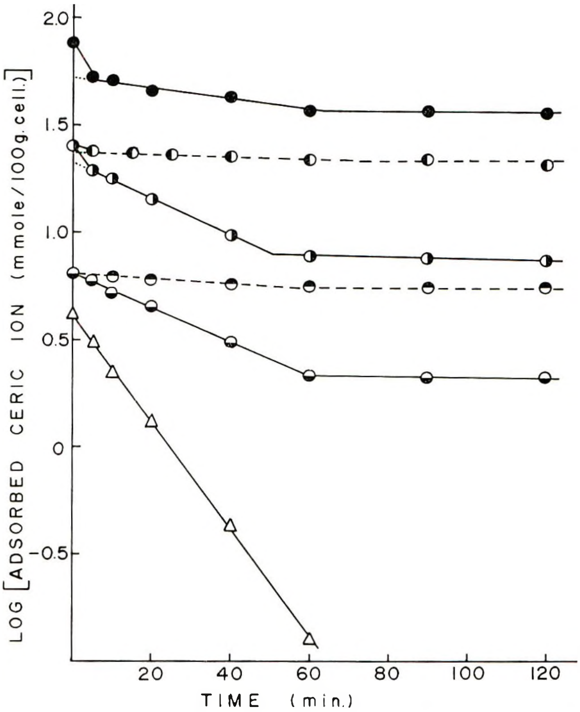

Fig. 1. Changes in ceric ion adsorbed with time, in N_2 at reaction temperature of 45°C. With irradiation (solid lines), adsorbed Ce^{4+} (mmol per 100 g of cellulose): (△) cotton, 4.10; (◒) SP, 6.48; (●) SCP_1, 75.4; (◑) SCP_2, 25.4. Without irradiation (dotted lines), adsorbed Ce^{4+} (mmol per 100 g of cellulose): (◓) SP, 6.48; (◐) SCP_2, 25.4.

lines with as many as two changes in the slopes. It is observed that ultraviolet light remarkably accelerates the reduction of adsorbed ceric ion.

In our previous work[1] it was shown that SCP containing a large amount of hemicellulose adsorbs two or three times as much ceric ion as does SCP containing the same molar amount of carbonyl groups and shows a different behavior in reduction from that of cotton and SP under ultraviolet light; that is, during irradiation for 0 to 60 min a linear relation is observed for for cotton and SP but two straight lines are observed for SCP. A reaction with a high reduction rate exists in the initial stage. The amounts of ceric ion with a higher reduction rate, obtained by the extrapolation of the two straight lines to the ordinate axis, were 11.0 and 4.2 mmol per 100 g of cellulose for SCP_1 and SCP_2, respectively. In the absence of ultraviolet light the initial higher reduction rate was observed also for SCP, and the amount was 0.8 mmol per 100 g of cellulose for SCP_2. It has been reported that by irradiation with ultraviolet light an aqueous solution of ceric salt gradually released oxygen and was reduced to cerous salt.[3,5] In our experiment the change of concentration of an aqueous solution of ceric salt in a system without cellulose is extremely small even under ultraviolet light, as shown in Figure 2.

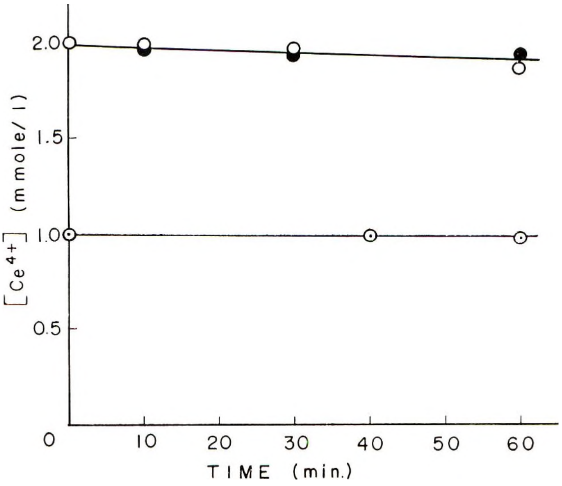

Fig. 2. Changes in concentration of ceric salt aqueous solution under ultraviolet light at reaction temperature of 45°C: (○) with 15 ml of 0.1N HNO$_3$ in N$_2$; (●) without 15 ml of 0.1N HNO$_3$ in N$_2$; ⊙ without ultraviolet light, in air.

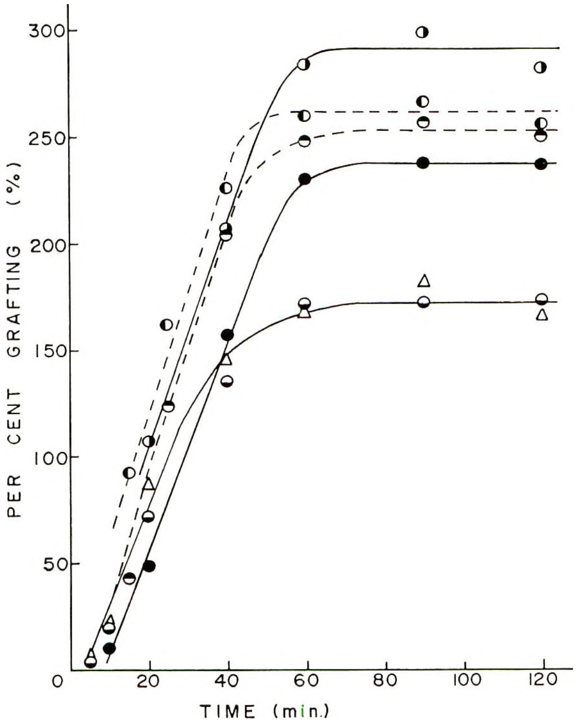

Fig. 3. Effect of ultraviolet light on per cent grafting at reaction temperature of 45°C. With irradiation (solid lines), adsorbed Ce^{4+} (mmol per 100 g of cellulose): (△) cotton, 4.10; (◒) SP, 6.48; (●) SCP$_1$, 75.4; (◑) SCP$_2$, 25.4. Without irradiation (dotted lines), adsorbed Ce^{4+} (mmol per 100 g of cellulose): (◓) SP, 6.48; (◐) SCP$_2$, 25.4.

Accordingly, ceric ion adsorbed on cellulose was clearly consumed through reduction with cellulose, and the rate of reduction is shown to be accelerated by ultraviolet light. It was observed that in irradiation times longer than 60 min the change of adsorbed ceric ion was very small.

Graft Copolymerization on Cellulose Sample Containing Adsorbed Ceric Ion

As seen in our previous work, from the reaction of cellulose containing adsorbed ceric ion with methyl methacrylate under nitrogen at 45°C for 60 min, graft copolymerization easily occurs. In the work reported herein the graft copolymerization on cellulose containing adsorbed ceric ion was examined under the irradiation of ultraviolet light.

Although the reduction rate of ceric ion was increased remarkably by irradiation with ultraviolet light, the effect of the light on the per cent grafting depended on the kind of cellulose, as shown in Figure 3. The per cent grafting clearly increases for SCP_2 but decreases remarkably for SP.

Number of Grafted Chains of Graft Copolymers

In the graft copolymerization on cellulose samples the common effect of ultraviolet irradiation is a decrease in the average molecular weight of the grafts. An average molecular weight of higher than 1,000,000 is reported for the grafts of copolymers initiated by adsorbed ceric ion.[7,8] In Table I the effect of the irradiation on the average molecular weight of the grafts

TABLE I
Effect of Irradiation with Ultraviolet Light on Average Molecular Weight of Grafts

Adsorbed ceric ion, mmole per 100 g of cell	Polymn. time, min	Avg. mol. wt.[a] of grafts ($\times 10^{-4}$)	
		No U.V.	With U.V.
Cotton			
4.10	60	724	307
SP:			
6.48	20	440	298
	40	507	333
	60	490	366
	90	475	346
	120	440	344
SCP_2:			
25.4	20	295	156
	40	320	190
	60	306	210
	90	375	220
	120	352	205

[a] Values determined viscometrically from equation of Chinai and co-workers.[9] Polymerization temp., 45°C; methyl methacrylate, 2.5 ml; total volume, 42.5 ml per 0.500 g of cellulose.

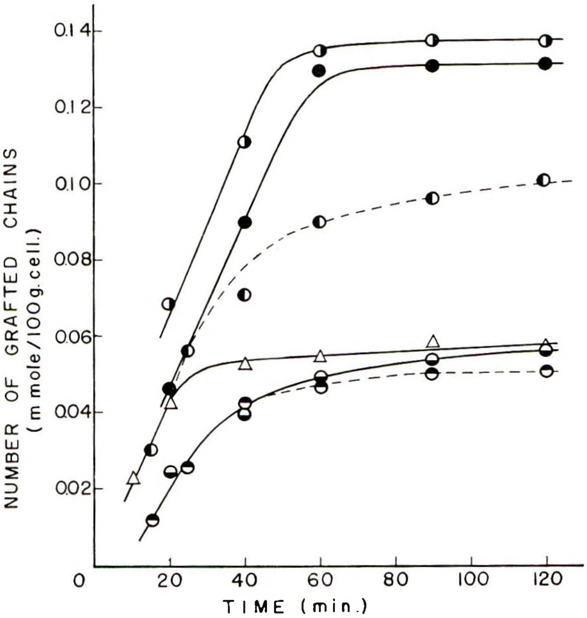

Fig. 4. Effect of ultraviolet light on number of grafted chains of graft copolymers at reaction temperature of 45°C. With irradiation (solid lines), adsorbed Ce^{4+} (mmol per 100 g of cellulose): (△) cotton, 4.10; (◒) SP, 6.48; (●) SCP_1, 75.4; (◑) SCP_2, 25.4. Without irradiation (dotted lines), adsorbed Ce^{4+} (mmol per 100 g of cellulose): (◓) SP, 6.48; (◐) SCP_2, 25.4.

is shown. The average molecular weight definitely decreases as a result of irradiation.

The relations between the number of grafted chains, as obtained from the per cent grafting and the average molecular weight of the grafts, and the polymerization time are shown in Figure 4. Regardless of irradiation, the number of grafted chains linearly increased in the initial stage of polymerization of each sample, and the equilibrium value was attained after about 60 min of polymerization.

Considering our results, the effect of ultraviolet light on the formation of grafts was observed to be considerable for SCP but not for SP.

Although the ceric ion in aqueous solution was very stable under ultraviolet irradiation, its reduction was remarkably accelerated in the presence of cellulose. It is supposed that there is a relation between the reduced amount of ceric ion and the number of grafted chains formed on the cellulose. The relation between the reduced amount of adsorbed ceric ion and the number of grafted chains in the graft copolymers is shown in Figures 5 and 6.

As is definitely seen in Figure 5, the results for cotton and SP are represented by the same straight line, but for SCP_1 and SCP_2 they are two different lines, both of which are separate from the former line. As shown in Figure 1, in the case of SCP the adsorbed ceric ions were reduced rapidly during the first 10 min of reaction time regardless of the irradiation. The effect of this reaction on the number of grafted chains is not considered to be important, judging from the results of Figure 4.

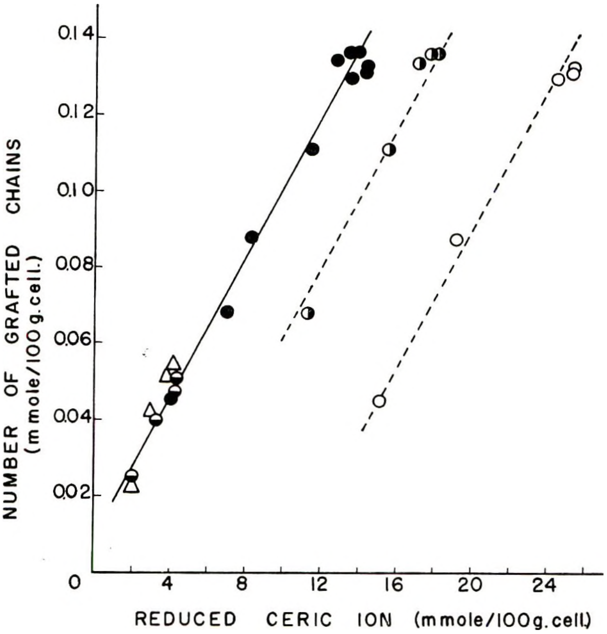

Fig. 5. Number of grafted chains of graft copolymers versus amount of reduced ceric ion adsorbed under ultraviolet irradiation: (△) cotton; (⊖) SP; (○) SCP$_1$; (◑) SCP$_2$; (●) modified values of amount of reduced ceric ion adsorbed, for SCP$_1$ and SCP$_2$.

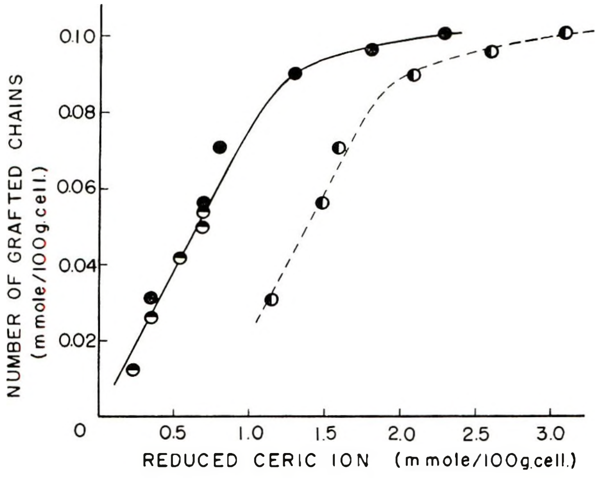

Fig. 6. Number of grafted chains of graft copolymers versus amount of reduced ceric ion adsorbed without ultraviolet irradiation: (◓) SP; (◐) SCP$_2$; (●) modified values of amount of reduced ceric ion adsorbed, for SCP$_2$.

Therefore, it is assumed that the adsorbed ceric ions reduced in this stage are not directly participating in the formation of grafts. Then for the purpose of modification this amount is subtracted from the reduced amount of adsorbed ceric ion at each stage of reaction, and a linear relation (Fig. 5) is obtained, representing cotton, SP, SCP_1, and SCP_2 together. The amounts to be subtracted are 11.0 mmol per 100 g of cellulose for SCP_1 and 4.2 mmol per 100 g of cellulose for SCP_2 in the presence of ultraviolet light, and 0.8 mmol per 100 g of cellulose for SCP_2 in the absence of ultraviolet light. As shown in Figure 6, when there is no irradiation and the same kind of modification is made in the reduced amount of adsorbed ceric ion, a common relation is obtained for the formation of grafts on SCP_2 and SP.

From the results mentioned above it is assumed that a reduction of adsorbed ceric ion that has no relation to the graft formation definitely exists. The amount is dependent upon the kind of cellulose. For SCP_2 with higher hemicellulose content the fairly large values of 4.2 mmol per 100 g of cellulose with irradiation and 0.8 mmol per 100 g of cellulose without irradiation were obtained. This is a factor that cannot be neglected in a discussion of the efficiency of graft formation. Such a reduction was not observed for cotton and SP.

From the slopes of the solid lines in Figures 5 and 6 a relation between the amount of adsorbed ceric ion participating in the graft formation and the number of grafted chains formed can be obtained. Without irradiation the ratio of these quantities was 12:1, but with irradiation it was 75:1 to 100:1, irrespective of the kind of cellulose. As clearly seen in Figure 4, even though the rate of reduction of adsorbed ceric ion is accelerated, the increase in the number of grafted chains is found to be very small.

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Kinetics of the Gamma-Radiation-Induced Polymerization of Ethylene in *tert*-Butyl Alcohol

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

Synopsis

The gamma-radiation-induced polymerization of ethylene in the presence of 13–30 ml of *tert*-butyl alcohol was carried out under a pressure of 120–400 kg/cm^2 at a dose rate of 1×10^3 to 2.5×10^4 rad/hr at 30°C with a 100 ml reactor. The polymerization rate and the molecular weight of the polymer increased with reaction time and pressure and decreased with amount of *tert*-butyl alcohol. The polymer yield increased almost proportionally with the dose rate, while the molecular weight was almost independent of it. These results were graphically evaluated, and the rate constants of initiation, propagation, and termination for various conditions were determined. No transfer was observed. On the basis of these results the role of *tert*-butyl alcohol in the polymerization is discussed.

INTRODUCTION

In previous papers[1,2] the effects of addition of various alcohols on the structure, rate of polymerization, and molecular weight of polymer were investigated, and it was found that in a polymerization with *tert*-butyl alcohol the rate is faster than in a bulk polymerization and that the molecular weight reduces to only one half. Accordingly, *tert*-butyl alcohol was deemed a useful solvent for the polymerization.

The purpose of this paper is to elucidate the effects of reaction conditions on the polymerization in *tert*-butyl alcohol, and to discuss the roles of *tert*-butyl alcohol in the initiation, propagation, transfer, and termination reaction from the viewpoint of kinetics.

EXPERIMENTAL

The reaction vessel, ethylene monomer, *tert*-butyl alcohol, irradiation facilities, and experimental procedure were the same as described in the previous papers.[1,2] The experiments were carried out under a pressure of 120–400 kg/cm^2, the dose rate was 1×10^3 to 2.5×10^4 rad/hr, and the temperature was 30°C. Since the polymerization was carried to a low conversion, less than 10%, the pressure remained essentially constant during the course of the reaction in all experiments.

RESULTS AND DISCUSSION

Effects of Reaction Conditions

The experimental results are summarized in Tables I, II, and III. Figure 1 shows the relation between the polymer yield and the reaction time. It is clear that the rate of polymerization is accelerated, since the plot of polymer yield versus reaction time is a concave, upward curve in all series of the experiments, and that the yield increases with increasing the reaction pressure during the whole period of reaction. As may be seen in Figure 2, the molecular weight increases with time under all conditions. This figure also shows that the molecular weight increases with pressure and decreases with amount of *tert*-butyl alcohol. Table IV gives the time exponents for

TABLE I
Effect of *tert*-Butyl Alcohol on Polymer Yield and Molecular Weight[a]

tert-Butyl alcohol, ml	Reaction time, hr	Polymerized monomer, mol/l	Molecular weight $\times 10^{-4}$
13	0.67	0.083	8.2
	1.0	0.173	11.8
	1.5	0.339	15.1
	2.0	0.594	19.8
30	0.5	0.067	6.0
	1.0	0.192	9.0
	1.5	0.375	11.4
	2.0	0.542	13.2

[a] Reaction conditions: pressure, 300 kg/cm^2; temperature, 30°C; dose rate, 2.5 $\times 10^4$ rad/hr; reactor volume, 100 ml.

TABLE II
Effect of Reaction Pressure on Polymer Yield and Molecular Weight[a]

Pressure, kg/cm^2	Reaction time, hr	Polymerized monomer, mol/l	Molecular weight $\times 10^{-4}$
120	1.0	0.058	2.1
	1.5	0.129	4.0
	2.0	0.189	4.4
	2.5	0.270	5.1
300	0.5	0.067	6.0
	1.0	0.192	9.0
	1.5	0.375	11.4
	2.0	0.542	13.2
400	0.67	0.193	11.8
	1.0	0.342	14.3
	1.33	0.512	14.4
	1.5	0.614	16.1

[a] Reaction conditions: temperature, 30°C; dose rate, 2.5 $\times 10^4$ rad/hr; *tert*-butyl alcohol, 30 ml; reactor volume, 100 ml.

TABLE III
Effect of Dose Rate on Polymer Yield and Molecular Weight[a]

Dose rate, $\times 10^4$ rad/hr	Polymer yield, mol/l	Molecular weight $\times 10^{-4}$
2.5	0.900	17.0
0.70	0.333	16.0
0.21	0.157	14.0
0.16	0.100	16.0
0.10	0.050	14.0

[a] Reaction conditions: pressure, 400 kg/cm^2; temperature, 30°C; time, 2 hr; *tert*-butyl alcohol 30 ml; reactor volume, 100 ml.

TABLE IV
Time Exponents of Polymer Yield and Molecular Weight[a]

Pressure, kg/cm^2	*tert*-Butyl alcohol, ml	Time exponent of polymer yield	Time exponent of molecular weight
120	30	1.69	0.75
300	30	1.58	0.57
400	30	1.42	0.35
300	13	1.79	0.76

[a] Reaction conditions: temperature, 30°C; dose rate, 2.5 × 10^4 rad/hr; reactor volume, 100 ml.

the yield and the molecular weight determined from the logarithmic plots of the results given in Tables I and II. From Table IV it is clear that the exponents both for the yield and for the molecular weight decrease with

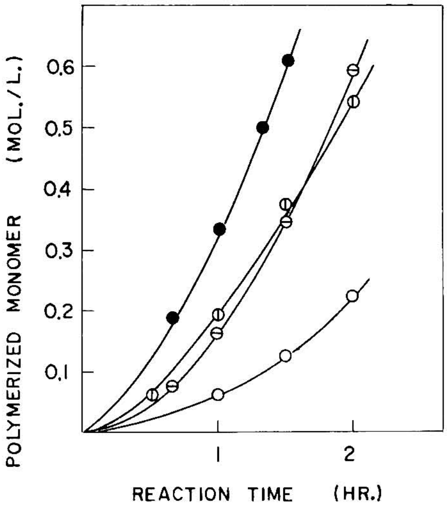

Fig. 1. Polymer yield versus reaction time. Reaction temperature, 30°C; dose rate, 2.5 × 10^4 rad/hr; reactor volume, 100 ml; pressure (kg/cm^2) and amount of *tert*-butyl alcohol (ml), respectively: (○) 120, 30; (⦶) 300, 30; (●) 400, 30; (⊖) 300, 13.

