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Grafting of Poly(ethylene oxide) on Poly(methyl Methacrylate) by Transesterification

MENAHEM A. TWAIK, MENASHE TAHAN, and ALBERT ZILKHA,
Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel

Synopsis

The grafting of the potassium alkoxide derivative of poly(ethylene oxide) on poly(methyl methacrylate) in homogeneous solution in toluene was studied. The alkoxide was prepared by reaction with potassium metal with methanolic potassium methoxide, or with potassium naphthalene. The last was the most suitable for the systematic investigation of the grafting process. Soluble graft polymers were formed, and essentially the initial poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) participated in the production of graft polymer. The composition of the graft polymers and the frequency of grafting of the side chains were determined by NMR. The solubility of the graft polymers in methanol and water increased with increasing PEO contents, while the melting ranges decreased. Fractionation of the crude graft polymers showed that the grafting reaction was random, and graft polymers containing one PEO side chain per about 10–170 MMA units were obtained.

INTRODUCTION

Graft polymers can be obtained either by grafting of monomers on a suitable polymeric backbone or by the attachment of a preformed polymer on the backbone. While the first method has been extensively investigated, the second has received only very limited attention.[1] The prime advantage of the latter lies in the possibility of obtaining graft polymers having side chains of predetermined molecular weight.

It was the object of the present work to study a representative case of this second method, namely the grafting of preformed poly(ethylene oxide) (PEO) on poly(methyl methacrylate) (PMMA) by the transesterification reaction between the terminal hydroxyl groups of the former with the ester groups of the latter.

Graft polymers of ethylene oxide on polyacrylates were obtained either by the reaction of ethylene oxide monomer with polyacrylates,[2] or acrylic monomers with PEO in the presence of suitable catalysts.[3,4]

The systematic investigation of the grafting was performed under homogeneous conditions in toluene by reacting the potassium alkoxide derivative of PEO with PMMA.

Poly(ethylene oxides) of different molecular weights were grafted, and graft polymers composed of different proportions of the two components were prepared. The polymers were fractionated; their composition and the frequency of grafting of the side chains were determined by NMR. Some of their physical properties were determined also.

EXPERIMENTAL

Materials

Poly(methyl methacrylate) (Matheson, practical), was dried *in vacuo* over phosphorus pentoxide, and a stock solution (1 g polymer, 8.8 ml solution), was prepared.

Diethylene glycol was fractionally distilled under argon. Poly(ethylene oxides) (B.D.H.), having two terminal hydroxyl groups per chain, were dried *in vacuo* over phosphorus pentoxide. Stock solutions of PEO in toluene were dried by azeotropic distillation. Toluene and tetrahydrofuran were dried as previously described.[5] Methanolic potassium methoxide[6] and potassium naphthalene in THF were prepared as described.

All solvents and stock solutions were kept under anhydrous conditions in a pure argon atmosphere.

Preparation of the Potassium Alkoxide Derivative of PEO

The metallation was performed by one of the following three methods. (*a*) Pure potassium metal was added to the dry solution of PEO in toluene and refluxed for 10 hr. The excess of potassium was removed and the concentration of the alkoxide solution was determined by titration. (*b*) The PEO solution was refluxed for 10 min with the proper amount of 5*N* methanolic potassium methoxide, and the methanol was completely distilled off. (*c*) An equivalent amount of potassium naphthalene in THF was added with stirring to the PEO solution in toluene. When the color of the reagent disappeared all the THF was distilled off.

Grafting and Isolation of the Graft Polymers

The proper amount of the PMMA stock solution was added to the solution of the potassium alkoxide derivative of PEO in toluene under argon and the mixture was heated under gentle reflux. The reaction mixture was neutralized with a slight excess of isobutyric acid, and the liberated methanol was slowly distilled off during about 2 hr until no more of it passed over. The methanol was trapped in a graduated receiver, cooled in an ice–salt mixture, and was quantitatively determined by gas chromatography.

The toluene was distilled off *in vacuo*, and the residue containing the reaction products was dissolved in chloroform (50 ml) and filtered. The filtrate was then added dropwise into ether (800 ml) cooled in a Dry Ice–acetone bath with constant vigorous stirring. The polymer which precipitated as a white powder was filtered and washed with ether.