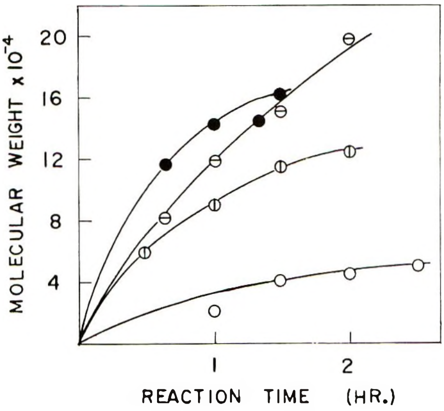

Fig. 2. Molecular weight versus reaction time. Reaction conditions same as in Figure 1.

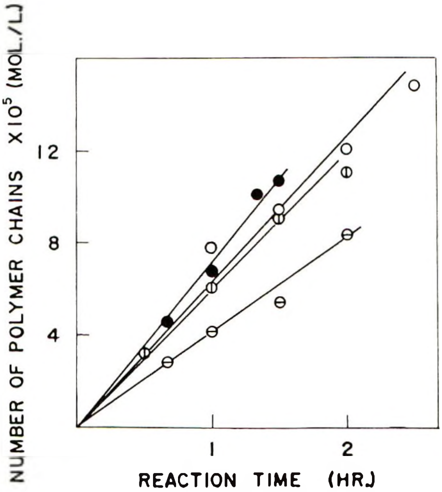

Fig. 3. Number of polymer chains versus reaction time. Reaction conditions same as in Figure 1.

increasing pressure and amount of *tert*-butyl alcohol and that the difference between the two exponents is nearly unity in each case.

From the data given in Table II the polymer yield and the molecular weight at 1 hr are found to be proportional to the 1.52th power of the ethylene pressure. As shown in Figure 3, the number of moles of the polymer chains (defined as the ratio of the polymer yield to the number-average molecular weight) increases proportionally with time, and the rate of the increment increases with the reaction pressure and the amount of *tert*-butyl alcohol. Figure 4 shows that the dose rate exponents are 0.90 for the yield and almost zero for the molecular weight. Accordingly, as shown in Figure 5, the number of moles of polymer chain is almost proportional to the dose rate.

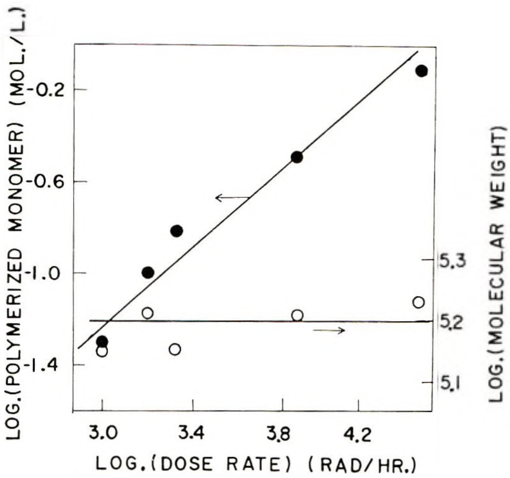

Fig. 4. Effect of dose rate on polymer yield and molecular weight. Reaction temperature, 30°C; pressure, 400 kg/cm²; time, 2 hr; *tert*-butyl alcohol, 30 ml; reactor volume, 100 ml.

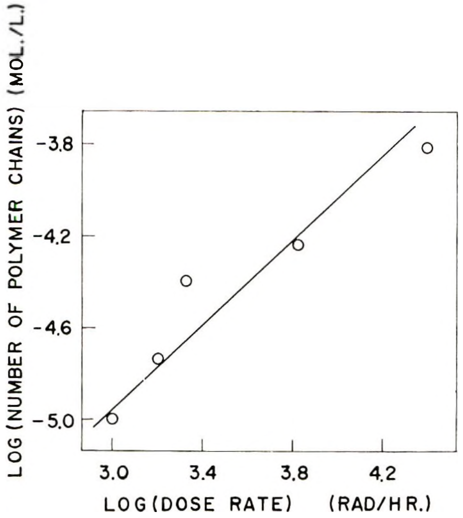

Fig. 5. Effect of dose rate on number of polymer chains. Reaction conditions same as in Figure 4.

The effects of the reaction conditions, such as reaction time, pressure, and dose rate, on the polymer yield and on the molecular weight are very similar to those in bulk polymerization at room temperature.[3–5]

Kinetics

Rate of Polymerization. As described above, since kinetic features similar to those in bulk polymerization were observed in this polymerization, the reaction mechanism shown in eqs. (1)–(5), which has already been proposed for bulk polymerization,[3] is assumed for this polymerization.

Mechanism

Initiation:

$$\mathrm{M} \underset{\mathrm{M}}{\rightsquigarrow} \mathrm{R}_1\cdot$$

$$\mathrm{S} \underset{\mathrm{M}}{\rightsquigarrow} \mathrm{R}_1\cdot$$

$$R_{\mathrm{i}} = I\, f(\rho_{\mathrm{M}}, \rho_{\mathrm{S}}) \tag{1}$$

Ethylene excitation:

$$\mathrm{M} \underset{\longleftarrow}{\rightsquigarrow} \mathrm{M}^*$$

$$\mathrm{M} + \mathrm{M}^* \rightleftharpoons \mathrm{M}_2^*, \qquad f_{\mathrm{M}2}^{*} = K_{\mathrm{e}} f_{\mathrm{M}}^{2} \tag{2}$$

Propagation:

$$\mathrm{R}_n\cdot + \mathrm{M}_2^* \rightarrow \mathrm{R}_{n+2}\cdot$$

$$R_{\mathrm{p}} = k_{\mathrm{p}}\, [\mathrm{R}_n\cdot]\, f_{\mathrm{M}2}^{*} \tag{3}$$

Transfer:

$$\mathrm{R}_n\cdot + \mathrm{Y} \rightarrow \mathrm{P}_n + \mathrm{Y}\cdot$$

$$R_{\mathrm{tr}} = k_{\mathrm{tr}}\, [\mathrm{R}_n\cdot]\, [\mathrm{Y}] \tag{4}$$

Termination:

$$\mathrm{R}_n\cdot + \mathrm{Z} \rightarrow \mathrm{R}_n\mathrm{Z}$$

$$R_{\mathrm{t}} = k_{\mathrm{t}}\, [\mathrm{R}_n\cdot]\, [\mathrm{Z}] \tag{5}$$

In the scheme M is ethylene monomer, S is *tert*-butyl alcohol, $\mathrm{R}_n\cdot$ is all the active polymer chain composed of n monomers, Y is the substance to which the activity of $\mathrm{R}_n\cdot$ is transferred, Z is the substance by which $\mathrm{R}_n\cdot$ is deactivated, P_n is a dead polymer composed of n monomers, M* is the excited ethylene monomer M_2^* is the excited ethylene dimer, f_{M} is the fugacity of ethylene monomer, $f_{\mathrm{M}2}^{*}$ is the fugacity of excited ethylene dimer, R_{i}, R_{p}, R_{tr}, and R_{t} are the rates of initiation, propagation, transfer, and termination, k_{p}, k_{tr}, and k_{t} are the rate constants of these reactions, ρ_{M} and ρ_{S} are the densities of ethylene and *tert*-butyl alcohol, respectively, $[\mathrm{R}_n\cdot]$, [Y], and [Z] are the concentrations of substances $\mathrm{R}_n\cdot$, Y, and Z, respectively, K_{e} is the equilibrium constant of the reaction between M and M* and I is the dose rate.

The continuous increase in polymerization rate and in molecular weight with time indicates that the kinetics of nonstationary polymerization[6] should be applied to the polymerization in *tert*-butyl alcohol. Since both ethylene and *tert*-butyl alcohol are excited by gamma-rays, and an energy transfer between them may take place, the rate of initiation is reasonably

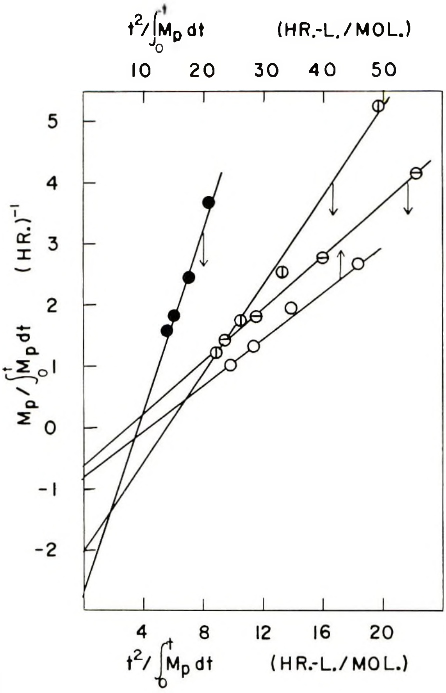

Fig. 6. $M_p/\int_0^t M_p\,dt$ versus $t^2/\int_0^t M_p\,dt$. Reaction conditions same as in Figure 1.

expressed as a function of the densities of both ethylene and *tert*-butyl alcohol; see eq. (1).

From the long-chain approximation the overall polymerization rate, R, is given as

$$R = R_p = k_pK_e[R_n^\cdot]f_M^2 \tag{6}$$

The concentration of active polymer chain, $[R_n^\cdot]$, is expressed as

$$[R_n^\cdot] = \int_0^t R_i\,dt - \int_0^t R_t\,dt = \int_0^t R_i\,dt - \int_0^t k_t[R_n^\cdot][Z]\,dt \tag{7}$$

where t is time and $[Z]$ is assumed to be constant throughout the polymerization. From eq. (6) the value of $[R_n^\cdot]$ is shown to be

$$[R_n^\cdot] = R_p/k_pK_ef_M^2 \tag{8}$$

When eq. (8) is introduced into eq. (7) and the integral terms are calculated, eq. (9) is obtained:

$$[R_n^\cdot] = R_it - (k_t[Z]/k_pK_ef_M^2)M_p \tag{9}$$

In this equation M_p represents polymer yield at time t $\left(\text{that is, } M_p = \int_0^t R_p\,dt\right)$ and f_M is considered to be independent of the reaction time, since the polymerization was carried out to low conversion, was stated earlier. Combining eqs. (6) and (9) results in

$$R_p = k_p K_e f_M^2 R_i t - k_t[Z]M_p \tag{10}$$

Integrating this equation and rearranging it gives

$$M_p \Big/ \int_0^t M_p\, dt = \tfrac{1}{2}\, k_p K_e f_M^2 R_i \left(t^2 \Big/ \int_0^t M_p\, dt \right) - k_t[Z] \tag{11}$$

Accordingly, the plots of $M_p / \int_0^t M_p\, dt$ versus $t^2 / \int_0^t M_p\, dt$ should be on a straight line. These plots are given in Figure 6. The value of $k_t[Z]$ can be obtained from the intercept on the ordinate, and the slope of the line represents the value of $\frac{1}{2} k_p K_e f_M^2 R_i$.

Degree of Polymerization. The degree of polymerization, $\bar{P}_n$, for the polymerization with no termination by recombination is expressed by

$$\bar{P}_n = \int_0^t R_p\, dt \Big/ \left(\int_0^t R_i\, dt + \int_0^t R_{tr}\, dt \right) \tag{12}$$

From eqs. (1), (4), (8), and (12) the reciprocal degree of polymerization, $1/\bar{P}_n$, is given by

$$1/\bar{P}_n = R_i t / M_p + k_{tr}[Y] / k_p K_e f_M^2 \tag{13}$$

where [Y] is assumed to be constant throughout the polymerization. By plotting $1/\bar{P}_n$ against t/M_p linear relations are obtained for every condition, as shown in Figure 7. The slope of the line represents the overall rate of initiation, R_i. In Figure 7 all lines are found to go through the origin; that is, all the values of $k_{tr}[Y]/k_p K_e f_M^2$ are zero. This means that the rate of transfer is negligible in this polymerization. The value of $k_p K_e f_M^2$ can be

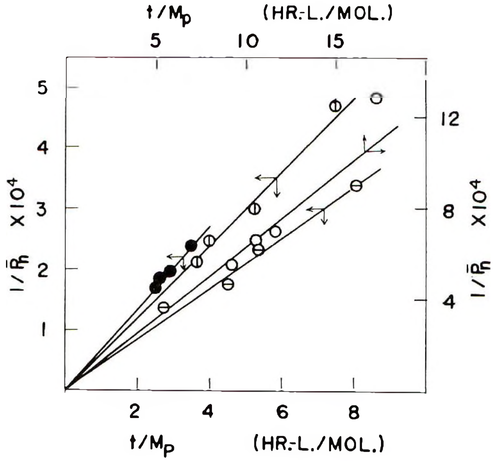

Fig. 7. $1/\bar{P}_n$ versus t/M_p. Reaction conditions same as in Figure 1.

obtained from the slopes of the lines given in Figures 6 and 7 by using eqs. (11) and (13).

The values determined according to this procedure are summarized in Table V.

TABLE V

Values[a] of R_i, $k_pK_ef_M^2$, and $k_t[Z]$

Pressure, kg/cm²	*tert*-Butyl alcohol, ml	R_i,[b] $\times 10^5$ mol/l-hr	$k_pK_ef_M^2$,[c] $\times 10^{-3}$ hr^{-1}	$k_t[Z]$,[d] hr^{-1}
120	30	6.36	2.49	0.80
300	30	6.00	12.9	2.00
400	30	7.00	23.1	2.78
300	13	4.29	11.8	0.60

[a] Reaction conditions: temperature, 30°C; dose rate, 2.5 × 10^4 rad/hr; reactor volume, 100 ml.

[b] Overall initiation rate.

[c] Product of rate constant k_p of the propagation, equilibrium constant K_e of reaction forming exited ethylene dimer, and square of ethylene fugacity f_M.

[d] Product of rate constant of the termination (k_t) and concentration of terminator ([Z]).

Initiation Reaction. As shown in Table V, the overall rate of initiation of the polymerization in *tert*-butyl alcohol increases with the amount of *tert*-butyl alcohol and the reaction pressure. The rate of initiation of the bulk polymerization has been reported to be represented as follows:[4]

$$R_{im} = k_{im} I \rho_M \tag{14}$$

where R_{im} and k_{im} are the rate and the rate constant of the initiation with ethylene. If k_{im} is not affected by *tert*-butyl alcohol, then in the presence of

TABLE VI

Rate and Rate Constant of Initiation[a]

Pressure, kg/cm²	*tert*-Butyl alcohol, ml	R_{im},[b] $\times 10^5$ mol/l-hr	R_{is},[c] $\times 10^5$ mol/l-hr	k_{is},[d] $\times 10^{10}$ rad^{-1}
120	30	1.37	4.99	5.83
300	30	1.59	4.41	5.15
400	30	1.67	5.33	6.24
300	13	1.92	3.42	6.87
300	0	—	—	0.465[e]

[a] Reaction condition: temperature, 30°C; dose rate, 2.5 × 10^4 rad/hr; reactor volume, 100 ml.

[b] Rate of initiation with ethylene.

[c] Rate of initiation with *tert*-butyl alcohol.

[d] Initiation rate constant with *tert*-butyl alcohol.

[e] Value of k_{im} from Machi et al.[4]

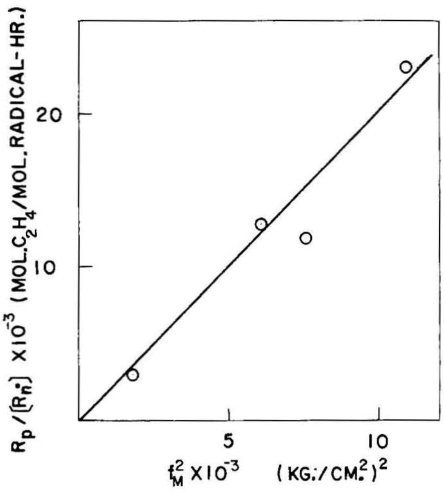

Fig. 8. Absolute propagation rate $R_p/[R_n]$ versus square of ethylene fugacity, f_M^2. Reaction temperature, 30°C; dose rate, 2.5 × 10^4 rad/hr; reactor volume, 100 ml.

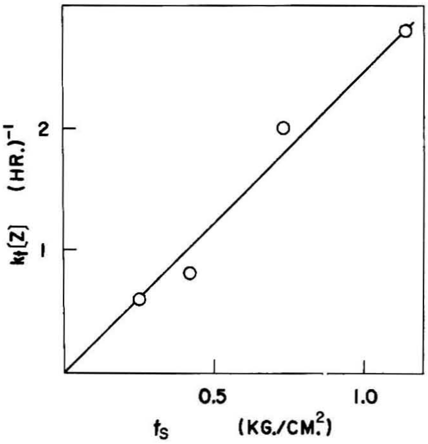

Fig. 9. Product of termination rate constant and concentration of terminator, $k_t[Z]$, versus fugacity of *tert*-butyl alcohol, f_s. Reaction conditions same as in Figure 8.

the alcohol R_{im} can be calculated by using the value of k_{im} determined from the data of the bulk polymerization,[4] and the rate of initiation with *tert*-butyl alcohol, R_{is}, can be evaluated as the difference between the overall initiation rate and R_{im}. The values of R_{im} and R_{is} calculated on the basis of this assumption are listed in Table VI.

As was mentioned, since the transfer is not observed, and the termination is first-order with respect to the concentration of growing radicals, the number of polymer chains per unit time is equal to the overall initiation rate. Since the number of moles of polymer chain increases almost proportionally with dose rate, as shown in Figure 5, the overall rate of initiation is found to be proportional to the dose rate. From this fact and from eq.

(14) the value of R_{is} also is considered to be proportional to the dose rate. These results indicate that the overall rate of initiation may be represented as follows:

$$R_i = R_{im} + R_{is} = I(k_{im}\rho_M + k_{is}\rho_S) \tag{15}$$

As shown in Table VI, the value of k_{is} calculated with eq. (15) is nearly ten times that of k_{im}.[4] These facts are consistent with the fact that the G_R values (G value for free-radical production) of such alcohols as methyl and isopropyl alcohols, 24.0 and 30.0,[7] are about ten times that of ethylene, 1.6;[4] and G value of the decomposition of *tert*-butyl alcohol is equal to those of methyl and isopropyl alcohols.[8]

Propagation Reaction. The value of $k_pK_ef_M^2$ given in Table V is equal to the absolute propagation rate, $R_p/[R_n^\cdot]$/(mol C_2H_4/mol radical hr). As is shown in Figure 8, $R_p/[R_n^\cdot]$ is proportional to the square of ethylene fugacity, f_M^2. This means that the mechanism of the propagation reaction is similar to that of the bulk polymerization.

Termination Reaction. As may be seen in Table V, the value of $k_t[Z]$ increases with the amount of *tert*-butyl alcohol and the reaction pressure. Figure 9 shows that $k_t[Z]$ is proportional to the fugacity f_s of *tert*-butyl alcohol. This indicates that the growing radical is terminated by the *tert*-butyl alcohol. In other words, the termination is considered to be a kind of degradative chain transfer.

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Olefin Polymerizations and Copolymerizations with Aluminum Alkyl–Cocatalyst Systems. I. Cocatalysis with Brönsted Acid Systems*

J. P. KENNEDY, *Central Basic Research Laboratory,*
Esso Research and Engineering Company, Linden, New Jersey 07036

Synopsis

Certain aluminum alkyls and aluminum dialkyl halides in conjunction with suitable simple cocatalysts generating proton or carbonium ion exhibit high polymerization activity and produce high molecular weight polyolefins, diolefins and/or copolymers at comparatively high temperatures. In this paper we report our investigations with $AlEt_2Cl$–Brönsted acid systems used for polymerizing isobutylene and copolymerizing isobutene–isoprene mixtures for high molecular weight products. The cocatalyst is not specific in these reactions. Highly active systems can be obtained with HCl, HBr, CCl_3COOH, etc. Evidently proton donors in general (Brönsted acids) may function as cocatalysts in this system. The sequence of polymerization initiation activity of various Brönsted acids in conjunction with $AlEt_2Cl$ is HCl, HBr $\gg$ HF, H_2O > CCl_3COOH $\gg$ CH_3OH > CH_3COCH_3. The effect of temperature on the molecular weights was studied. In contrast to linear plots of log molecular weight versus $1/T$, obtained for polyisobutylene or isobutylene–isoprene copolymers with conventional Friedel-Crafts halides in the −30 to −100°C range, this Arrhenius plot showed a marked maximum near −70°C for polymers prepared with $AlEt_2Cl$–HCl catalyst systems. Features of this polymerization reaction are discussed.

INTRODUCTION

During the last few years great progress has been made in the understanding of the mechanism of low-temperature cationic polymerizations in general and the isobutylene–$AlCl_3$ system in particular.[1-3] Some time ago we discovered that high molecular weight polyisobutylenes and isobutylene–isoprene copolymers (butyl rubbers) can be prepared at comparatively high temperatures with certain aluminum alkyl halide catalysts in the presence of suitable cocatalysts.[4] This paper describes experimental studies directed toward the characterization and development of novel, homogeneous, cationic catalyst systems, i.e., catalysts soluble in hydrocarbons, alkyl halides, etc. and giving high molecular weight polyisobutylenes and isobutylene–diene copolymers in the temperature range −30 to −70°C. Commercial isobutylene–isoprene copolymerizations (butyl rubber) are

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carried out in alkyl halide solvents in the presence of $AlCl_3$ catalyst at $-100°C$.

Soluble polymerization catalyst systems offer a number of advantages over their insoluble counterparts (ease of catalyst preparation, ease of catalyst concentration control, improved catalyst uniformity and reproducibility, convenient catalyst storage, handling, etc.). Other more subtle problems might also arise with sparingly soluble catalysts (e.g., $AlCl_3$). Since $AlCl_3$ is insoluble in hydrocarbon-rich methyl chloride mixtures, it is conceivable that immediately after catalyst introduction into a polymerization system containing a large amount of olefin $AlCl_3$ precipitation occurs. This precipitation cannot be observed, because polymerization ensues instantaneously. However, precipitation becomes noticeable when $AlCl_3$ dissolved in methyl chloride is introduced into an isobutane–methyl chloride mixture, e.g., a mixture in which the isobutylene monomer has been replaced with isobutane. Further, the precipitating polyisobutylene molecule encapsulates active catalyst and thus lowers catalyst efficiencies and creates an ill-controlled situation.

Conventional solid $AlCl_3$ always contains small amounts of unidentified hydrolysis products ($AlCl_2OH$, $AlOCl$, etc.) and HCl. These materials undoubtedly affect the mechanism of polymerization, but the mode of interference is largely unknown.

Newly discovered aluminum alkyl halide—cocatalyst systems such as $AlEt_2Cl/HCl$ eliminate these problems and in addition provide excellent high molecular weight products at higher temperatures than was possible before.

The $AlEt_2Cl$–HCl system is a soluble, highly active polymerization initiator. The $AlEt_2Cl$ catalyst can be purified readily (distillation and complexing with NaCl to remove traces of $AlEtCl_2$), it is miscible in all proportions with hydrocarbons, lower alkyl chlorides, and CS_2, and in dilute solutions its freezing point can be lowered to $-130°C$.

The literature concerning pure aluminum dialkyl halide catalyst systems is quite meager. Aluminum dialkyl halides have been used in the polymerization of vinyl ethers.[5] Two patents[6,7] disclosed the synthesis of high molecular weight polyisobutylene with the use of $AlEt_2Cl$ alone. Russian workers[8] investigated the polymerization of various olefins and diolefins with AlR_2Cl–cocatalyst systems. These investigators used CH_3COOH and hydrated salts such as $LiCl \cdot XH_2O$ and $MgCl_2 \cdot XH_2O$ as cocatalyst.

This paper concerns studies carried out with various $AlEt_2Cl$–Brönsted acid catalyst combinations to give high molecular weight polyisobutylenes and isobutylene–isoprene copolymers (butyl rubber).

EXPERIMENTAL

All experiments were carried out under nitrogen atmosphere in a stainless-steel enclosure.[9] The purity and analysis of isobutylene, methyl chloride, aluminum chloride,[10] and ethyl chloride[9] have been described.

Isoprene was freshly distilled before use. $Al(C_2H_5)_2Cl$ (Texas Alkyls, Inc.) was freshly distilled and treated with NaCl at 80°C for 2 hr to remove traces of $AlEtCl_2$.

RESULTS AND DISCUSSION

Comparison of Cocatalysts

Olefins such as isobutylene and styrene or diolefins such as butadiene and isoprene or mixtures of these monomers in bulk or in solution can be stirred in the presence of $AlEt_2Cl$ in the temperature range +30 to −100°C without any reaction. However, polymerization commences instantaneously when small amounts of HCl, HBr, or other Brönsted acids are introduced into the quiescent mixture. Depending on the amount of cocatalyst added, a smooth controlled polymerization or, with large amounts of cocatalyst, very fast reactions, even explosions, can be obtained.

The cocatalyst is not specific in this reaction. Similar results were obtained with HCl, HBr, CCl_3COOH, H_2O, CH_3OH, etc. In fact, it seems that in agreement with the theory of cocatalysis in cationic polymerizations proton donors (e.g., Brönsted acids) in general can act as cocatalysts. This system is ideally suited to cocatalyst research. Polymerization starts only when cocatalysts are added, and chemical manipulations can be carried out conveniently and rapidly in an enclosure.

Table I shows some results for isobutylene–isoprene (3 vol-%) mixtures. Table II gives physical properties of the vulcanized copolymers (butyl rubbers) whose syntheses are described in Table I.

Thus, experiments 1 and 2 show that no polymerization takes place in mixtures of isobutylene–isoprene (3 vol-%), methyl chloride, and $AlEt_2Cl$; however, polymerization commences immediately when traces of HCl are added.

Similar results were obtained in experiments 3 and 4 with ethyl chloride diluent. Ethyl chloride (treated with molecular sieves and BaO) always contains appreciable amounts of HCl coming from the manufacturing process. When ethyl chloride is first purified by refluxing over KOH pellets and then used as the diluent (experiment 4, Table I), the polymer yield decreases significantly. However, even with highly purified ethyl chloride slow isobutylene polymerization proceeds (this finding will be treated in more detail in a forthcoming publication). By contrast, no polymerization at all occurs in pure methyl chloride as solvent. However, immediate and vigorous polymerization commences in methyl chloride diluent as soon as small amounts of HCl are introduced.

Montecatini patents[6,7] claim that polymerization of isobutylene can take place only in solvents of dipole moments higher than 1 (e.g., ethyl chloride and chlorobenzene). According to these claims, no polymerization can take place in hydrocarbon solvents. Contrary to this our results show that the dipole moment of the diluent does not affect the success or failure of the polymerization, and the reaction can be initiated with greatest velocity in

TABLE I

Polymerization of Isobutene–Isoprene (3 vol-%) Mixtures with $AlEt_2Cl$ Catalyst[a]

Expt. No.	Diluent	Conc., ml	Temp.,[b] °C	React. cond.	Cocatalyst solution	Observations, Remarks	Yield		Mol. wt.[b] ($\times 10^{-3}$)	Unsat.-mol-%
							g	%		
1	CH_3Cl	100	-50	monomers added dropwise to catalyst and solvent charge	none	no polymn. (90 min)	—	—	—	—
2	CH_3Cl	75	-75 ↑	monomers and catalyst stirred for 10 min	1 ml of CH_3Cl containing 4×10^{-3} mol of HCl	explosive polymn. on HCl addition	—	100	↑	—
3	C_2H_5Cl	100	-50	monomer feed added dropwise to catalyst and solvent	undetermined amount of HCl in C_2H_5Cl	slow polymerization	54.5	72.0	465	—
4	C_2H_5Cl	100	-50	as in expt. 3, except C_2H_5Cl treated with KOH to remove HCl	C_2H_5Cl treated with KOH	very slow polymn. for 100 min	11.0	16	447	2.0
5	C_2H_5Cl	250	-45	as in expt. 3	as in expt. 3	slow polymn. for 60 min	34.5	48.5	330	—
6	n-pentane	100	-50 ↑	as in expt. 3	0.07 ml of *n*-pentane containing 1.5×10^{-4} mol of HCl	explosive polymerization on HCl addition	—	≈100	↑	—

7	CS_2	100	−50 ↑	as in expt. 3	small amount of HCl in 0.07 ml of CH_3Cl	immediate reaction on HCl addition	—	high	↑	—
8	CH_3Cl	100	−75 ↑	monomer feed + catalyst stirred for 60 min	0.025 mol of HF in 20 ml of CH_3Cl added	immediate polymn. on HF addition, run for 60 min	56.0	80	↑	—
9	CH_3Cl	100	−50 ↑	as in expt. 3	about 1 ml of CH_3Cl containing $\approx 1.3 \times 10^{-4}$ mol of HBr added	immediate polymn. on HBr addition, run for 2 min	7.0	9.9	↑	—
10	CH_3Cl	100	−50	as in expt. 3 no polymn. for 300 min	0.4 ml of CH_3Cl containing 2.2×10^{-4} mol of CH_3COOH added	immediate slow polymn. started; run for 90 min	13.0	18.3	144	1.48
11	CH_3Cl	87.6	−100	as in expt. 3	H_2O saturated stream of N_2	slow polymn. of H_2O–N_2 introduction	15.0	21.0	471	1.43
12	CH_3Cl	100	−50	as in expt. 3	25 ml of CH_3Cl containing 1.87×10^{-3} mol of CH_3OH	immediate initiation (haziness) on CH_3OH addition, very slow polymn. (245 min)	0.81	1.1	271	1.46
13	CH_3Cl	100	−50	as in expt. 3	25 ml of CH_3Cl containing 1.36×10^{-2} mol of CH_3COCH_3	slow initiation on CH_3COCH_3 addition (polymn. for 180 min)	0.06	0.1	151	—

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[a] Conditions: monomer mixture (97 ml of isobutene + 3 ml of isoprene) stirred in the presence of 0.01 mol of $AlEt_2Cl$ for about 30 min; cocatalyst solution added to the quiescent mixture; polymerization terminated by introducing precooled methanol.

[b] Arrow indicates temperature runaway; consequently, molecular weights would be meaningless.

TABLE II
Physical Properties of Polymers Described in Table I[a]

	Mooney viscy., 8 min, 212 °F	Cure 30 min at 308°F			Cure 60 min at 308°F		
		300% Mod., psi	Tensile, psi	Elong., %	300% Mod., psi	Tensile, psi	Elong., psi
Enjay Butyl 218							
avg. of 5 tests	≈70	805	2905	632	1257	2824	553
3	67	1200	2550	700	1400	2600	600
5	79	1200	3057	600	1615	3000	497

[a] Cure recipe (in parts): polymer 100, HAF 50, ZnO 5, stearic acid 2, S 1.25, Tuads 1.

solvents whose dipole moment is certainly much less than 1, such as in hydrocarbons (*n*-pentane) or CS_2, provided a suitable cocatalyst is present (see experiments 6 and 7, Table I), or polymerization can be completely excluded in solvents whose dipole moment is much higher than 1 provided the proton or carbonium ion generating cocatalyst is absent.

Good product quality and easily controlled reactions were obtained in experiments with water as cocatalyst (experiment 6, Table I). The introduction of water as cocatalyst presented some problems, since these experiments were run much below the freezing point of water, and the solubility of water in hydrocarbon–methyl chloride mixtures is extremely low. After some preliminary experimentation we learned how to introduce water in an extremely finely dispersed form to obtain an efficient catalyst system. Thus, a moisture-laden nitrogen stream was passed into the stirred cold reaction mixture. This technique can be used even at −80 or −100°C. The velocity of gas stream determines the water dispersion. Reaction control is conveniently attained by adjusting the rate of introduction of cocatalyst. The extent of conversion depends on the amount of cocatalyst introduced.

Experiments with trichloroacetic acid cocatalyst gave fundamentally similar results. Polymerization initiation was immediately noticeable by the haziness developing on cocatalyst introduction, but no heat evolution occurred, and the rate of the reaction was much slower than observed in previous runs with hydrogen halides.

In experiments 12 and 13 methanol and acetone were used as cocatalyst, respectively. With methanol immediate initiation occurred (haziness); however, polymerization was extremely slow with acetone as cocatalyst.

These results are qualitatively summarized in Table III. The cocatalyst concentrations are approximate, since it was difficult to determine such low quantities accurately under the experimental conditions employed. Reaction times vary because termination times were judged subjectively or were dictated by external factors. Yields are expressed as approximate conversions usually obtained with a particular cocatalyst. It is significant that explosive polymerizations were obtained only with HCl or HBr

TABLE III
Cocatalytic Efficiency of Brönsted Acid in Conjunction with $AlEt_2Cl$ Catalyst

Cocat.	Approx. conc., mol	Reaction time, min	Order of magn. of yields	Polymn. rate
—	—	—	—	no reaction
HCl	10^{-4}	<1	100	very fast
HBr	10^{-4}	<1	100	very fast
HF	10^{-2}	150	80	medium
H_2O	?	60	80	medium
CCl_3COOH	10^{-4}	90	20	medium
CH_3OH	10^{-3}	250	1	slow
CH_3COCH_3	10^{-2}	180	0.1	extremely slow

cocatalysts. However, these reactions can easily be slowed down by diluting the cocatalyst. The rates obtained with less active cocatalysts cannot be accelerated by employing higher concentrations, since at higher concentrations ill-define side reactions start to compete.

These results provided the basis of a qualitative series of cocatalytic efficiencies for the polymerization of isobutylene–isoprene mixtures in conjunction with $AlEt_2Cl$ catalyst at low temperatures:

$$HCl, HBr \gg HF, H_2O > CCl_3COOH \gg CH_3OH > CH_3COCH_3$$

This sequence follows approximately the acidity function of the materials involved. It is peculiar that water appears to be more effective than CCl_3COOH. Acetone possibly acts as a proton donor through its enolic form (or perhaps traces of some unidentified acidic impurity provided the cocatalyst).

Effect of Temperature

The effect of temperature on the molecular weight of polyisobutylene and isobutylene–isoprene copolymers has been investigated extensively.[2] The molecular weight of polyisobutylene is much higher than that of isobutylene–isoprene copolymers obtained under essentially identical experimental conditions.[2] The plot of log molecular weight versus $1/T$ of polymers prepared with conventional Friedel-Crafts catalysts is linear in the temperature range -30 to -100°C. By contrast, this plot of the Arrhenius type with polymers obtained in the presence of the $AlEt_2Cl^-$ cocatalyst system shows a marked maximum at about -70°C. Figure 1 shows the effect of temperature on the logarithm of molecular weights of isobutylene–isoprene copolymers obtained with $AlCl_3$, $AlEtCl_2$, and $AlEt_2Cl$–HCl cocatalyst systems, respectively. (These runs were carried out by a semicontinuous technique, i.e., by adding the monomer feed and the catalyst solutions separately to a stirred reservoir of pure methyl chloride solvent. With the $AlEt_2Cl$/HCl run the monomer and $AlEt_2Cl$ were mixed and introduced separately but simultaneously with a HCl cocatalyst stream.) Significantly, isobutene–isoprene copolymers prepared with the $AlEt_2Cl$–HCl system have much higher molecular weights at the same temperature level in the range of −30 to −70°C than copolymers obtained with the conventional catalysts. For example, the molecular weight of a copolymer prepared with $AlEt_2Cl$-HCl at −60°C is ≈250,000, whereas that produced with $AlCl_3$ or $AlEtCl_2$ catalysts is only ≈70,000. All these copolymers contained about 1.5 mole-% unsaturation (e.g., isoprene units) at low conversions. Even higher molecular weights and correspondingly excellent vulcanizates can be obtained by the conventional technique.

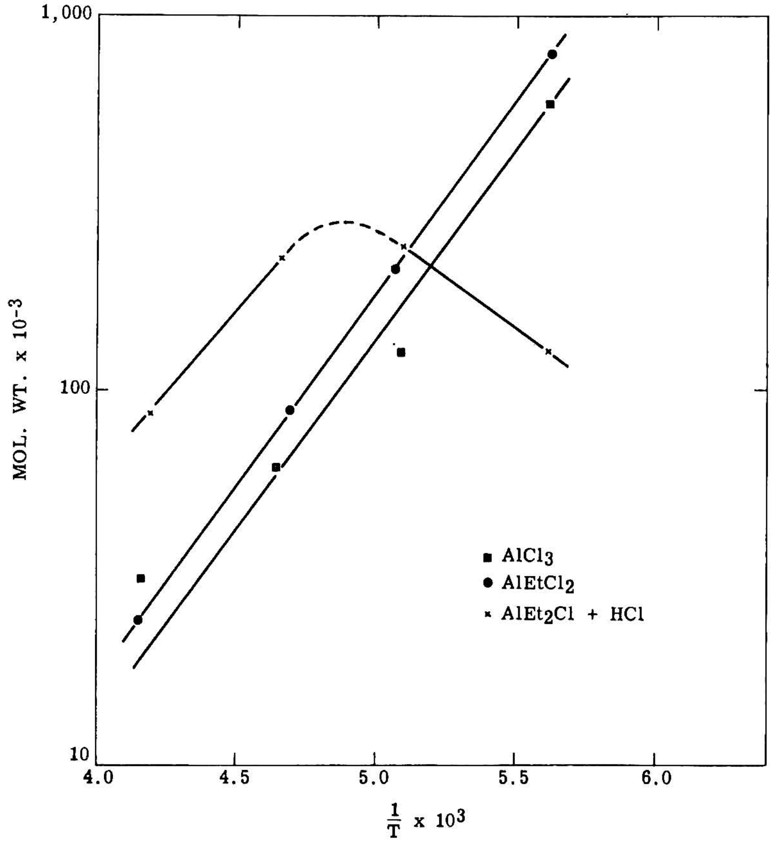

Fig. 1. Dependence of molecular weight of isobutylene–isoprene copolymers on reciprocal temperature, obtained with $AlCl_3$, $AlEtCl_2$, and $AlEt_2Cl$-HCl in MeCl solvent.

Thus in another series of experiments two monomer concentration charges (2.89 and 9.69 mol/l) of isobutene–isoprene (3 vol-%) were mixed with $AlEt_2Cl$ and stirred in methyl chloride at various temperatures. Polymerization was initiated by introducing HCl in methyl chloride solution (e.g., conventional technique). Temperature control was extremely difficult with the high monomer concentration charge. Table IV and Figure 2 show the results, and Table V gives physical properties of vulcanized copolymer samples obtained at −65, −78, and −85°C of the high monomer concentration series.

TABLE IV
Copolymerization of Isobutylene–Isoprene Mixtures with $AlEt_2Cl$–HCl Initiator System at Various Temperatures[a]

Monom. conc., mol/l	Temp.,[b] °C	Cocat. added, mols HCl (× 10^3)	Yield g	Yield %	Mol. wt. (× 10^{-3})	Unsatn., mol-%
2.89	−30	0.25	7	33.3	73	1.50
2.89	−48	0.51	16	75	—	1.68
2.89	−63	0.31	11	51.5	101	1.69
2.89	−76	0.48	13.5	63.5	127	1.60
2.89	−83	0.52	8.5	39.9	149	1.6
2.89	−96	0.96	3.5	16.4	69	1.49
9.69	−35 (−24)	0.052	14.5	20.5	143	1.41
9.69	−50 (−28)	0.067	20.0	28.1	168	1.33
9.69	−65 (−55)	0.045	21.0	30	397	1.49
9.69	−78 (−72)	0.031	9.5	13.5	626	1.44
9.69	−85 (−77)	0.052	20.0	28.1	561	1.43
9.69	−100 (−96)	0.66	19.5	27.9	167	1.51

[a] Conditions: charges were (first six runs) 97 ml of isobutylene + 3 ml of isoprene + 30 ml of methyl chloride + 0.005 mol of $AlEt_2Cl$ and (second six runs) 29.1 ml of isobutylene + 0.9 ml of isoprene + 100 ml of methyl chloride + 0.005 mol of $AlEt_2Cl$; charges stirred at selected temperature, then cocatalyst solution (0.024 mol/l of HCl in methyl chloride) added dropwise.

[b] Temperatures in parentheses are maximum temperatures reached during run.

TABLE V
Physical Properties of Isobutene–Isoprene Copolymers (Butyl Rubbers)[a] Prepared with $AlEt_2Cl$–HCl Catalyst

	30 min at 308°F			60 min at 308°F		
Temp. of synthesis, °C.	300% Mod., psi	Tens., psi	Elong., %	300% Mod., psi	Tens., psi	Elong., %
−65 to −55	981	2898	633	1385	2969	535
−78 to −72	517	2677	740	776	2690	680
−85 to −77	1083	2970	623	1557	3067	550

[a] Cure recipe as in Table II.

Interestingly, the curves of molecular weight versus $1/T$ in Figures 1 and 2 show pronounced maxima and, moreover, the molecular weight maximum seems to depend on the monomer concentration employed. According to Figure 2, highest molecular weight product is obtained at about −70°C with a monomer concentration of 9.69 mol/l, but the maximum shifts to about −85°C with a monomer concentration of 2.89 mol/l. In contrast to this phenomenon, with conventional catalysts such as $AlCl_3$, BF_3, and $AlEtCl_2$ the molecular weight versus $1/T$ is linear in the temperature range of −35 to −100°C; at −100°C there is a break in the line, and the line assumes a lesser slope but does not drop.[2]

TABLE VI
Isobutene–Isoprene Copolymerizations in Bulk[a]

Monomer charge, ml		AlEt$_2$Cl	Cocatalyst soln.[b]		AlEt$_2$Cl–	Yield		Mol. wt.	Gel,	Unsatn,
Isobutene	Isoprene	mol	ml	mol HCl ($\times 10^{-3}$)	HCl, mol	g	%	($\times 10^{-3}$)	%	mol-%
96	3	0.02	3	0.0042	4760	9.0	12.0	544	9.2	1.9
95	5	0.02	100	0.14	143	28.0	20.0	323	4.7	3.21
92	8	0.02	100	0.14	143	18.0	13.5	211	70	5.42

[a] Conditions: all experiments at −98°C; cocatalyst solution added last.

[b] Cocatalyst solution prepared by absorbing dry HCl gas in the particular monomer mixture used.

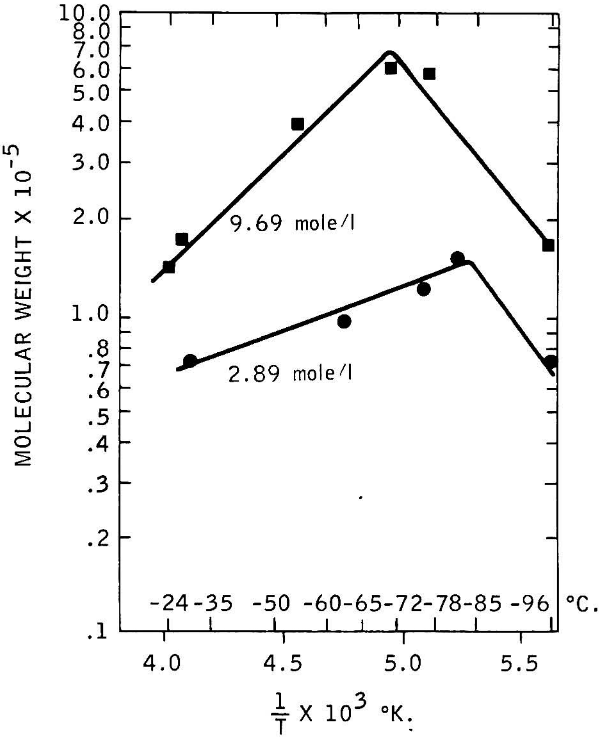

Fig. 2. Dependence of molecular weight of isobutylene–isoprene copolymers on reciprocal temperature, obtained with $AlEt_2Cl$–HCl initiator system at various monomer concentrations.