The solubility of the crude graft polymers in methanol and water was examined. Complete solubility of the polymer indicated complete grafting of the PMMA, since it is insoluble in these solvents. In case the graft polymer was only partially soluble, it was extracted thoroughly with methanol and the presence of grafted PEO in the residue was confirmed from its infrared and NMR spectra.

Fractionation of the Graft Polymers

The crude reaction products were fractionated to elucidate the distribution of the grafted side chains, and to detect the presence of homopolymers.

Fractional precipitation was accomplished by using the solvent–nonsolvent system chloroform–ether. Blank tests on PMMA and on PEO ($\bar{M}_n$ = 4330) showed that from a 1% solution of the homopolymers in chloroform, the former precipitated completely at nonsolvent:solvent ratios of 3.2–4.2 and the latter at ratios of 6.5–8.

On the basis of these results four fractions were precipitated from 2% solutions of the reaction products at nonsolvent:solvent ratios of 4.5, 6.0, 7.0, and 8.5 (denoted fractions A, B, C, and D, respectively). The remaining polymer was recovered on evaporation of the solvents giving a fraction denoted E.

Infrared spectra of the fractions showed the presence of both PEO and PMMA (Fig. 1). The compositions of all the fractions were determined by NMR.

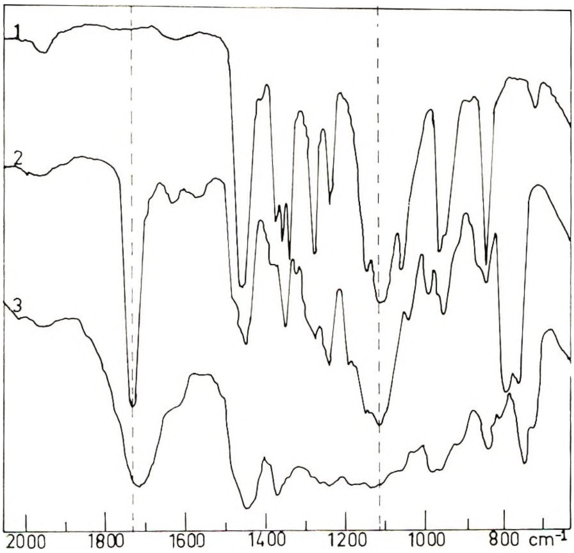
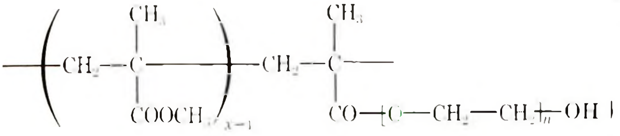


Fig. 1. Infrared spectra of poly(ethylene oxide)–poly(methyl methacrylate) graft polymer and homopolymers: (*1*) PEO; (*2*) graft polymer; (*3*) PMMA.

NMR Study of the Graft Polymers

The NMR spectra were recorded on a Varian A-60 instrument using samples of fresh concentrated solutions of the graft polymers in dry pyridine containing traces of hydrogen chloride gas. Under these conditions PEO shows two resonance peaks at δ = 3.7 ppm (internal —CH_2—O—groups) and $\delta = 3.9$ (terminal $—CH_2OH$ groups). Since atactic poly-MMA shows resonance peaks[9–11] at $\delta = 1.04$ (α-methyl group), $\delta = 1.86$ (methylene) and $\delta = 3.60$ (methyl ester), it follows that the resonance of the methylene protons of the PEO falls in the same region as that of the ester methyl of PMMA and thus each cannot be separately recorded. Therefore, the composition of the graft polymers was determined from the ratio of the peak areas of the different protons according to the model (I) of the recurring unit of the graft polymers, as follows:



$$\left(-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}- \right)_{X-1} -CH_2-\overset{CH_3}{\underset{CO-[O-CH_2-CH_2]_n-OH}{C}}-$$