Isobutene–Isoprene Copolymerizations in the Absence of Solvent

Isobutene–isoprene copolymerizations were carried out with charges containing, 3, 5, and 8 vol-% isoprene in the absence of solvent, i.e., with the unreacted monomers as diluent. Rate of reaction and conversion can be controlled by judicious cocatalyst introduction. Table VI shows representative data. The physical properties of vulcanizates were excellent.

In these experiments the catalyst was added to the monomer charge, and the cocatalyst (HCl) was absorbed in a separate batch of the particular monomer mixture (undiluted monomers) charged in the reactor. This monomer–cocatalyst mixture then was added to the quiescent monomer–catalyst charge. By controlling the rate of introduction or the concentration of the monomer–cocatalyst mixture very vigorous (explosive) or slow reactions can be maintained. All these experiments were carried out at −98°C, and the polymerization was "quasihomogeneous"; e.g., the product was partially in solution and grew probably in the swollen phase. It does not seem to be possible to conduct completely homogeneous butyl polymerizations even in very dilute hydrocarbon solvent system at −98°C.

Apparently, high molecular weight products are partially forced out of solution. The extent of the reaction was largely determined by the viscosity of the mixture. No serious heat problems were encountered at the conversion levels at which we terminated these reactions ($\approx 15\%$).

CONCLUSIONS

Cationically highly active monomers such as isobutylene, isoprene, and mixtures thereof may be made to come in contact with $AlEt_2Cl$ without polymerization initiation. However, on the introduction on even minute amounts of proton sources ($Al/HX \gg 1000$) immediate and vigorous polymerization commences.

It is highly unlikely that $AlEtCl_2$ formed in the reaction $AlEt_2Cl + HCl \rightarrow AlEtCl_2 + Et$ is responsible for initiation. The true initiating species is probably the proton generated by $AlEt_2Cl + HCl \rightarrow H^{\oplus}AlEt_2Cl^{\ominus}$. Studies concerning mechanism details will be published in subsequent papers.

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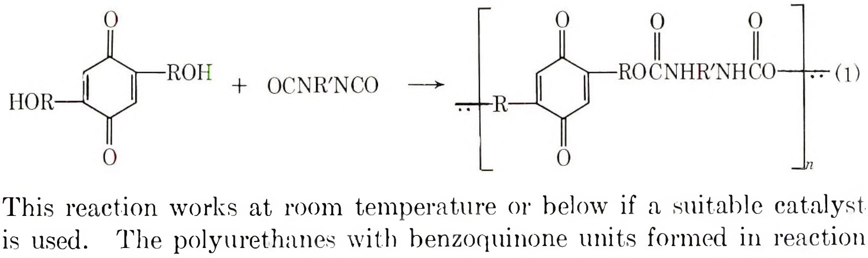
Electron-Transfer Polymers. XXXIV. Redox Polyurethanes from *p*-Benzoquinone-2,5-diols and Diisocyanates

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

Synopsis

It is possible to prepare polyurethanes from *p*-benzoquinone-diols and diisocyanates by using dibutyltin diacetate catalyst at room temperature or below, since the benzoquinone group does not react with isocyanate under these conditions. This permits preparation of new redox polymers. In preparing the polyurethanes excess isocyanate groups must be destroyed at the end of the reaction time in order to prevent crosslinking during work-up. These polymers are readily reduced by aqueous hydrosulfite. Good viscosity numbers are obtained; and, in general, upon reduction the viscosity increases over that of the oxidized form. There is no evidence of crosslinking. When oxidized and reduced forms of these polymers are mixed there is no evidence of charge transfer.

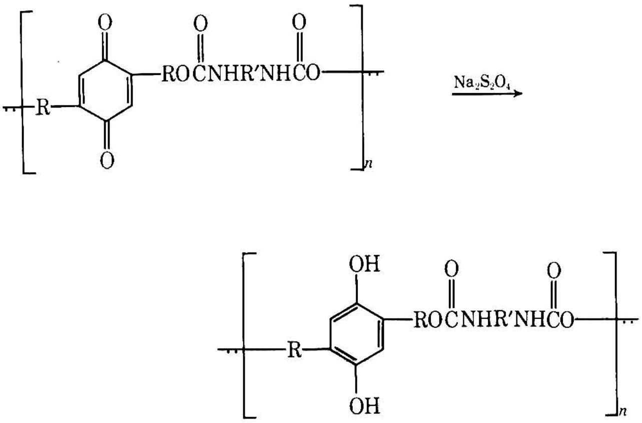
The purpose of this paper is to show that the oxidized form of a redox polymer may be prepared directly without using protecting groups during the polymerization step.[1] Since benzoquinones do not react with isocyanates at normal temperatures, it is possible to prepare polyurethanes from *p*-benzoquinonediols and diisocyanates according to eq. (1):



(1)

This reaction works at room temperature or below if a suitable catalyst is used. The polyurethanes with benzoquinone units formed in reaction (1) can easily be reduced according to eq. (2) by shaking a solution of the polymer in an organic solvent with a solution of sodium hydrosulfite in water (see top of next page). The urethane linkages are not attacked during reduction.

Preparation of 2,5-bis(2′-hydroxyethyl)-1,4-benzoquinone and 2,5-bis(3′-hydroxypropyl)-1,4-benzoquinone is described elsewhere.[2] The quinones were recrystallized from a mixture of acetone and *n*-hexane and dried *in vacuo* before use. Hexamethylenediisocyanate and methylene-



(2)

bis(4-phenylisocyanate) were distilled *in vacuo*. DDI-diisocyanate was used without further purification (supplier: General Mills, Chemical Division, Kankakee, Ill. 60901). Tetrahydrofuran (THF) was dried over sodium and distilled.

EXPERIMENTAL

Polycondensation, General Procedure

Benzoquinone-2,5-diol (5.00 mmole) and a diisocyanate (5.00 mmole) were dissolved together under strictly anhydrous conditions in 25 ml of THF. The mixture was placed in a water bath at 30°C and the catalyst was added. Care was taken to exclude moisture during the polycondensation step. Triethylamine or dibutyltin diacetate or a mixture thereof were used as catalysts. The reaction was stopped after the given time by pouring the reaction mixture into an excess of *n*-hexane. In an alternative method, 2.0 ml of ethanol was added at the end of the reaction time and the mixture then poured into *n*-hexane (Table I). The polymer precipitated from *n*-hexane as brown-yellow flakes. These were washed several times with *n*-hexane and then dried for 48 hr *in vacuo*.

Reduction, General Procedure

A 0.5-g portion of the polymer was dissolved in 25 ml THF previously saturated with concentrated ammonium chloride solution. This was shaken for about 5 min with two portions of a 10% solution of sodium hydrosulfite in THF-saturated ammonium chloride solution. The bright yellow color of the polymer solution turned colorless or faint yellow. The polymer solution in THF was washed with concentrated ammonium chloride solution and then precipitated from the 10-fold amount of distilled water. The filtered polymers formed white powders after drying over sulfuric acid *in vacuo*. Polymer 3 (Table II), being insoluble in THF was reduced by using 90% formic acid as solvent.

TABLE I

Polyurethanes from Benzoquinone-2,5-diols and Diisocyanates: Influence of Reaction Conditions upon Polymer Formation and Solubility[a]

No.	Diol[b]	Diiso-cyanate[c]	Catalyst		Reaction time, min[e]	Solubility after precipitation of polymer			Solubility after 48 hr drying		
			Type[d]	Vol, ml		THF	DMF	FA[f]	THF	DMF	FA[f]
1	I	HMDI	TEA DBTA	0.1 0.01	60	−	+	+	−	−	−
2	I	HMDI	TEA	0.1	20	+	+	+	+	+	+
3	I	HMDI	DBTA	0.05	15	−	+	+	−	−	+
4	I	MBPI	DBTA	0.01	40	+	+	−	+	+	−
5	II	MBPI	TEA	0.01	145	+	+	+	−	−	−
6	II	MBPI	DBTA	0.1	5	+	+	−	−	+	−
7	I	DDI	DBTA	0.05	360	+	+	−	+	+	−
8	II	DDI	DBTA	0.01	240	+	+	−	+	+	−

[a] Generally 5.0 mmole of each reactant was dissolved together in 25 ml THF at 30°C.

[b] I: 2,5-(2′-hydroxyethyl)-1,4-benzoquinone; II: 2,5-(3′-hydroxypropyl)-1,4-benzoquinone.

[c] HMDI: hexamethylenediisocyanate; MBPI: methylenebis(4-phenylisocyanate); DDI: OCN-R-NCO, where R is a C_{35} hydrocarbon group.

[d] TEA: triethylamine; DBTA: dibutyltin diacetate.

[e] The reaction was stopped with 2 ml ethanol in the cases of Nos. 2, 3, 4, 6, 7, 8.

[f] Formic acid.

TABLE II
Structure and Properties of Redox Polyurethanes from *p*-Benzoquinone-2,5-diols and Diisocyanates

					IR data, frequencies, cm^{-1}[f]			
No.[a]	State[b]	η_{sp}/c, cm^3/g[c]	UV data λ_m, $m\mu$[d]	$\epsilon \times 10^{-3}$[e]	Quinone	Amide I	Amide II	Amide III
3	Ox.	4.9	260	11.0[g]	1654 1660	1695	1540	1265
	Red.	12.8	299	3.9	none	1712 1660	1540	1268
4	Ox.	9.6	250	18.5	1655	1720	1538	1225
	Red.	17.7	292	4.3	none	1705	1530	1230
7	Ox.	16.8	256	14.8[h]	1660	1705	1540	1250[i]
	Red.	19.8	299	3.7	none	1695	1540	1265[i]
6	Ox.	—	252	21.2	1650 1655	1710	1530	1225
	Red.	15.8	292	4.4	none	1700	1525	1230
8	Ox.	21.1	258	16.9[h]	1651 1660	1690	1540	1260
	Red	25.4	298	4.9	none	1690	1530	1260[g]

[a] The structures are identified by the numbers in Table I.

[b] Ox. denotes the oxidized state, Red. the reduced state.

[c] In 95% THF, unless otherwise indicated, at 25.0°C, concentration = 5.0 g/l.

[d] In 95% THF.

[e] Molar extinction coefficient based on the repeating unit.

[f] Sample dissolved in KBr matrix.

[g] In 98% formic acid.

[h] In methylene chloride.

[i] Film cast from THF on NaCl plate. All samples prepared with dibutyltin diacetate as catalyst.

Measurements

Viscosities were measured with a Cannon-Fenske-Ostwald type viscometer. Ultraviolet data were obtained by using a Bausch and Lomb Spec-

TABLE III
Elemental Analyes of Polyurethanes

			Analysis					
			Calculated			Found		
Number			C,%	H,%	N,%	C,%	H,%	N,%
3	Ox.	$C_{18}H_{24}N_2O_6$	59.33	6.64	7.69	60.08	7.31	7.36
4	Ox.	$C_{25}H_{22}N_2O_6$	67.25	4.97	6.28	67.90	6.57	5.24
6	Ox.	$C_{27}H_{26}N_2O_6$	68.52	5.49	5.87	68.40	5.74	5.88
7	Ox.	$C_{48}H_{84}N_2O_6$	73.40	10.78	3.57	73.14	10.53	3.48
	Red.	$C_{48}H_{86}N_2O_6$	73.23	11.01	3.56	72.97	10.82	3.53
8	Ox.	$C_{50}H_{88}N_2O_6$	73.84	10.91	3.46	73.55	10.88	3.26
	Red.	$C_{50}H_{90}N_2O_6$	73.66	11.13	3.44	73.44	11.09	3.17

tronic 505 spectrometer; infrared data were obtained with a Perkin-Elmer Model 421 spectrometer. Elementary analyses are given in Table III.

DATA AND DISCUSSION

Table I shows the influence of reaction conditions upon polymer formation and solubility of the resulting polymers. In order to get stable polymers all excess isocyanate groups which are still present at the end of reaction time must be destroyed. Isocyanate groups would hydrolyze during work-up, giving amino groups. These amino groups react with the quinone units in the polymer backbone to produce crosslinks. The polymer then becomes insoluble. That is the reason why polymers 1 and 5 become insoluble rather quickly.

Triethylamine proved to be a rather sluggish catalyst, e.g., the molecular weight of polymer 2 (Table I) was very low. Dibutyltin diacetate, however, gave good results. Polymers formed with that catalyst showed good viscosity numbers (Table II). The yield was quantitative in all cases. THF was used as solvent because the more conventional DMAc gave more color in the product, DMSO is sensitive to oxidation, and was avoided on principle.

All polymers obtained in this work could be reduced quantitatively with sodium hydrosulfite, giving polyurethanes with hydroquinone units in the polymer backbone [eq. (2)]. In Table II viscosity numbers and spectra are compared for oxidized and reduced forms of several polyurethanes. Generally upon reduction viscosity increases. Thus far no indication has been found for any crosslinking during the reduction procedure. The increase in viscosity might indicate an increased hydrogen bonding due to interactions of the newly formed phenolic hydroxyls with the urethane links. Absorption maxima and extinction coefficients in the ultraviolet are not different from low molecular model substances. In the reduced polymers no quinone absorption can be detected in the ultraviolet, thus indicating a 100% conversion. The infrared spectra show the expected pattern[3] (Table II). In the spectra of the quinone groups containing polymers there are also bands around 1350, 1120, 1020, and 920 cm^{-1} due to the 2,5-substitution pattern at the benzoquinone ring.[4] Upon reduction these bands disappear, as well as the quinone carbonyl absorption around 1650 cm^{-1}. The bands due to the urethane linkages do not change their position very much. All polymers show a strong absorption around 3330 cm^{-1}, thus indicating hydrogen bonding through N—H groups.

Thus far no indication of charge-transfer interaction has been found upon mixing the reduced and the oxidized form of the polymers together, as has been described for other redox polymers.[1,5] Further work is in progress to evaluate the redox potential of the described polymers.

We thank Mr. T. Keyes for taking the infrared spectra and Mrs. Irmlind Stronkowski for technical assistance. The work was supported by a Research Grant GM 10864, Research Grants Branch, National Institute of General Medical Sciences, Public Health Service. We wish to express our thanks for this support.

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Vinyl Monomer Polymerization Mechanism in the Presence of Trialkylboranes

J. GROTEWOLD, E. A. LISSI, and A. E. VILLA, *Labóratorio Central de Química, Universidad Técnica del Estado, Santiago, Chile*

Synopsis

The polymerization of methyl methacrylate in the presence and in the absence of triethylborane and different inhibitors was carried out. An ethyl radical displacement reaction between the inhibitor radical (produced through the reaction between a radical chain and the inhibitor) and the triethylborane is postulated. This new chain-transfer reaction explains the large excess of inhibitor which must be added in the presence of triethylborane in order to suppress the production of high molecular weight polymer. The results are in agreement with a typical free-radical mechanism.

It has been suggested that the polymerization of vinyl monomers in the presence of organoboron compounds proceeds through the formation of a free-radical–organoboron complex.[1] This mechanism was postulated to explain the fact that, even in the presence of substantial amounts of free-radical inhibitors, polymerization occurred when trialkylboron compounds were present. There are, however, several reasons that make such a mechanism rather doubtful and still seem to favor a free-radical process:

(*1*) Nearly all of the inhibitors used are not very effective in methyl methacrylate polymerization (2,6-di-*tert*-butyl-*p*-cresol, hydroquinone, *N*-phenyl-1-naphthylamine).[2]

(*2*) It was found that the oxidation of alkylboron compounds proceeds through a free-radical process,[3] and this was the explanation of methyl methacrylate polymerization in the presence of trialkylboranes and oxygen.[4]

(*3*) We have found that free-radical displacement reactions occur with trialkylboranes.[5] They seem to be extremely fast when the attacking radical has an oxygen atom or resonance contribution, as would be the case with the radicals produced by hydrogen abstraction or addition to conjugated double bonds in the inhibitors. In none of Arimoto's runs did the ratio of inhibitors to trialkylborane seem to warrant the nondepletion of the inhibitor when such a displacement reaction occurred twice or even three times on each trialkylborane molecule.

For these reasons the polymerization of methyl methacrylate (MMA) in the presence and in the absence of trialkylborane and different inhibitors was studied. Special attention was given to the selection of inhibitors, which seemed to be a rather unfortunate one in Arimoto's work.[1]

Experimental

Commercial methyl methacrylate was washed with sodium hydroxide solution and distilled water. A certain amount (20 cm.^{3}) was then degassed and distilled into a container attached to a conventional high-vacuum system for gas kinetics. Attached to the vacuum system was a burette, for measuring the amount of MMA to be used, and the tubes containing the already weighed amounts of initiator and inhibitor. The monomer was then vacuum-distilled, first into the burette and then into the reaction tubes. The solids, which always contained a certain amount of air, were dissolved in the monomer and then degassed thoroughly (by repeated thawing and freezing) to less than 1.10^{-4} torr. When necessary, triethylborane, stored in the high vacuum apparatus, was added after having been measured by vaporizing a certain amount into a known volume and reading the corresponding pressure. The reaction tubes, about 7 cm.^{3} in volume, were then sealed under vacuum and placed in a thermostat at 70° ± 0.05°C. After the reaction had taken place, they were cooled to room temperature and broken off, and the mixtures were poured into a beaker containing 45 cm.^{3} of methanol and 5 cm.^{3} of concentrated ammonium hydroxide. The solid precipitate was filtered, washed, and dried at 50°C to constant weight. The molecular weight was determinated by specific-viscosity measurements with the parameters given by Flory[6] at 25°C. In all cases the reactants were commercially available reagents of analytical grade, with the exception of phenothiazine, which was prepared by the usual technique.[7] After two recrystallizations from ethanol its melting point was 186–187.5°C.

Results and Discussion

The experimental results obtained are shown in Table I. The polymer formed usually had a high molecular weight (about 1×10^5), the only exception being the products formed in runs 13–19, which had molecular weights of 1×10^4 or less; when water was added to the filtered liquid, which presumably consisted of methanol, ammonium hydroxide, and unreacted monomer, a small quantity of solid product was obtained, indicating the presence of extremely low molecular weight polymer, which was soluble in the original quenching mixture. The polymerization rate has nevertheless been calculated from the yield of solid obtained before the addition of water.

A higher molecular weight product (about 2.5×10^4) was observed, however, in run 15, in which the ratio of trialkylborane to benzoquinone was 0.91. This result is important in connection with the mechanism discussed below. In order to clarify the discussion it will be useful at this stage to mention the differences between Arimoto's work[1] and ours.

It is our opinion that his choice of inhibitors was inadequate: the results from the use of 2-6-di-*tert*-butyl-*p*-cresol with benzoyl peroxide as initiator or of hydroquinone or phenothiazine with peroxyboron compounds are by no means conclusive, as it is known that peroxides or peroxy radicals react readily with these substances, that is are antioxidants but not inhibitors.[2,8a,9]

TABLE I
Polymerization[a] of Methyl Methacrylate at 70°C

Run No.	Init. and concn., mole/l	Inhib. and concn., mole/l	Convsn., %	Time, sec.	$k \times 10^4$, $l^{1/2}$ mole$^{-1/2}$ sec^{-1}	
1	Bz_2O_2, 0.025		6.4	800	5.17	
2	" 0.025		11.2	1,590	4.72	
3	" 0.025		15.8	2,130	5.06	
4	" 0.025	DPhA, 0.05	—	7,500		
5	" 0.025	HQ, 0.05	—	15,000		
6	AIBN, 0.01		7.7	310	8.30	
7	" 0.06	DPhA, 0.05	16.3	710	9.30	
8	" 0.06	" 0.05	24.7	1,200	9.62	
9	" 0.06	HQ, 0.15	8.3	420	8.35	
10	" 0.06	HQ, 0.15	20.0	960	9.30	
11	" 0.06	PhT, 0.05	15.2	710	9.32	
		HQ, 0.09				
12	" 0.06	PhT 0.05	17.3	955	8.16	
		HQ, 0.09				
13	" 0.06	BQ, 0.06	8.0	12,200	0.28	
14	" 0.06	" 0.15	1	16,000	0.02	
15	" 0.06	" 0.06	26	1,620	7.57	
	Et_3B, 0.06					
16	AIBN, 0.07	" 0.15	—	4,140		
	Et_3B, 0.03					
17	AIBN, 0.043	" 0.13	3.7	3,320	0.68	
	Et_3B, 0.035					
18	AIBN, 0.06	" 0.15	—	3,420		
	Et_3B, 0.025					
19	AIBN, 0.06	" 0.15		15,000		A
20	" 0.06	PhT 0.05	11	10,800	0.44	A, sa
		HQ, 0.09				
21	" 0.06	PhT 0.05	—	7,000		A, va
		HQ, 0.09				
22	" 0.06	PhT 0.05	40	7,000	2.3	A, wa
		HQ, 0.09				

[a] Conversion/[Initiator]$^{1/2}$· time = k; Bz_2O_2, benzoyl peroxide; AIBN, azobisisobutyronitrile; Et_3B, triethylborane; DPhA, diphenylamine; HQ, hydroquinone; BQ, benzoquinone; PhT, phenothiazine; A, in the presence of air; a, agitation; s, slight; v, vigorous; w, without.

No polymerization could therefore be observed in runs 4 and 5 when hydroquinone (HQ) or diphenylamine (DPha) were used together with benzoyl peroxide (Bz_2O_2). However, under similar conditions we did observe polymerization when azobisisobutyronitrile (AIBN) was used as initiator instead of Bz_2O_2, as may be seen in runs 7–10.

The differences between Arimoto's data and ours with phenothiazine (Pth) and Pth-HQ mixtures and AIBN as initiator (runs 11 and 12) seem to be less clear. Our experimental conditions were almost the same as those reported in his paper,[1] but our results differ. Instead of the total inhibition observed by Arimoto in 3 hr. we were unable to find even a measureable retardation at the same temperature. We did observe a strong retardation after 3 hr., but only when the reaction was carried out in the presence of air, as may be seen in runs 20 and 21.

Thus, Arimoto's choice of these substances as good inhibitors in the absence of oxygen is not very understandable, since there seems to be no reason for these compounds or mixtures of them to be much more effective than DPha[8a] or HQ, for example. Nor does any interaction between them that might suggest a strong synergetic effect seem to have been observed.

In the presence of oxygen the situation becomes clearer, since Pth and HQ are good antioxidants and, if O_2 is present, the chain radicals will give peroxyradicals, which in turn react readily with these compounds. Our results seem to agree with this, because we could not find any measurable inhibiting effect of these mixtures in the absence of oxygen (runs 11 and 12), but we did find a strong retardation in its presence; this effect was notably influenced by agitation of the reaction tubes.

Runs 21 and 22 were carried out under almost the same conditions, the first with strong and continuous agitation and the second without; they gave after 100 min 0% and 40% polymerization yield, respectively.

We are unable to explain the differences between our data and Arimoto's regarding this mixture. The arguments given above, together with the fact that the presence of impurities would explain an inhibiting effect much more easily than a specific inhibiting action of these antioxidants, make us more confident in our results with Pth and HQ.

For these reasons none of the compounds employed by Arimoto could be used by us to test the effect of triethylborane (Et_3B) on the inhibited polymerization. Therefore, benzoquinone (BQ), known to be one of the best inhibitors of MMA polymerization,[8b] was selected as the retarder.

Provided that the ratio $R = 2$ [initiator decomposed] $+ 3[Et_3B]/[BQ]$ was less than 1, no polymerization could be observed in 69 and 51 min in runs 16 and 18, respectively. If, however, the ratio R was considerably greater than 1, as in run 15, and as it happens to be in most of Arimoto's experiments, polymerization did occur. It must be pointed out that, although the rate constant obtained in run 15 nearly agrees with the corresponding rate constants for uninhibited polymerization in runs 6–12, the observed molecular weight is considerably lower (about 2.5×10^4) than those obtained with initiator alone (about 1×10^5). The results with Et_3B and BQ show conclusively that no polymerization occurs when the inhibitor is in large excess over Et_3B and initiator. This cannot be explained by the mechanism proposed by Arimoto, which involves an organoboron–radical complex rendered sufficiently inactive to be unaffected by the presence of inhibitors, a complex in whose presence polymerization should have occurred.

Nevertheless, to explain the fact that, as in Arimoto's work, polymer is obtained by the addition of Et_3B to systems that otherwise would not polymerize, such as 2-6-di-*tert*-butyl-*p*-cresol with Bz_2O_2 or HQ or Pth with peroxyboron compounds, and results such as those obtained in runs 15 and 17 of the present paper, the following free-radical mechanism is proposed:

$$M_x\text{—}R\cdot + PhO_2 \rightarrow RM_xPhO_2\cdot \tag{1}$$

$$RM_xPhO_2\cdot + Et_3B \rightarrow RM_xPhO_2BEt_2 + Et\cdot \tag{2}$$

$$Et\cdot + M \rightarrow Et\text{—}M\cdot \tag{3}$$

$$RM_xPhO_2\cdot + RM_xPhO_2BEt_2 \rightarrow (RM_xPhO_2)_2BEt + Et\cdot \tag{4}$$

where $RM_x.$ is the chain radical, M the monomer, and $RM_xPhO_2.$ the radical produced by the reaction of $RM_x.$ with BQ, whose precise structure is still speculative. That reaction (2) can be operative is supported by the occurrence of similar reactions such as

$$CH_3CO\cdot + BR_3 \rightarrow CH_3COBR_3 + R\cdot \tag{5}$$

$$ROO\cdot + BR_3 \rightarrow ROOBR_2 + R\cdot \tag{6}$$

which seem to be extremely fast.[3,5] From the evidence of oxidation reactions[3] reaction (4) cannot be disregarded; one would expect its rate to be smaller than that of (2) but still competitive with radical termination reactions. Although a further substitution reaction is possible, its occurrence under these conditions remains doubtful. The reaction of $(RM_xPhO_2)_nB(C_2H_5)_{3-n}$, where n is 1 or 2, with air when the reaction tubes were broken off would be responsible for the observed low molecular weight products.

The results of Runs 15 and 17 (it is important to note that in the latter the ratio R is greater than in runs 16 and 18 and close to 1) are clearly understood in connection with the data of runs 13, 14, and 19 (carried out without Et_3B) according to the above mechanism. In reaction (1) the growing chain radical is transformed into a resonance-stabilized radical that is unable to continue chain growth in the absence of Et_3B but participates only in termination steps by combination with other radicals. Although these radicals are too weakly reactive to attack the monomer, they give a facile transfer reaction with Et_3B, whereby they are transformed into very reactive ethyl radicals. In this way the rate-diminishing effect of BQ is partly compensated for by this chain-transfer reaction; in this sense the mechanism here proposed closely resembles the one suggested by Breitenbach and Schindler[10] for the effect of transfer agents on the degradative chain transfer in vinyl chloride polymerization.

These arguments would also explain the fact that Arimoto did observe polymerization when Et_3B was added to systems that otherwise would be inhibited by the presence of antioxidants, since the resonance-stabilized radicals formed in these systems would readily interact with Et_3B, giving the reactive ethyl radicals, as proposed in the above mechanism.

The rate, nature, and stoichiometry of the interaction of peroxy and other resonance-stabilized radicals with Et_3B in the gas and liquid phase are under investigation in this laboratory and will be published elsewhere.

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Preparation of Poly(diphenyl Phosphazene)

J. R. MacCALLUM and J. TANNER, *Department of Chemistry, University of St. Andrews, St. Andrews, Fife, Scotland*

Synopsis

The preparation of substituted polyphosphazenes has been briefly surveyed. A method of synthesis of a fully substituted poly(diphenyl phosphazene) has been investigated. The product has been characterized and thermogravimetric analysis carried out. The volatile products of pyrolysis have been identified and the hydrolytic stability of the polymer tested.

The polyphosphazenes of general formula $(pX_2 = N)_n$ are an interesting and potentially useful group of inorganic polymers. The halides, X = Cl, Br, or F, have been known for some time, and when n is large they are elastomeric in nature. More recently, methods of synthesizing polymers containing organic substituents have been developed. There are three general routes available. In the first route the reaction of either lithium or sodium azides with a halophosphine and then heating of the intermediates so formed gives high polymers along with lower molecular weight species.[1,2] This method involves a certain hazard in that the azide/halophosphine reaction can be explosive. The second synthesis follows the reaction scheme,

$$R_2PNH_2 + Cl_2 \rightarrow R_2P(Cl_2)NH_2$$
$$R_2P(Cl_2)NH_2 + NR_3 \rightarrow R_2PN + NHR_3Cl$$

The polymer is obtained in moderate yields along with trimer and tetramer which must be removed to obtain pure polymer.[3] A third method involves substitution of the chloro group in poly(dichloro phosphazene) by a suitable nucleophilic reagent, for example CH_3ONa or C_6H_5ONa. This method has been applied to both soluble and insoluble polymer samples.[4,5]

Poly(dimethyl phosphazene) has also been prepared by the pyrolysis of dimethyldiaminophosphonium chloride with ammonium chloride.[6]

In this note we wish to report the synthesis of poly(diphenyl phosphazene) by the third method, and also some of the physical and chemical characteristics of the polymer. A similar method of preparation has been attempted previously, but only 95% substitution was achieved, and the product was not characterized.[7-10]

Experimental and Results

In preparation of poly(diphenyl phosphazene), a 25 g portion of hexachlorophosphazene (mp 112.5–114°C) was evacuated in a clean dry glass tube to a pressure of 10^{-4} torr and sealed off. The tube and contents were then heated at 250°C for 24 hr, 70% of the trimer being converted to polymer. After cooling and opening the tube, excess trimer was removed by vacuum sublimation. Soluble polymer was dissolved in dry benzene and the solution carefully decanted from residual gel, which comprised 10% of the sample. A solution of phenyllithium in dry diethyl ether under nitrogen was prepared in a twice molar excess with respect to the replaceable chloride in the benzene solution. This benzene solution was then added drop by drop to the phenyllithium and thoroughly mixed. After refluxing the reaction mixture for 48 hr, during which time the solution deepened in color from light buff to dark brown, the benzene and diethyl ether were distilled off under reduced pressure and the residue thoroughly washed with water. The soluble portion of the polymer was further purified by precipitation from acetone solution by the addition of water and was then dried in a vacuum oven at 60°C for several hours. The overall yield was 22% relative to the starting material. The infrared spectrum of the dried polymer was measured on a Perkin-Elmer 621 grating spectrophotometer by using the pressed KBr disk technique.

Infrared absorption bands for poly(diphenyl phosphazene) were observed at 3040 (m), 1585 (m), 1475 (m), 1435 (s), 1200 (v. broad, vs), 1115 (s), 1024 (m), 995 (m), 915 (broad, m), 740 (s), 715 (s), 693 (vs), and 540 (broad, vs).

The spectrum obtained agrees closely with the spectrum of a sample of hexaphenylphosphazene kindly sent to use by Dr. D. L. Herring. It differs only in that there is a general broadening and diffuseness of peaks as expected for a high polymer.

Elemental analysis yielded the following results.

ANAL. Calcd. C, 72.36%; H, 5.02%; N, 7.03%; P, 15.59%. Found: C, 66.14%; H, 4.87%; N, 6.08%; P, 13.40%.

It appeared from the infrared spectra that there was present in the polymer samples water which could not be removed simply by pumping out for prolonged periods. The presence of bonded water might reasonably account for the discrepancies in the above analysis.

ANAL. Calcd. for $(PPh_2 = N,H_2O)_n$: C, 66.36%; H, 5.53%; N, 6.45%; P, 14.29%.

A sample of the solid polyphosphazene was heated *in vacuo* at 130°C for 6 hr and removed, under vacuum, to a dry box in which a Nujol mull was prepared (the Nujol having previously been dried by heating with sodium metal). This sample was found by infrared spectroscopy not to have water present. In all other respects it was identical with the infrared data given above.

Thermogravimetric analyses were obtained by using a Du Pont 950 thermogravimetric analyzer. Figure 1 illustrates a typical thermogram. The major volatile products of degradation were, water, ammonia, benzene, and low molecular weight homologs. The residual polymer was a brittle, dark brown glass which showed no change in infrared spectrum from the parent polymer, but was insoluble.

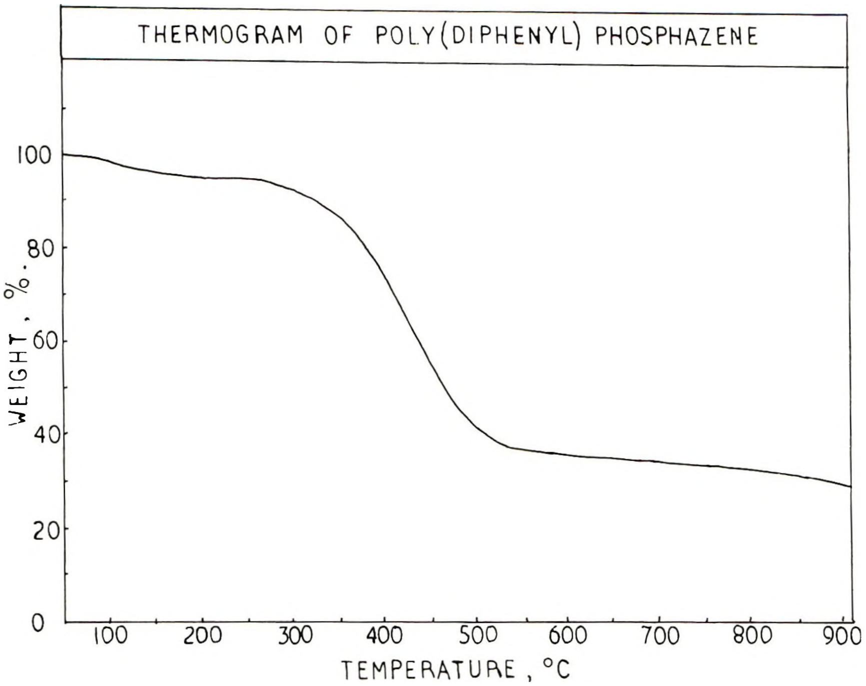

Fig. 1. Thermogram of poly(diphenyl phosphazene) heated at 10°C/min in an N_2 atmosphere.

The hydrolytic stability of poly(diphenyl phosphazene) was tested by refluxing samples in 0.1*M* nitric acid and 0.1*M* sodium hydroxide for 48 hr with no resultant change in character of the polymer. Potentiometric titration of the boiled solutions with $AgNO_3$ solution gave negative results, indicating complete substitution of the parent poly(dichlorophosphazene).

Further investigation of the properties of a variety of substituted polyphosphazenes prepared by the above method is being carried out.

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NOTES

Aryl End-Capping of 2,6-Dimethyl-1,4-polyphenylene Oxide

2,6-Dimethylpolyphenylene oxide (PPO) is a linear polymer[1] with a terminal phenolic endgroup.[2] Because of the reactivity of phenols, this endgroup is a likely point of attack by oxygen and other chemical reagents. In fact, the redistribution reaction of PPO with monomeric or dimeric phenols depends on the presence of a phenol endgroup.[3] An investigation was begun to convert the hydroxyl endgroup to a phenoxy group which should have about the same chemical reactivity as the other ether linkages along the polymer chain.

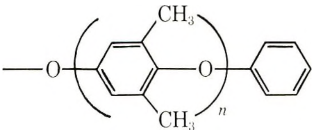
One method for preparing a diaryl ether is the Ullmann reaction.[4] However, this reaction is not quantitative, and any aryl end-capping process must be so. Therefore, we directed our efforts towards investigating the use of this reaction quantitatively to cap the polymer but first needed an analytical method to determine whether or not the reaction was occurring. Since concentrated solutions of PPO in carbon disulfide exhibit an infrared hydroxyl absorption at 3610 cm^{-1} and a transparent region at 3710–3720 cm^{-1}, it is possible to measure the hydroxyl absorption by the difference between these two frequencies.* In this manner the course of the reaction could be followed by the decrease in hydroxyl absorption which must occur if hydroxyl is converted to phenoxide.

A number of reactions were run to determine the conditions for the reaction. Toluene proved to be a suitable solvent, since it dissolved both the sodium and potassium salts of PPO. In order to complete the reaction within 30–60 min, it was found necessary to heat the polymer salt solution in a sealed tube at 250°C with an excess of bromobenzene and in the presence of an amine and a soluble copper salt.

Table I summarizes the results. It was found convenient to convert the polymer to its salt by titrating a toluene solution of polymer with the dialkali salt of benzophenone in benzene[6] containing some amine or by the addition of solid potassium *tert*-butoxide. The soluble copper salt was then added and the tube evacuated and sealed. After the reaction, the polymer was isolated by filtration and precipitation. The final drying was carried out at 60°C and 20 mm pressure overnight before the infrared measurements were determined.

A value of about 15–20 abs/g × 100 units appears to be the background absorbance at 3610 cm^{-1} in a 2,6-dialkyldiaryl ether, since 2,6-dimethylphenyl phenyl ether indicates some absorbance at 3610 cm^{-1} compared to 3710 cm^{-1} (Table I).

Proof that the decrease in hydroxyl absorption observed is due to ether formation rather than reduction was provided by the infrared spectra of the product in runs 1, 4, and 5. A small band appeared at 690–700 cm^{-1} which can be assigned to the C—H out-of-plane deformation for five adjacent free hydrogen atoms on an aromatic ring.[7] This region is transparent in PPO. The absorbance in the capped polymer is not due to residual toluene since redrying does not remove it. Therefore, it must be caused by the benzene group introduced.



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* An infrared analytical method for determining hydroxyl content has been developed in this laboratory by Howe.[5]

TABLE I

Run	Time, hr	Temp, °C	Concentration	Salt-amine	Abs/g × 100[a]
1	0.5	250	0.25 g PPO in 2.5 ml of 1:1.5 bromobenzene: toluene	$K^{\oplus}$ with diethylamine and Cu_2Br_2	18.4
2	"	"	"	$K^{\oplus}$ with triethylamine and Cu_2Br_2	16.0
3	"	"	0.25 g PPO in 2.5 ml bromobenzene	Same as run 1	20.8
4	"	"	"	Same as run 2	15.2
5	"	"	"	"	14.4
6	—	—	2,6-dimethylphenyl phenyl ether (Two different samples)		20.0 19.0
7	—	—	PPO starting material (MW 18,500)		74.2

[a] Solutions made from 0.125 g of solid/5 ml solution in CS_2. Absorbance is difference between 3710–3720 and 3608 cm^{-1}.

The phenyl-capped polymer was stable when submitted to the conditions of the redistribution reaction.[3] Within experimental error, it was quantitatively recovered when compared to a sample which was not redistributed but was reprecipitated.

The infrared measurements were performed by Miss D. V. McClung. Information concerning the preparation and use of various dialkali salts of benzophenone in benzene was provided by Dr. A. S. Hay.

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ROBERT A. JERUSSI
MICHAEL R. MCCORMICK

Research and Development Center
General Electric Company
Schenectady, New York 12301

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Aliphatic Polyphenylquinoxalines

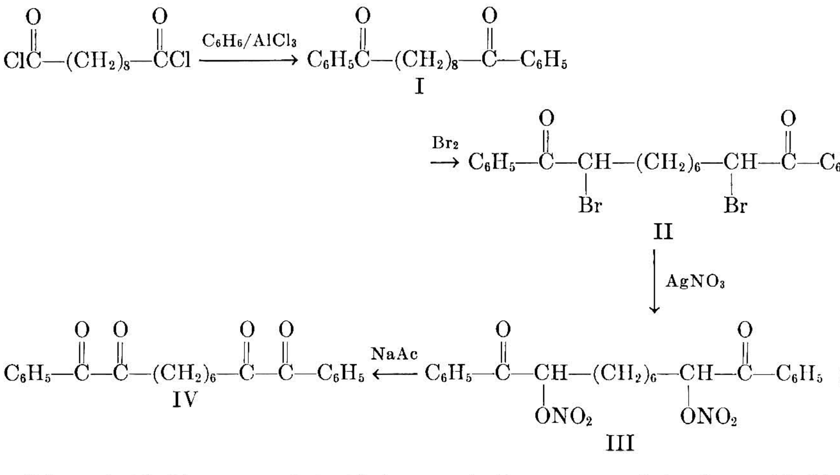
INTRODUCTION

Research on wholly aromatic polyquinoxalines[1-6] has provided high molecular polymers of excellent thermal stability. This work has been extended to the ladder-type polyquinoxalines[7-10] and the polyphenylquinoxalines.[11] Although ladder-type polyquinoxalines containing a nonaromatic segment in the polymer chain have recently been reported,[10] the synthesis of aliphatic polyquinoxalines has not been disclosed. This communication reports the successful preparation of two aliphatic polyphenylquinoxalines from the reaction of 1,10-diphenyldecane-1,2,9,10-tetraone with 3,3′-diaminobenzidine and with 3,3′,4,4′-tetraaminodiphenyl ether.

DISCUSSION AND RESULTS

Reactants

1,10-Diphenyldecane-1,2,9,10-tetraone was synthesized as shown in eq. (1) by modifying a known procedure[12] employed for the synthesis of similar compounds. Characterization of the various intermediates and reactants is shown in Table I.



$$\mathrm{ClC(=O)-(CH_2)_8-C(=O)Cl} \xrightarrow{\mathrm{C_6H_6/AlCl_3}} \underset{\mathrm{I}}{\mathrm{C_6H_5C(=O)-(CH_2)_8-C(=O)-C_6H_5}} \xrightarrow{\mathrm{Br_2}} \underset{\mathrm{II}}{\mathrm{C_6H_5-C(=O)-CH(Br)-(CH_2)_6-CH(Br)-C(=O)-C_6H_5}}$$

$$\xrightarrow{\mathrm{AgNO_3}} \underset{\mathrm{III}}{\mathrm{C_6H_5-C(=O)-CH(ONO_2)-(CH_2)_6-CH(ONO_2)-C(=O)-C_6H_5}} \xrightarrow{\mathrm{NaAc}} \underset{\mathrm{IV}}{\mathrm{C_6H_5-C(=O)-C(=O)-(CH_2)_6-C(=O)-C(=O)-C_6H_5}} \quad (1)$$

Sebacoyl chloride was reacted with benzene in the presence of aluminum chloride to provide a near-quantitative yield of 1,8-dibenzoyloctane (I). Bromination was performed in the conventional manner in carbon tetrachloride using a catalytic amount of aluminum chloride. 1,8-Dibromo-1,8-dibenzoyloctane (II) was converted to the corresponding nitrate ester (III) in good yield by reaction with silver nitrate in acetonitrile. Reaction of 1,8-dibenzoyloctyl-1,8-dinitrate with sodium acetate in warm dimethyl sulfoxide provided a crude yellow solid which was recrystallized several times from *n*-hexane to afford pale yellow crystals of 1,10-diphenyldecane-1,2,9,10-tetraone (IV).

3,3′-Diaminobenzidine (V) was purchased from a commercial source and purified by recrystallization from water.

3,3′,4,4′-Tetraaminodiphenyl ether (VI) was prepared according to the procedure of Foster and Marvel.[14]

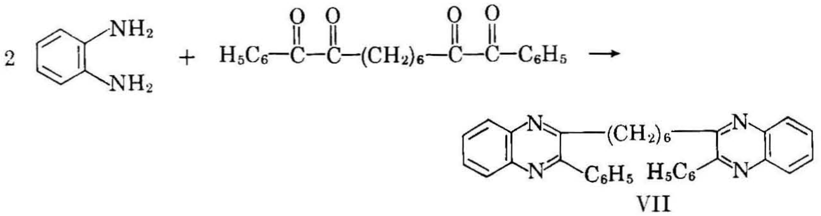
Model Compound

2,2′-Hexamethylenedi(3-phenylquinoxaline) (VII) was prepared in quantitative yield by the melt condensation of *o*-phenylenediamine and 1,10-diphenyldecane-1,2,9,10-tetraone as shown in eq. (2).

TABLE I
Characterization of Intermediates and Reactants

Reactant	Mp, °C	Formula	Elemental analysis							
			Calculated				Found			
			C, %	H, %	N, %	Br, %	C, %	H, %	N, %	Br, %
I	97–98[a]	$C_{22}H_{26}O_2$	81.95	8.13	—	—	81.96	8.01	—	—
II	126–127	$C_{22}H_{24}O_2Br_2$	55.02	5.04	—	33.28	54.86	4.87	—	33.10
III	111–112	$C_{22}H_{24}N_2O_8$	59.45	5.44	6.30	—	59.67	5.34	6.19	—
IV	63–64	$C_{22}H_{22}O_4$	75.40	6.33	—	—	75.28	6.36	—	—
V	177.5–178	$C_{12}H_{15}N_4$	67.26	6.59	26.15	—	67.18	6.47	26.11	—
VI	150–151	$C_{12}H_{14}N_4O$	62.58	6.13	24.35	—	62.41	6.03	24.12	—
VII	151.5–152.5	$C_{34}H_{30}N_4$	82.56	6.11	11.33	—	82.46	6.14	11.45	—

[a] Literature reports mp 91–92°C.[13]

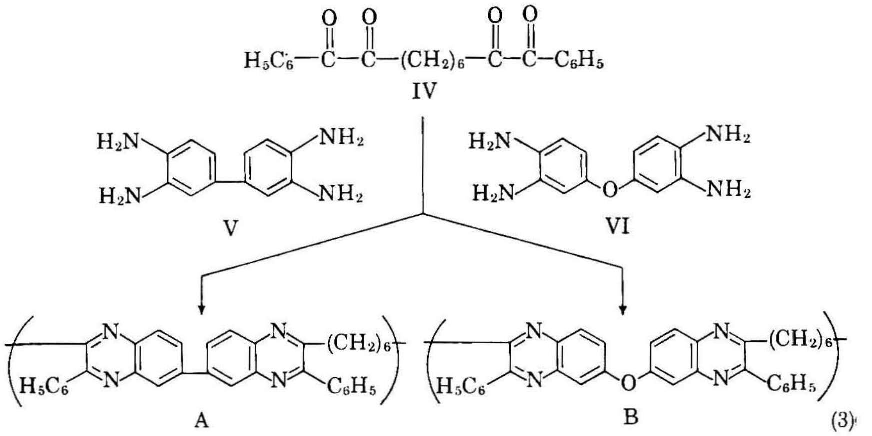


VII

(2)

Polymer

The polymerization of 1,10-diphenyldecane-1,2,9,10-tetraone with 3,3′-diaminobenzidine (V) and with 3,3′,4,4′-tetraaminodiphenyl ether (VI) was performed via melt and solution techniques to afford poly[2,2′-(hexamethylene)-6,6′-di(3-phenylquinoxaline)] (A) and poly[2,2′-(hexamethylene)-6,6′-oxydi(3-phenylquinoxaline)] (B) and isomers thereof respectively as shown in eq. (3).



(3)

Melt condensations were performed by introducing an intimate mixture of stoichiometric quantities of 1,10-diphenyldecane-1,2,9,10-tetraone and 3,3′-diaminobenzidine or 3,3′,4,4′-tetraaminodiphenyl ether in a polymerization tube under nitrogen into a preheated oil bath at 200°C. The temperature was increased to 300°C during 1.5 hr and maintained at 300°C for 1 hr. The resulting glassy brown polymer exhibited excellent adhesion, by pulling the glass away from the side of the polymerization tube when cooled. The polymers were extremely tough and difficult to pulverize. The inherent viscosities (0.5% H_2SO_4 at 25°C) of the polymer prepared in this manner from 3,3′-diaminobenzidine and 3,3′,4,4′-tetraaminodiphenyl ether were 1.16 and 1.04, respectively.

Solution polymerizations were conducted by adding the tetracarbonyl compound to a stirred slurry of a stoichiometric amount of tetraamine in *m*-cresol (final solids concentration 16%) at ambient temperature under nitrogen. The temperature of the resulting clear viscous solution was increased to 80°C and maintained at 80°C for 1 hr. A sample of the polymer at this stage was isolated as a fibrous yellow solid by quenching with methanol, followed by drying at 100°C for 1 hr under pump vacuum. The remaining polymer solution was stirred to reflux temperature (202°C) and maintained at reflux under nitrogen for 1 hr followed by isolation of the polymer as previously described. Clear yellow films which exhibited good toughness and flexibility were cast from the *m*-cresol and dried under nitrogen to 200°C. The molecular weight of the polymer as indicated by inherent viscosity measurement as reported in Table II failed to increase appreciably in *m*-cresol from 80°C to 202°C. However, further polymer advancement

TABLE II
Polymer Characterization

Poly-mer	Inherent viscosity, dl/g[a]			PDT, °C[b]		Elemental analysis[c]		
	80°C in *m*-cresol	202°C in *m*-cresol	300°C in melt	Air	He-lium	C, %	H, %	N, %
A	0.44	0.45	0.72	445	450	82.14	5.36	11.72
B	0.64	0.69	0.77	450	450	81.03	5.11	10.57

[a] 0.5% H_2SO_4 solution at 25°C.

[b] PDT = Polymer decomposition temperature, $\Delta T = 6.67°C/min$.

[c] Calcd for $(C_{34}H_{28}N_4)_x$ (A): C, 82.90%; H, 5.73%; N, 11.37%. Calcd for $(C_{34}H_{28}N_4O)_x$ (B): C, 80.29%; H, 5.55%; N, 11.08%.

to an inherent viscosity as high as 0.77 dl/g was effected by heating the isolated fibrous yellow solid under nitrogen for 1 hr at 300°C.

The final polymers were characterized as shown in Table II. The infrared spectra of the polymers were completely consistent with that expected from the proposed structure of the polymer. Polymer decomposition temperatures in air and in helium were ~450°C as determined on a Stanton thermobalance.

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PAUL M. HERGENROTHER*

Narmco Research and Development Division
Whittaker Corporation
San Diego, California 92123

Received February 6, 1968
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* Present address: Boeing Scientific Research Laboratories, Seattle, Washington 98124.

The Peroxide-Induced Degradation of Sulfonated Polystyrenes Crosslinked with m- *and* p-*Divinylbenzenes*

The peroxide-induced degradation of sulfonated polystyrenes crosslinked with "commercial," *para*-, or *meta*-divinylbenzene proceeds at varying rates. The sulfonated, *meta*-DVB crosslinked resin degrades the most slowly for reasons possibly related to its more uniformly crosslinked network.

It has been known for some time that sulfonated polystyrenes crosslinked with divinylbenzene are readily degraded by peroxide.[1] We wish to record experiments with this type of degradation which are designed to correlate the rate of degradation with the nature of the crosslinking as varied by the use of pure *meta*-, pure *para*-, and commercial divinylbenzene in the styrene copolymerization. Comparison data for a commercial ion-exchange resin of the same type are included.

Experimental Part

The methods used for the separation[2] and characterization of the divinylbenzene isomers; for the bead copolymerization;[3] and for the sulfonation[4] have been described in detail in previous publications. The isomeric monomers used in the present study were 99.8% pure by GLC (flame ionization detector). Twenty mesh beads prepared at 80°C with carboxymethylcellulose ether sodium salt as suspending agent and 1 wt-% dibenzoylperoxide as initiator were used. Sulfonations were run at 80°C with 98% sulfuric acid on beads swollen in ethylene dichloride. The total capacity, determined by the method used previously[4] was 5.16 meq/g for the polystyrene crosslinked with 8 mole-% pure *para*-divinylbenzene; for the material crosslinked with 8 mole-% pure *meta*-DVB and with 8 mole-% commercial-DVB these values were 4.97 and 5.14 meq/g, respectively.

The degradation process was conducted as follows. The sulfonated resins were washed repeatedly with distilled water to remove completely all absorbed acid. Five milliliters of hydrogen peroxide solution (3%) were used to flush 1 g. of the beads together with 2.48 mg of ferrous sulfate $\cdot 7H_2O$ (10 ppm) through a long stemmed funnel into a flask containing 45 ml of the same hydrogen peroxide solution (3% solution, Am. Peroxide Co.) maintained at the degradation temperature (75°C) in a constant temperature bath at 75°C. The flask was equipped with a magnetic stirrer and a reflux condenser. Aliquot parts (1 ml) of the liquid phase of the reaction mixture were taken out at regular intervals and diluted with 50 ml of water. The amount of sulfonic acid groups in the solution was then determined by titration with $0.01N$ sodium hydroxide solution versus phenolphthalein as an indicator. The titration values were adjusted for the decreased reaction volume as the successive 1-ml samples were withdrawn during the course of the experiment, by taking the product of the residual volume and the equivalents of base required for neutralization of the aliquot. The data are summarized in Figure 1 and Table I. The resins become soluble during the degradation and are completely dissolved by the end of the experiment. A faint ferric chloride enol test color was noted for the solution of the degraded polymer.

The amount of hydrogen peroxide in the aliquot samples was determined at regular intervals by thiosulfate titration of the iodine liberated from added iodide. In a typical experiment the amount of the hydrogen peroxide was decreased from its initial value to 88.9% in 180 min, 82.5% in 240 min, and 68% in 300 min.

Discussion

The results of these experiments show that there is a significant difference in the rates of peroxide-induced degradation of sulfonated polystyrenes in terms of the nature of the crosslinkage. The *para*-DVB crosslinked resins degrade more rapidly than the *meta*- or commercial-DVB crosslinked resins. The latter two are not greatly different. The commercial ion-exchange resin degrades more rapidly than the *para*-DVB crosslinked sample but this may be attributed to a different sample history. We assume

TABLE I
Degradation of Sulfonated Polystyrene Beads Crosslinked with 8% of Different Divinylbenzenes

Time, min	Sulfonic acid groups,[a] meq, sulfonated polystyrene crosslinked with: *meta*[b]			Resin[c]
	meta[b]	*para*[b]	Commercial[b]	
60	0.23	0.21	0.22	0.47
105	—	—	0.57	2.78
120	0.71	0.87	0.78	3.28
135	0.90	1.24	1.01	3.66
150	1.13	1.76	1.30	3.91
165	1.50	2.71	1.68	4.23
180	1.78	3.33	2.36	4.40
195	2.30	3.71	3.05	4.59
210	3.13	3.97	3.57	4.68
225	3.75	4.20	3.94	4.74
240	4.07	4.35	4.15	4.84
270	4.51	4.70	4.46	—
300	4.73	4.90	4.63	—

[a] Meq of acid, as determined by titration of aliquots from the peroxide reaction mixture, from 1.0 g of resin crosslinked with 8% of the indicated DVB.

[b] Divinylbenzene.

[c] Resin-50W-X8, Lot No. 22467.

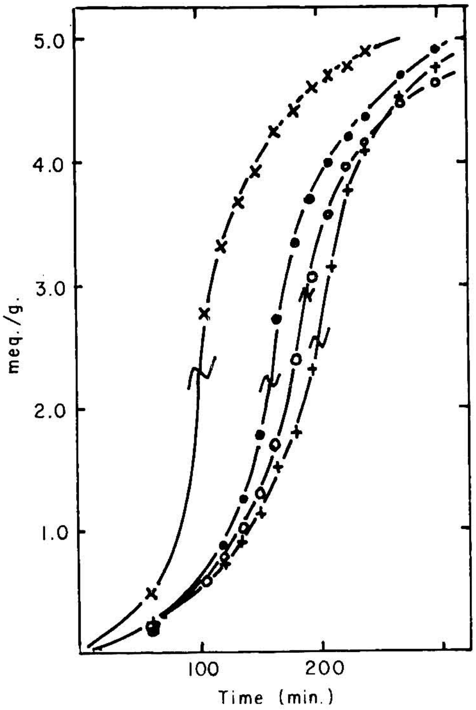

Fig. 1. Rate of formation of acid in peroxide-induced degradation of sulfonated styrene–divinylbenzene resins; meq acid liberated per g resin vs. time. Inflection points from differential plots: (+) *meta-*, (●) *para-*, (O) commercial-DVB; (X) resin (commercial)-50W-x8.

that the difference in rates of degradation is related, in part, to different rates of diffusion of the peroxide through the resin matrix and, in part, to alteration (decrease) in the rate as the degradation, assumed to be a depolymerization, reaches a point of crosslinkage. Our previous data indicate that there are longer sequences of polystyrene units in the *para*-DVB crosslinked resin. These presumably give a greater overall degradation rate than is observed with the less lengthy polystyrene segments in the more uniformly crosslinked *m*-DVB resins. The degradation is thought to involve depolymerization principally because the resins dissolve during the course of the experiment. The degradation is not induced by acid under comparable conditions. It is also noted that the peroxide-induced degradation of the unsulfonated resins is not observed under comparable conditions.

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RICHARD H. WILEY
E. REICH

Department of Chemistry
Hunter College
City University of New York

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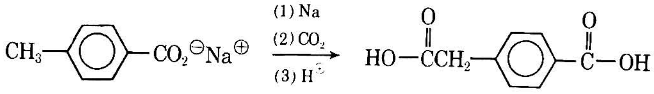
Polyamide and Polyester Derivatives of Homoterephthalic Acid

INTRODUCTION

During the course of some work on sodium metallation, DePree[1] found that homoterephthalic acid could be readily prepared from sodium *p*-toluate:



The availability of homoterephthalic acid by this simple sequence of reactions prompted an investigation of its polyamide and polyester derivatives. The presence of both aromatic and aliphatic carboxyl groups in homoterephthalic acid could lead to an interesting series of polymeric derivatives. Edgar and Hill[2] prepared polyethylene homoterephthalate and found this unsymmetrical polyester showed no significant sign of crystallinity, whereas polyethylene terephthalate and polyethylene *p*-phenylene diacetate crystallized readily. These differences in crystallinity were ascribed to differences in symmetry. Copolyesters[3] and copolyamides[4] containing homoterephthalic acid have also been reported. The work reported here describes the synthesis and differential thermal analysis of polyamides and polyesters derived from homoterephthalic acid.

EXPERIMENTAL

Dimethyl Homoterephthalate, Homoterephthalic Acid, and Homoterephthaloyl Chloride

Dimethyl homoterephthalate (Ethyl Corporation) was fractionated at 10 mm Hg pressure. Vapor phase chromatography showed the minimum purity of the distillate to be 99.5%. Some of the physical data on this ester include: b.p., 163–164°C at 10 mm Hg n^{25}_{4}, 1.5185 d^{25}_{4}, 1.1693.

Homoterephthalic acid was prepared by the alkaline hydrolysis of dimethyl homoterephthalate. Following acidification and three recrystallizations from water, a white crystalline product was obtained, m.p. 245°C.

ANAL. Calcd. for $C_9H_8O_4$: C, 60.00%; H, 4.48%. Found: C, 59.87%; H, 4.64%.

Homoterephthaloyl chloride was prepared by heating homoterephthalic acid with excess thionyl chloride at 90–95°C until a clear solution resulted. After removal of the excess thionyl chloride the acid chloride was recrystallized from a carbon tetrachloride–hexane (1:1) solution, m.p. 35–36°C.

Polymerizations

The polyamides, with the exception of the piperazine polyamide, were prepared by solution polymerization at 200–230°C. Generally 200°C was a satisfactory reaction temperature; however, in some cases temperature $\leq$230°C were required to maintain homogeneity. The acid–diamine salts were heated in *m*-cresol for 72–100 hr at atmospheric pressure while a slow stream of nitrogen was bubbled through the solution. The reaction times were governed by the viscosity of the reaction solution. A series of condensers and traps were used to prevent excessive diamine losses. The polyamides were precipitated by acetone, then collected and dried. The dry polymers were either white or light-yellow in appearance. The piperazine polyamide was prepared by interfacial polycondensation at room temperature using homoterephthaloyl chloride.

The polyesters, with the exception of the 4,4′-isopropylidene diphenol polyester, were prepared by melt polymerization. The initial ester exchange between the dimethyl

TABLE I
Homoterephthalic Acid Polyamide Homopolymers and Copolymers

Acid	Diamine	Polymer code	Logarithmic viscosity number, dl/g	T_g, °C	T_m, °C	T_{dec}, °C
Homoterephthalic	Ethylenediamine	2-H	0.18^{a}	—^{b}	221	309
Homoterephthalic	1,3-Propanediamine	3-H	0.12^{a}	109	281	295
Homoterephthalic	1,4-Butanediamine	4-H	0.11^{a}	84	221	236
Homoterephthalic	1,5-Pentanediamine	5-H	0.25^{a}	103	216	271
Homoterephthalic	1,6-Hexanediamine	6-H	0.48^{a}	104	227	347
Homoterephthalic	Piperazine	Pip-H	0.74^{c}	—^{b}	—^{b}	197
Homoterephthalic, 50 mol-% Adipic, 50 mol-%	1,6-Hexanediamine	6-6/H	0.45^{c}	99	—^{b}	330

[a] In *m*-cresol at 30°C and 0.5 g/100 ml solvent.

[b] None detected.

[c] In *m*-cresol at 25°C and 0.5 g/100 ml solvent.

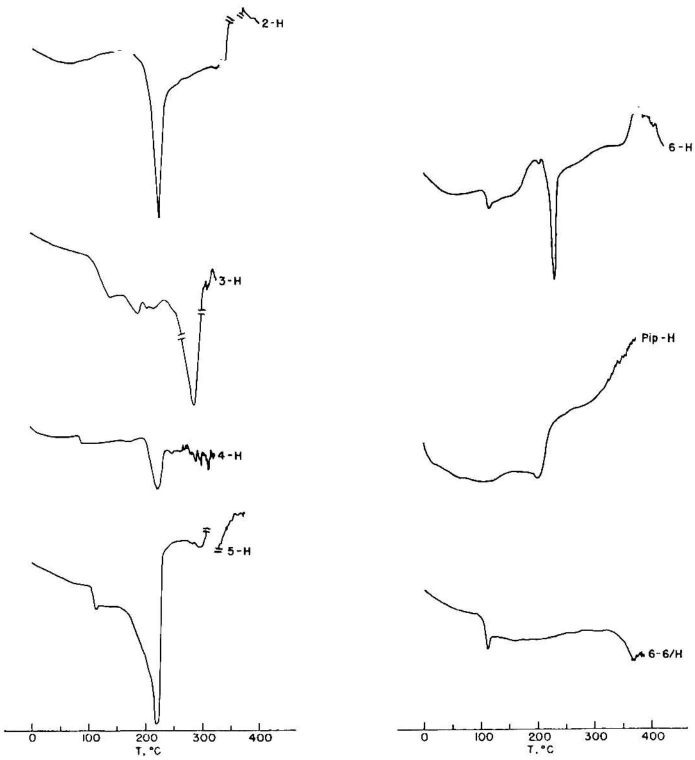


Fig. 1. DTA thermograms of homoterephthalic acid polyamides.

TABLE II
Homoterephthalic Acid Polyester Homopolymers and Copolymers

Acid	Diol	Polymer code	Logarithmic viscosity number, dl/g	T_g, °C	T_m, °C	T_{dec}, °C
Homoterephthalic	Ethylene glycol	E-H	0.69[a]	24	—[b]	334
Homoterephthalic	4,4′-Isopropylidene diphenol	I-H	0.14[a]	85	—[b]	338
Homoterephthalic	*p*-Xylylene glycol	X-H	0.72[a]	47	—[b]	347
Homoterephthalic	Neopentyl glycol	N-H	—[c]	33	—[b]	339
Homoterephthalic, 10 mol-% Terephthalic, 90 mol-%	Ethylene glycol	E-9T/H	0.30[d]	60	230	345
Homoterephthalic, 20 mol-% Terephthalic, 80 mol-%	Ethylene glycol	E-8T/H	0.67[a]	57	206	345
Homoterephthalic, 40 mol-% Terephthalic, 60 mol-%	Ethylene glycol	E-6T/H	0.48[a]	55	—[b]	303
Homoterephthalic, 50 mol-% Bibenzoic, 50 mol-%	*p*-Xylylene glycol	X-5B/H	0.38[a]	71	246	298
Homoterephthalic, 90 mol-% Bibenzoic, 10 mol-%	*p*-Xylylene glycol	X-B/H	0.84[a]	45	—[b]	343
Homoterephthalic, 20 mol-% Terephthalic, 80 mol-%	Neopentyl glycol	N-8T/H	0.49[a]	64	—[b]	308

[a] In phenol–tetrachloroethane (60:40) at 25°C and 0.5 g/100 ml solvent.

[b] None detected.

[c] Not completely soluble in phenol–tetrachloroethane.

[d] In phenol–tetrachloroethane (60:40) at 30°C and 0.5 g/100 ml solvent.

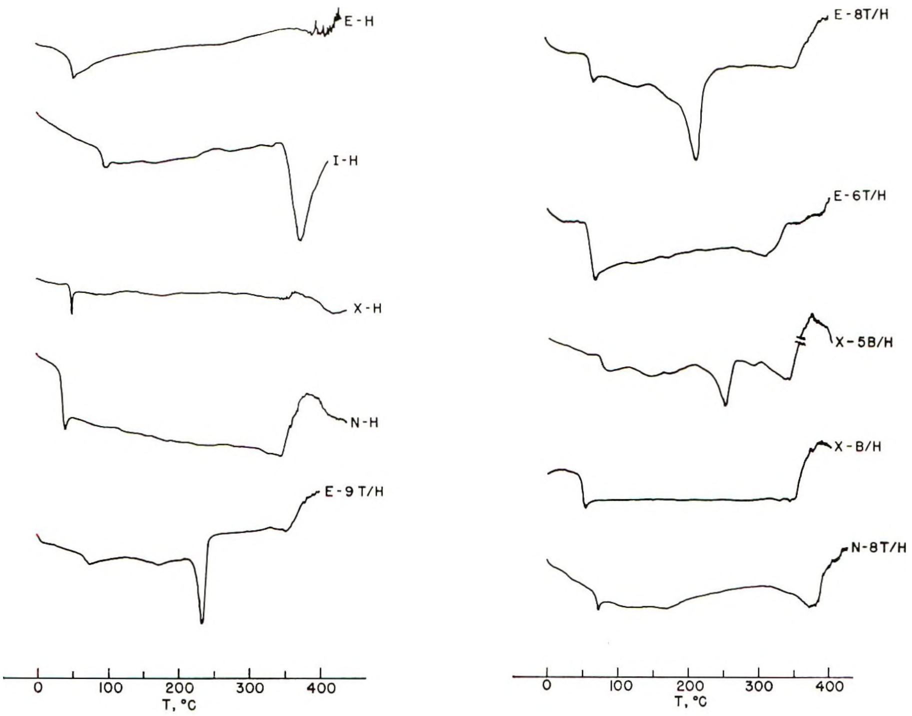


Fig. 2. DTA thermograms of homoterephthalic acid polyesters.

esters and excess glycol at 125–200°C under nitrogen was followed by heating at 200–250°C while the pressure was reduced at 1.0–0.1 mm Hg. The total reaction time varied from 7–80 hr, depending on the viscosity of the melt. This procedure gave polyesters ranging in color from white to amber. Reaction temperatures exceeding 250°C invariably resulted in gelation. The 4,4′-isopropylidenediphenol polyester was prepared by interfacial polycondensation at room temperature using homoterephthaloyl chloride.

Differential Thermal Analysis

Thermal analyses were run on a DuPont 900 Differential Thermal Analyzer at a programmed heating rate of 20°C/min. Crystalline melting points, T_m, were defined as the maxima in the melting endotherms. Decomposition temperatures, T_{dec}, were taken as the points at which the curves began to depart erratically from the baseline at elevated temperatures.

RESULTS AND DISCUSSION

Polymers prepared from homoterephthalic acid and diamines or glycols by conventional methods of synthesis would be expected to have structures of limited order.[5] The dependence of crystalline melting point on the spacing of polar groups has been well documented for both aliphatic[6] and aromatic[7] polyamides but such a clear relationship would not be expected in the homoterephthalate polyamides. Considering the large spread in molecular weight among the polyamides, the data summarized in Table I and Figure 1 agree rather well with the predicted behavior for unsymmetrical polyamides. The series (2-H through 6-H) of homopolymers prepared from aliphatic diamines shows no dependence of either the T_m or T_g on the spacing of polar groups. The small variation in T_m with increasing aliphatic diamine chain length can be explained by assuming that each polyamide in the series has about the same amount of interchain hydrogen bonding. The absence of a detectable T_m together with the high T_g found for the adipic acid–homoterephthalic acid–hexamethylenediamine copolymer illustrates the dominant effect of the homoterephthalate units on the copolyamide properties. The aromatic rings probably contribute greatly to the high T_g values.

Homoterephthalate polyester homopolymers would be expected to be highly amorphous materials. Furthermore, the placement of homoterephthalate units in the highly crystalline polyesters of terephthalic or bibenzoic acid should drastically lower the crystallinity, melting points and glass transition temperatures. The polyester data summarized in Table II and Figure 2 substantiate these predictions. The absence of crystalline melting points indicates that the homoterephthalate homopolyesters are indeed highly amorphous. Increasing the homoterephthalate content from 10 to 40 mol-% in the ethylene glycol–terephthalic acid polyester eliminated the T_m but had little effect on the T_g. The T_m disappeared and the T_g decreased appreciably in the *p*-xylylene glycol–bibenzoic acid polyester as the homoterephthalate content was increased from 50 to 90 mole-%. Assuming limited order, one can explain the effect of the homoterephthalate unit on the crystalline melting point of polyesters solely on the basis of symmetry.

The author wishes to express his appreciation to Dr. E. D. Hornbaker, Dr. O. E. Klopfer, and Dr. G. N. Grammer for many valuable suggestions and criticisms. A further debt of gratitude is due Mr. D. O. DePree whose excellent synthesis work provided the stimulus for this research program.

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Donald A. Holmer

Research and Development Department
Ethyl Corporation
Baton Rouge, Louisiana 70821

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Polymerization of Cyclic Acetals. I. Polymerization of 2-Vinyl-1,3-dioxane and 2-Isopropenyl-1,3-dioxane

Recently there has arisen a great interest in ring-opening polymerization of heterocyclic compounds, particularly of cyclic ethers.[1–3]

A similar type of compound is formed by cyclic unsaturated acetals. Tada and coworkers[4] reported studies concerning a cationic polymerization of 2-vinyl-1,3-dioxolane at low temperature. The present experiment investigates the polymerization of 2-vinyl-1,3-dioxane and 2-isopropenyl-1,3-dioxane by means of cationic catalysts.

Experimental

2-Vinyl-1,3-dioxane (VDOX) and 2-isopropenyl-1,3-dioxane (ISDOX) were synthesized by the method of Fischer,[5] distilled under deoxygenated nitrogen, and collected in a flame-dried glass flask, then saturated with nitrogen. The product of VDOX distilling at 64–66°C/44 mm Hg, n_D^{20} = 1.4433 and the product of ISDOX distilling at 84–86°C/72 mm, Hg n_D^{20} = 1.4488 were used.

The catalysts $TiCl_4$, $SnCl_4$, and BF_3Et_2O were distilled over P_2O_5 under a nitrogen atmosphere prior to use. The $TiCl_4$ and $SnCl_4$ were used as 0.4 and 0.67*M* solutions in *n*-heptane, respectively; boron trifluoride diethyl etherate was used as a 0.59*M* solution in ethylene dichloride. All solutions were stored under nitrogen in bottles and were transferred with hypodermic syringes. The polymerization was carried out under nitrogen. The monomer was dissolved in *n*-heptane, then catalyst solution was added at the polymerization temperature, and the mixture was allowed to stand for the desired time of reaction. To stop the polymerization, ethanol containing an amount of NH_3 equimolar to the catalyst, was added. The reaction mixture was washed with water. Solvents and the unreacted monomer were distilled off at 30–40°C under reduced pressure, and the polymeric residue was dried *in vacuo* after washing with water.

The process of polymerization is greatly influenced by the temperature and the kind and concentration of the catalyst. Polymerization of VDOX and ISDOX was carried out at temperatures ranging from −78°C to 18°C in *n*-heptane or ethylene dichloride. At temperatures of −78°C to −30°C no polymer was obtained, and at higher temperatures the polymerization proceeded to give polymer in a good yield.

A crosslinked structure for both polymers has been obtained, when $BF_3 \cdot Et_2O$ of different concentrations was used at room temperature or at 0°C.

$SnCl_4$ causes crosslinking of both monomers at room temperature. At 0°C only VDOX undergoes crosslinking at a $SnCl_4$ concentration of more than 80×10^{-3} mole/l.

$TiCl_4$ gives products of low molecular weight and low conversion. The decomposition point of some such polymers was about 190–210°C for VDOX and 220–230°C for ISDOX. The polymers were soluble in most organic solvents; intrinsic viscosity $[\eta] = 0.02$–0.1.

Table I records the results for several runs. The structure of polymers was studied by means of the infrared and chemical analyses.

Double bond contents on the average of 30–40%, and ester contents of 5–56% were determined by means of chemical analysis. In the case of ester content this was achieved by saponification for several hours with 0.5*N* KOH. Carboxyl groups were absent in all the examined polymers.

In general, the infrared spectra of VDOX and ISDOX exhibited bands at 1040–1175 cm^{-1}, indicative of the C—O—C group and at 915 and 990 cm^{-1} indicative of the vinyl group. In the spectra of the polymers, PVDOX and PISDOX a C=O stretching band at 1720 cm^{-1} is seen, as well as an absorption band at 1040–1175 cm^{-1}, associated with the cyclic C—O—C group and bands at 915 and 990 cm^{-1} characteristic for a vinyl group (Figs. 1 and 2); the intensity of the latter two is somewhat decreased.

The results of the polymerization of VDOX and ISDOX show that the process of increasing the molecules may be carried out according to several mechanisms, particularly by: (*1*) consumption of double bonds; (*2*) formation of ester units; (*3*) breaking of the acetal ring.

TABLE I

	Reaction conditions					Polymer					
							Conversion, %				
Monomer	[M], mole/l.	Catalyst	[Cat], mmole/l.	Time, hr	Temp., °C	[η] (25°C)	Soluble[a]	Insoluble	Ester units, mole-%	Double bonds, mole-%	Appearance of polymer
2-Vinyl 1,3-dioxane (VDOX)	1.6	$SnCl_4$	80	70	0	—	17.8	—	7.2	30.6	Brown oil
	2.3	"	139	70	0	—	—	29.2	5.7	22.0	Dark brown oil
	4.3	"	124	16	0	—	—	22.2	6.8	27.0	Light yellow semisolid, M-507[b]
	2.3	$TiCl_4$	52	70	0	0.02	23.4	—	8.6	19.4	Brown oil
	2.3	$BF_3 \cdot Et_2O$	52	70	0	0.06	13.8	26.5	20.8[b]	29.7[b]	White powder, crosslinked[b]
	2.3	$SnCl_4$	17.5	70	+18	—	1.1	13.4	14.1[b]	40.1[b]	Light semisolid[b]
	2.3	$SnCl_4$	49.0	70	+18	—	4.65	44.7	13.2[b]	32.9[b]	Light semisolid[b]
	2.3	$TiCl_4$	50.0	70	+18	0.08	12.7	7.94	7.2	36.4	Brown oil, M-390[b]
	1.8	$BF_3 \cdot Et_2O$	32	70	+18	0.1	3.1	9.7	27.9[b]	32.9	White powder crosslinked[b]
2-Isopropenyl-1,3-dioxane (ISDOX)	2.2	$SnCl_4$	56	70	0	—	12.5	—	2.71	18.7	Yellow oil
	2.2	$TiCl_4$	56	70	0	0.08	26.0	—	14.1	50.1	Semisolid oil
	2.2	$BF_3 \cdot Et_2O$	56	70	0	0.1	7.8	10.8	53.6	30.1	Light yellow powder[b]
	2.0	$SnCl_4$	56	70	+18	—	14.8	—	12.8	29.7	Dark brown oil
	2.0	$TiCl_4$	56	70	+18	—	31.1	—	11.7	36.1	Dark brown oil
	2.0	$BF_3 \cdot Et_2O$	56	70	+18	—	21.5	10.1	56.1	30.1	Light yellow powder[b]

[a] Data for polymer soluble in heptane.

[b] Data for polymer insoluble in heptane.

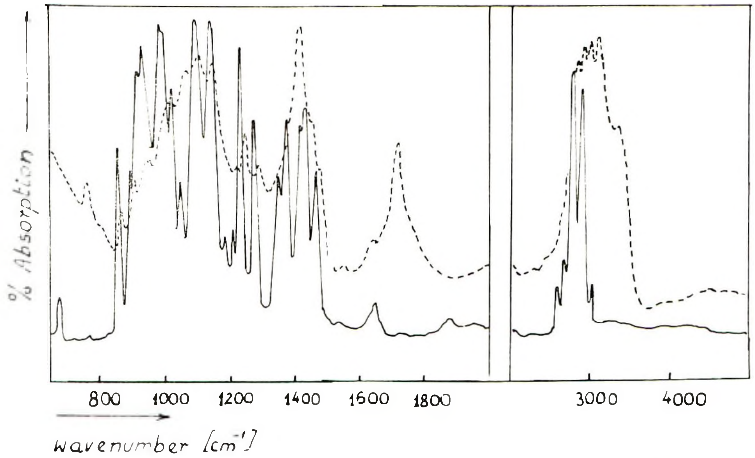

Fig. 1. Infrared spectra of 2-vinyl-1,3-dioxane and its polymers: (——) monomer; (- -) polymer.

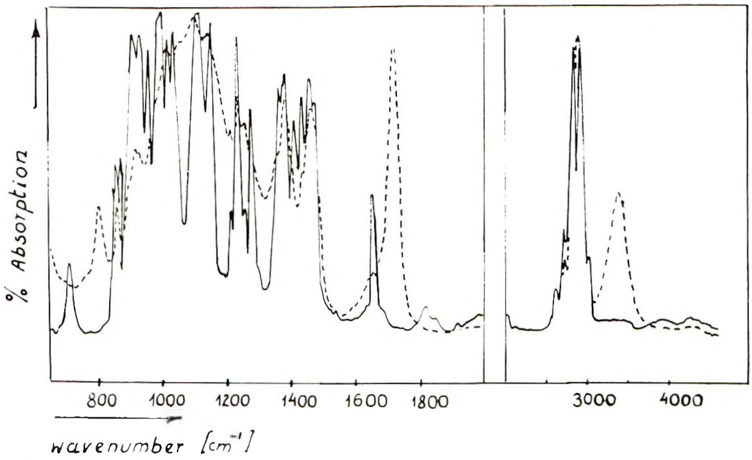

Fig. 2. Infrared spectra of 2-isopropenyl-1,3-dioxane and its polymer: (——) monomer; (- -) polymer.

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Zbigniew Jedlinski
Jolanta Maslinska-Solich

Department of Polymers Technology
Silesian Institute of Technology
Gliwice, Poland

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Electrochemical Synthesis of Living Anions

Since the pioneering work of Szwarc and co-workers[1] concerning the formation of living anions from hydrocarbon monomers by using a sodium–naphthalene complex as initiator, a growing literature has developed on electrochemical methods for obtaining these same living anions. The monomers studied most extensively are styrene[2–4] and α-methylstyrene.[5,6]

Certain questions arise when these systems are discussed from an electrochemical viewpoint. Some of these questions have been recognized by the workers given above, but not all have been answered. These questions include: (*1*) What solvents are satisfactory? (*2*) What electrolytes can be used? (*3*) Is the mechanism of initiation dependent on the electrolyte used?

In regard to the first of these questions, Yamazaki and co-workers[5] have discussed the solvent problem in general terms, and no additional comment seems warranted. In addition to the solvents which have been used successfully, we have found in our laboratory that hexamethylphosphoramide (HMPT) is also a suitable solvent. This solvent has previously been described as being quite stable in the presence of various anions.[7]

Polymerization reactions were carried out in an H-type cell in the middle of which was a medium-porosity sintered glass disk. Smooth platinum electrodes, each with a surface area of 1 in.^{2}, were sealed into the electrode compartments. Each electrode compartment could hold a volume of up to 150 ml. After attaching the cell to a vacuum line and evacuating, solvents and monomer were distilled onto electrolytes in the cell. Atmospheric pressure was then restored using prepurified nitrogen. The monomer used was styrene in all cases.

With HMPT as the solvent, purification was achieved by distillations *in vacuo* from calcium hydride and barium oxide followed by passage through a molecular sieve column. A syringe, previously heated to 110°C. and then cooled while purging with nitrogen, was used to transfer the HMPT to the cell attached to the vacuum line. The transfer was effected with the use of diaphragms on the column receiver and the cell. All of the above operations were conducted under a blanket of prepurified nitrogen.

With regard to electrolyte suitability, Baizer[8] has discussed the parameters for electrolyte choice (in particular the cation) for the electrochemical reduction of a monomer. In general these parameters would also apply to living anion systems. An additional factor in the latter systems, however, is the possibility of the living anions reacting with the electrolyte. With the use only of reduction potentials as a criterion for electrolyte choice, it would seem that all tetraalkylammonium salts would be suitable as their potentials are more cathodic than that of styrene. Such is not the case, however, as living anions will react with tetraalkylammonium salts when at least one of the alkyl groups contains a β-hydrogen. This type of reaction has been observed before. For example, Wawzonek and Duty[9] have reported that benzyl carbanions will abstract a proton from the tetrabutylammonium ion.

Electrolysis of styrene in tetrahydrofuran by use of sodium tetraphenylboron as the electrolyte was carried out under conditions similar to those described by Funt et al.[4] The characteristic orange color associated with living polystyryl anions soon developed at the cathode surface and quickly permeated the whole of the catholyte solution. Addition of a small amount of tetrabutylammonium perchlorate resulted in the rapid disappearance of the color indicating that the living anions had been quenched. A second electrolysis under similar conditions, except that the tetrabutylammonium salt was used as the electrolyte, produced no living anions as evidenced by the complete absence of the orange color. Workup of the experiment gave no solid polystyrene.

Previous workers used alkali metal cations in the electrolyte almost exclusively with the styrene system. With such a cation, sodium, for example, two modes of initiation can be visualized. One possibility is that sodium cation is reduced to the metal followed by reaction with monomer to give styrene anion radical. The alternative would seem to be direct electron transfer to monomer resulting in the same anion radical. The propagation reaction should be similar, if not identical, in both cases.

Polarographic reduction potentials of sodium cation (the salt was sodium tetraphenylboron) and styrene were determined at a rotating platinum electrode with the use of *N*,*N*-dimethylformamide containing 0.1*N* tetrabutylammonium iodide as supporting electrolyte. The half-wave potential of sodium ion was −2.2 v. (vs. SCE), whereas that of styrene was −2.32 v. (vs. SCE). Although one cannot rule out the possibility that both modes of initiation occur simultaneously due to the close proximity of the reduction potentials, it would seem that the mode involving participation of sodium metal should predominate.

Based on the polarographic study, the question arose as to whether a system could be devised in which living polystyryl anions were definitely formed by direct electron transfer to monomer. Tetramethylammonium ion was shown to reduce at −2.7 v. (vs. SCE) under the polarographic conditions previously described. In addition, this cation should not be readily attacked by the living anions due to the absence of β-hydrogens on the alkyl groups. The conditions of a typical electrolysis using the tetramethylammonium ion are described in Table I. The data are consistent with a living anion system.

TABLE I
Electroinitiated Living Polystyrene[a]

Monomer, g.	Current passage, F. × 10^4	$\bar{M}_n \times 10^{-4}$ From electrol. data[b]	$\bar{M}_n \times 10^{-4}$ From intrinsic viscosity
8.2	2.9	5.66	5.22

[a] Total volume of monomer and HMPT, 110 ml., $N(CH_3)_4B(C_6H_5)_4$, 1.0 g.

[b] Molecular weight calculated from the equation:[5]

$$\bar{M}_n = \text{Monomer (g.)}1/2I\ \text{(F.)}$$

After completion of this work, Yamazaki and co-workers[10] reported a similar study involving α-methylstyrene. Their findings were very consistent with those of this work.

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JAMES D. ANDERSON

Monsanto Company
Central Research Department
St. Louis, Missouri 63166

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Polymerization with Hydrogen Migration of Acrylamide

It is known that the base-catalyzed polymerization of acrylamide does not give a vinyl-type polymer, polyacrylamide, but gives poly-β-alanine; there occurs a so-called polymerization with hydrogen migration.

This type of polymerization is not peculiar to acrylamide but occurs with other monomers (ethylenesulfonamide,[1] methyl vinyl ketone,[2] isobutene,[3] *N*-monosubstituted acrylamides,[4,5] *p*-styrenesulfonamide[6]).

Breslow,[1] who first studied the base-catalyzed polymerization of acrylamide, obtained, during the polymerization, a compound which was thought, on the basis of analytical data (hydrogen absorption and NH_2 content) to be an acrylamide dimer containing an acrylic double bond in the molecule; hence the author proposed a mechanism for the initiation and propagation steps of the polymerization.

Later other authors[7-11] who studied both the initiation and the propagation steps of this polymerization, failed to confirm the presence of products of this kind. Ogata[8] particularly refers to not finding a double bond either in the product of the reaction between acrylamide and sodium alkoxide, or in the products obtained in the initial stage of the polymerization.

Tani et al.,[10] moreover, observe that all the authors interested in this subject were unable to isolate acrylamide oligomers in a sufficiently pure state for identification.

The present work reports the results obtained by polymerizing acrylamide in the presence of several alkali catalysts.

In each polymerization a product was obtained which was crystallized and analyzed; the results indicated the structure I for the product:

$$CH_2{=}CHCONHCH_2CH_2CONH_2$$

I

that is, β-acrylamidopropionamide or acrylamide dimer. In some polymerizations it is possible to obtain product I in yields as high as 40% based on the initial monomer.[12]

Product I can be polymerized by free-radical initiation,[12] thus yielding polymers and copolymers having the following structural unit II:

$$\left[\begin{array}{l} CH_2CH \\ \quad | \\ CONHCH_2CH_2CONH_2 \end{array}\right]_n$$

II

The same product can be polymerized in the presence of alkali catalysts giving poly-β-alanine[1] (III)

$$\left[CH_2CH_2CONH \right]_n$$

III

the same product obtained from the base-catalyzed polymerization of acrylamide.

Among the reaction products of the base-catalyzed polymerization of acrylamide, besides acrylamide dimer, was another which was isolated and analyzed; the results seem to indicate the structure IV,

$$CH_2{=}CHCONHCH_2CH_2CONHCH_2CH_2CONH_2$$

IV

which is an acrylamide trimer. Product IV can be polymerized by free-radical initiation thus giving polymers and copolymers containing the structural unit V:

$$\left[\begin{array}{l} CH_2CH \\ \quad | \\ CONHCH_2CH_2CONHCH_2CH_2CONH_2 \end{array}\right]_n$$

V

Again if polymerized in presence of alkali catalysts, product IV gives poly-β-alanine.

On the basis of these results, some considerations about the polymerization of acrylamide with hydrogen migration can be drawn.

EXPERIMENTAL

Monomer

Acrylamide was crystallized from chloroform each time before polymerization; in some cases the monomer was purified by sublimation *in vacuo* before use.

Solvent

In each polymerization, dioxane was used as solvent; this was dried with sodium and distilled, then treated with potassium benzophenone ketyl and distilled again.

Catalysts

Sodium *tert*-butoxide was prepared by reacting sodium and dry *tert*-butyl alcohol according to the standard technique of preparation of alkali alkoxides. The product was then heated at 160°C. at 0.1 torr for 1 hr. in order to remove all the excess alcohol. *n*-Butyllithium was used as a solution in *n*-heptane; the titer was determined before use according to Gilman.[13] Alkali benzophenone ketyls were prepared by reacting alkali metals with benzophenone in dry dioxane (previously treated with potassium benzophenone ketyl); upon stirring at room temperature the mixture soon became dark blue. The concentration of the ketyl was determined by titration of hydrolyzed, filtered solutions. Lithium naphthalene was prepared by reacting lithium metal and naphthalene in dry tetrahydrofuran (previously treated with potassium benzophenone ketyl).

Procedure

All experiments were performed in a glass tube which was filled in a dry box with dry monomer, solvent, and catalyst; in some cases phenyl-β-naphthylamine was added as inhibitor of free-radical polymerization. The tube was then sealed in a nitrogen atmosphere and heated according to the conditions of Table I.

At the end of each polymerization, there was a solid white product on the walls of the reaction tube. This product was separated from the polymerization solvent and then treated with boiling dioxane (which contained a small amount of phenyl-β-naphthylamine) in order to extract acrylamide dimer and the acrylamide trimer if present; both products, in fact, dissolve in boiling dioxane and by cooling it is possible to obtain them in a crystalline form.

The solubility of product I in dioxane at room temperature is very low (3.1×10^{-2} mole/l.); product IV is practically insoluble under the same conditions. The solid residue of this extraction was examined in order to evaluate the amount of water-soluble or insoluble polymer; other analytical tests were also performed (infrared spectrum, melting point, sometimes X-ray diffraction and the ninhydrin reaction on the hydrolyzed product).

To the polymerization solvent remaining after removing the solid product, small amounts of water were added in order to destroy the catalyst present; the solvent was then allowed to come to room temperature and to stand overnight. Under these conditions, in the polymerizations carried out at higher temperatures (see Table I), it is still possible to obtain in some cases both crystallized acrylamide dimer and acrylamide trimer. The polymerization solvent was then evaporated to dryness *in vacuo* to detect monomer and small amounts of acrylamide dimer.

To separate I from IV the mixture of products was repeatedly extracted with dioxane at 60°C. From each extraction acrylamide dimer was separated by cooling; it was then weighed and crystallized for analysis. The residue insoluble under these con-

TABLE I
Polymerization of Acrylamide

Monomer[b] concn., mole/l.	Inhibitor[a]	Solvent	Catalyst	Catalyst concn. × 10^2, mole/mole monomer	Temp., °C.	Time, hr.	Acrylamide dimer yield, %	Polymer yield, %	Yield of polymer insoluble in water, %
4.3	PBNA	Dioxane	Sodium *tert*-butoxide	1.84	100	0.25	7	80	2
4.3	PBNA	"	Sodium *tert*-	1.84	100	15	Trace	92	65
1.8	PBNA	"	*n*-Butyllithium	2.8	60	0.25	30	40	0
1.8	PBNA	"	*n*-Butyllithium	2.8	60	6	5	85	0
1.8	—	"	*n*-Butyllithium	2.8	20	24	42	48	0
1.8	—	"	Lithium benzophenone ketyl	2.8	20	24	40	52	0
1.8	—	"	Potassium benzophenone ketyl	2.8	20	24	Trace	68	0
1.8	—	"	Lithium naphthalene	2.8	20	24	38	22	0

[a] PBNA = phenyl-β-naphthylamine. [b] The amount of acrylamide used in each polymerization was 1 mole.

ditions (in some cases 2% or 3% with respect to the initial mixture) was then recrystallized from boiling dioxane–ethanol (4:1 in volume). Product IV was obtained in form of a white powder; it was further crystallized for analysis. Paper chromatography was performed with butanol–acetic acid–water (4:1:5 in volume); the compounds were detected by means of their ultraviolet absorption. Whatman No. 1 paper was used.

RESULTS

The experimental conditions of polymerization and the catalysts employed are given in Table I. In this table are also listed the percentages of acrylamide dimer obtained from each polymerization.

Acrylamide dimer, obtained according to the procedure described in the Experimental Section, was recrystallized from dioxane and analyzed.

ANAL. Calcd for $C_6H_{10}N_2O_2$: C, 50.6%; H, 7.1%; N, 19.7%. Found: C, 50.5%; H, 7.0%; N, 19.5%.

One gram of the product absorbed 1.11 g. of bromine (calcd. for $C_6H_{10}N_2O_2$: 1.125 g).

A determination of the molecular weight, carried out with a Mechrolab Model 301 A osmometer, gave a value of 140.8 (calcd value: 142.16). The infrared spectra of the dimer and its polymers are shown in Figure 1.

The infrared spectrum of acrylamide dimer (spectrum *1*, Fig. 1) showed absorptions at 950 and 980 cm.$^{-1}$ that may be attributed to the C=C double bond, absorption at 1555 cm.$^{-1}$ characteristic of the second band of the secondary amides, and absorption at 1635 cm.$^{-1}$ characteristic of the second band of the primary ones. The melting point of the product after recrystallization from dioxane is 149–150°C. The chromatographic analysis (eluent phase: butanol–acetic acid–water) showed it was a well defined product having $R_f = 0.63$.

Free radical polymerization of product I in a methanol solution (with α,α'-azobisisobutyronitrile and ultraviolet radiation as catalyst) gave a 95% yield of polymer which still showed the characteristic bands of primary and secondary amide groups (spectrum *2*, Fig. 1) while the bands of the double bond had disappeared. The polymer was water-soluble and softened at 150–200°C.

The base-catalyzed polymerization of I in *N*-methylpyrrolidone for 4 hr. at 100°C. with sodium *tert*-butoxide as catalyst and phenyl-β-naphthylamine as inhibitor of free radical polymerization gave 90% yield of a polymer insoluble in water, soluble in formic acid, melting with decomposition at temperatures higher than 300°C. The infrared spectrum (spectrum *3*, Fig. 1) showed it to be poly-β-alanine.

Acrylamide trimer, obtained according to the previously described procedure, gave the following analytical results: 1 g. of product absorbed 0.68 g. of bromine (calcd. for $C_9H_{15}N_3O_3$: 0.75 g). The determination of the molecular weight carried out with a Mechrolab Model 301A osmometer gave a value of 222 (calcd. value: 213.2). The melting point is 179–181°C. The differences among analytical and calculated values are attributed to difficulties in obtaining the product in a sufficiently pure state, difficulties, mainly, in removing small quantities of products which have probably analogous structures and higher molecular weights. (The chromatographic analysis showed it was a well defined product with traces of presumably higher oligomers; in fact in the chromatograph of acrylamide trimer, besides the main spot, the R_f of which is 0.54, there can be noted a second spot of very low intensity with $R_f = 0.44$).

The spectrum of the product is given in Figure 1, spectrum *4*.

Absorptions at 950 and 980 cm.$^{-1}$ may be attributed to the double bond; the absorption at 1550 cm.$^{-1}$ is characteristic of the second band of secondary amides and that at 1635 cm.$^{-1}$ of the second band of primary amides.

Acrylamide trimer, like acrylamide dimer, can be further polymerized. For example, treating it at 50°C. in a 10% methanol solution with α,α'-azobisisobutyronitrile yielded after 15 hr., a 40% yield of water-soluble polymer. The infrared spectrum (Fig. 1) of this polymer revealed bands peculiar to the primary and secondary amide groups while

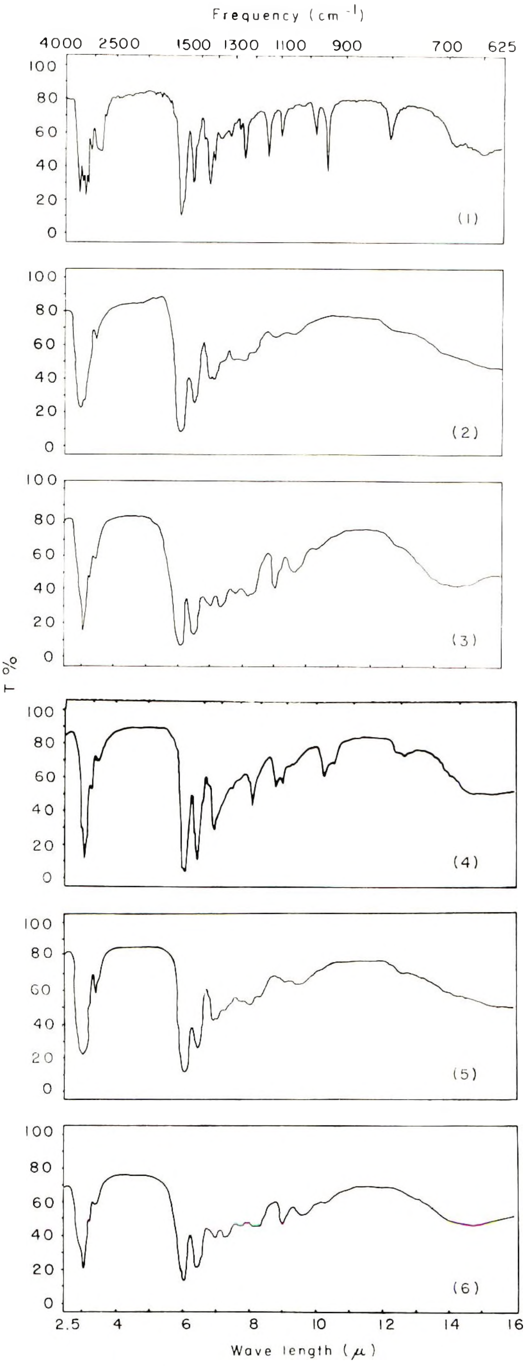

Fig. 1. Infrared spectra: (*1*) acrylamide dimer; (*2*) polymer of the acrylamide dimer obtained by free radical-catalyzed polymerization; (*3*) polymer of the acrylamide dimer obtained by base-catalyzed polymerization; (*4*) acrylamide trimer; (*5*) polymer of the acrylamide trimer obtained by free radical-catalyzed polymerization; (*6*) polymer of the acrylamide trimer obtained by base-catalyzed polymerization. Spectrophotometer, Beckman IR 8; KBr disk.

TABLE II
Properties of Acrylamide and Its Oligomers

	Mol. wt.	Melting point, °C.	Solubility[a]					
			R_f	Water	Ethanol	Dimethylformamide	Dioxane	Acetone
Acrylamide	71.08	84–85	0.78	+	+	+	+	+
Acrylamide dimer	142.16	149–150	0.63	+	+	+	0	0
Acrylamide trimer	213.24	179–181	0.54	+	+	+	−	−

[a] Solubility: (+) soluble (−) insoluble, (0) slightly soluble at room temperature.

those of the double acrylic bond had disappeared. The polymer softened in the range of 100–150°C.

By base-catalyzed polymerization (e.g., *N*-methyl pyrrolidone at 100°C. for 1 hr. with sodium *tert*-butoxide catalyst and phenyl-β-naphthylamine as inhibitor of free-radical polymerization) compound IV yielded a polymer which is water-insoluble, but soluble in formic acid; it melts at over 300°C. The infrared spectrum (Fig. 1, spectrum *6*) showed it was a pure poly-β-alanine, that is, the same product obtained by base-catalyzed polymerization of acrylamide and acrylamide dimer.

Table II summarizes some physical characteristics of acrylamide and of oligomers obtained from base-catalyzed polymerizations of acrylamide.

DISCUSSION

Table I shows that virtually each polymerization gives acrylamide dimer. Many factors influence the yields of this product; the main ones seem to be catalysts, temperature and polymerization time. It has been observed, for example, that by using lithium-benzophenone ketyl as catalyst and a temperature of 20°C. it is possible to obtain acrylamide dimer in very high yield and that under the same conditions but using potassium benzophenone ketyl, the yield of acrylamide dimer is remarkably lower. In the presence of *n*-butyllithium catalyst, the yield of acrylamide dimer is closely related to the polymerization conditions. For example, high yields of product I can be obtained by polymerizing at different temperatures (20 or 60°C.) provided that the polymerization time has been suitably chosen. On the other hand, at the same temperature (60°C.), the polymerization time influences greatly the yields of acrylamide dimer.

It is interesting to notice that, according to the experimental conditions of Table I, only with sodium *tert*-butoxide catalyst at 100°C. was a water-insoluble polymer (soluble in formic acid probably because of a high molecular weight) obtained. Under these conditions a polymerization of 15 hr. gives acrylamide dimer in extremely low yield while the yield of the water-insoluble polymer is high (65% with reference to the initial acrylamide). If the polymerization time is reduced to 15 min., the yield of acrylamide dimer increases (7%), while the yield of the water-insoluble polymer is considerably reduced (2%). This seems to suggest that, in the course of the polymerization process, the initially formed products, having a low molecular weight, tend to react giving polymer with a higher molecular weight. This reaction requires severe conditions and, presumably, occurs in a nonhomogeneous state since the polymer chains formed at the first stage are insoluble in the polymerization solvent.

Our results confirm the mechanism originally proposed by Breslow et al.[1]

In particular, the possibility of a further base-catalyzed polymerization of product IV to poly-β-alanine seems to confirm the hypothesis of a chain transfer prevailing during the propagation stage. In fact it seems difficult to think, according to Ogata[8] (who does not consider the possibility of an intermolecular hydrogen migration during the polymerization) that the poly-β-alanine molecule could be formed by an intramolecular hydrogen migration; in this case such migration should take place from position 12 to position 2 of the molecule.

Note added in proof: Since our manuscript was submitted, a summary of a paper by Okamura and co-workers [*Polymer Previews*, **3**, 27 (1967)] has come to our attention. They have confirmed the formation of dimer under certain conditions and seem to agree, at least in part, with our results.

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ALVARO LEONI
SIMONE FRANCO
GUIDO POLLA

Research Laboratories, Ferrania, S.p.a.
Ferrania, Italy

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BOOK REVIEWS

Conformations of Macromolecules (High Polymers, Vol. XXII). T. M. Birshtein and O. B. Ptitsyn (translated from the Russian by Serge N. Timasheff and Marina J. Timasheff). Interscience, New York, 1966. xiv + 350 pp. $14.50.

This volume is a very timely, interesting, and authoritative book. It extends the treatment of configurational statistics of polymer chains as developed in the treatise of Volkenstein. It also treats the problem of the helix-coil transition in biopolymers. The use of matrix methods, Markoff chains, and Ising problems are concisely presented. Much illustrative material is given. The book is highly recommended to all who are interested in polymer structure.

Arthur V. Tobolsky

Frick Chemical Laboratory
Department of Chemistry
Princeton, University
Princeton, New Jersey 08540

Introduction to Organic Chemistry. Charles H. De Puy and Kenneth L. Rinehart, Jr. Wiley, New York, 1967, 392 pp. $8.95.

In this book the authors provide us with an attractive text for a one term course in organic chemistry aimed primarily at nonmajors. The emphasis in the book is on compounds of biological interest with many examples of functional group types being taken from natural products. This slant is further demonstrated by the devotion of five chapters out of the sixteen in the book to carbohydrates, acids and lipids, amino acids, peptides and proteins, biochemical reactions and metabolism, and biosynthesis and the chemistry of natural products. Fundamental concepts of organic chemistry are not neglected, however. Reaction mechanisms, stereochemistry, and the molecular orbital picture of bonding are among the topics which form an integral part of the discussion of the subject. The presentation is lively and interesting. Color is used in formulas and equations in the text to emphasize functional groups, reaction sites, and general relationships between molecules. There are good problems in and at the end of each chapter, and answers are provided at the end of the book.

The topic of polymerization is introduced by a chapter on free radical addition and polymerization early in the book. Many other polymerization reactions are covered in other chapters as the different functional groups are introduced. For a textbook of this size, it would seem that there is an exceptionally good coverage of the variety of polymers that can be made and of their present and increasing practical importance.

Seyhan N. Ege

Department of Chemistry
University of Michigan
Ann Arbor, Michigan

Reinforcement of Elastomers, Gerard Kraus, Ed. Interscience, New York, 1965. xv + 611. pp. $19.50.

While several hundred papers have been published on the subject of elastomer reinforcement in the past decade, there has not been a single volume available which could be recommended as a reference for those recently concerned with this important aspect of rubber technology. *Reinforcement of Elastomers,* edited by Gerard Kraus and published by Interscience, very adequately provides this reference. In addition to "newcomers," those who have been active in the field will also find it most interesting reading.

The first nine chapters cover the theoretical and experimental aspects of reinforcement, while the remaining eight chapters cover the production and applications of reinforcing fillers. Each chapter has been written by recognized authorities in the field and all have carried out their commission most adequately. As the Editor points out in the Preface, differences of opinion and interpretation will occasionally be encountered in the first nine chapters. This is to be anticipated in a field as complex and still as far from "closed" as elastomer reinforcement. The present reviewer leans toward the views expressed by Rehner in Chapter 9, to the effect that a final elucidation of reinforcement awaits clarification of the phenomenon of vulcanization.

The chapter by Hess on microscopy of reinforced rubber stocks is particularly lucid and interesting.

Merton Studebaker has provided an excellent chapter on compounding with carbon black. It should prove invaluable to those recently concerned with this important aspect of rubber technology. The inclusion of practical information on "noncarbon" fillers, particularly the silicas, is very timely. Information on these reinforcing pigments has not been as readily available as that for carbon blacks. While the chapters on "noncarbon" fillers emphasize the fact that reinforcement is not a property unique to carbon black, the last two chapters on carbon black–polyethylene compounds make it evident that reinforcement in its broadest sense in not confined to elastomers.

The Appendix contains valuable information, previously not readily available, relating to the production and producers of reinforcing fillers.

Although 22 authors have contributed to this volume, the style throughout is generally uniform; indicative of the excellent task of editing which Dr. Kraus has performed. *Reinforcement of Elastomers* is a valuable and long needed contribution to the literature of rubber technology. Dr. Kraus and his authors are to be complimented for their excellent efforts.

W. R. Smith

Cabot Corporation
Billerica, Massachusetts

Testing of Polymers, Vol. 2. J. V. Schmitz, Ed. Interscience, New York, 1966. 440 pp. $19.00.

Volume 2 of Schmitz's series is a valuable collection of scientific and technological data about physical properties as well as testing of polymers.

Stress relaxation and other mechanical properties are discussed by R. L. Vergen, Jr. and by D. H. Kaelble in two useful reviews. J. J. Bikerman treats the wetting properties of plastics surfaces, For the space and radiation scientists, there are chapters on cryogenic testing by J. H. Lieb and R. E. Mowers, and radiation resistance of polymers by D. J. Metz. The latter author adds a convenient listing of commercial sources of radiation equipment.

Flexural tests (H. S. Loveless) are becoming more important with the increasing use of sandwich construction. Flammability tests (L. B. Allen and L. N. Chellis) are also of immediate interest, in view of the accelerated use of plastics in building.

The chapter on hardness and wear (J. J. Gouza) reveals no fewer than 26 tests. The chapter on surface appearance, by R. S. Hunter and L. Boor, includes a discussion of Hunter's own widely used glossmeter. E. Weiss discusses ozone resistance, with particular emphasis on the unsaturated elastomers.

Processing of Numerical Test Data, by J. Mandel and T. W. Lashof, is a salutary review of the principles of statistical analysis and planning of experiments.

Irving Skeist

Skeist Laboratories, Inc.
Newark, New Jersey

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 6 (1968)

ERRATUM

Steady-State Drawing of Polymer Melts

(article in *J. Polym. Sci. A-1*, **6**, 247–251, 1968)

By GREGORY M. FEHN

Engineering Research Department, Owens-Illinois Technical Center,
Toledo, Ohio 43607

On page 249, eq. (8) should read $E_l = F_l v_l v_0/[Q(v_l - v_0)]$.

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