I

Let the average number of methyl methacrylate units per grafted chain of PEO be X, the sum of the resonance areas of the $—OCH_2—$ and $—OCH_3$ protons A, and the sum of the $—CH_3$ and $—CH_2—$ groups of the poly(methyl methacrylate) B (Fig. 2). It follows that

$$A \propto 3(X - 1) + N$$

and

$$B \propto 5X$$

where 5 is the number of the $—CH_2—$ and $—CH_3$ protons in a methyl methacrylate unit, 3 is the number of the protons of the ester methyl and N

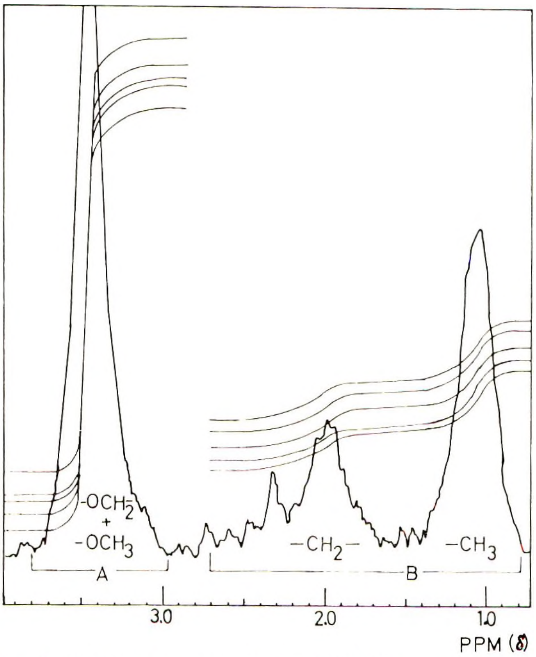


Fig. 2. NMR spectrum of PEO–PMMA graft polymer.

is the number of protons present in a PEO side chain of known molecular weight. It follows that

$$A/B = [3(X - 1) + N]/5X$$

On using poly(ethylene oxide) having $\overline{M}_n = 4330$, the equation becomes

$$A/B = (3/5) + (78/X)$$

Thus from the ratio of the areas A to B it is possible to calculate X. From X it is possible to calculate the molecular weight of the recurring unit, M_s, in the graft polymer according to the equation:

$$M_s = 100X - 31 + M$$

where 31 is the molecular weight of the —OCH_3 group which was substituted by a graft polymer chain and M is the average molecular weight of the PEO side chains. The percentage of poly(ethylene oxide) in the graft polymer is then 100 M/M_s. It may be mentioned that essentially no degradation of the PEO occurred under the conditions of the grafting process, as seen from blank experiments in which the alkoxide derivative of poly(ethylene oxide) was heated in toluene in the absence of PMMA; the $\overline{M}_n$ of the recovered, as seen from acetylation,[12] remained unchanged.

In conclusion, the information obtained from the NMR spectra permits the calculation of the frequency of the grafting of the side chains X, the molecular weight of the recurring unit M_s, and the composition of the graft polymers.

RESULTS AND DISCUSSION

Preliminary experiments on the grafting of PEO on PMMA were made by known methods and catalysts employed in the transesterification of nonpolymeric compounds.[13–21]

In some experiments, PMMA was heated with poly(ethylene oxides) of various molecular weights ($\overline{M}_n$ = 100, 4000, and 6000) in melt at 180°C for 16 hr followed by 4 hr *in vacuo,* in the presence of litharge as catalyst and *tert*-butyl hydroquinone as antioxidant. In other experiments aluminum isopropylate was used as catalyst, and the reaction time was doubled. Other experiments were made in toluene solution under homogeneous conditions with *p*-toluene-sulfonic acid as catalyst while slowly distilling off the solvent to remove any liberated methanol. In all these reactions no graft polymer was formed, as seen from the extraction of the crude product with methanol which led to separation of the PMMA from ungrafted PEO.

The failure of these catalyst systems in the transesterification is probably due to factors associated with the macromolecular nature of the reactants, such as viscosity and diffusion, as well as to the heterogeneity of some of the catalysts used.

To enhance the possibility of reaction of the terminal hydroxyl groups of PEO with ester groups, they were converted to the potassium alkoxide derivatives and reacted with PMMA in toluene under homogeneous condi-

TABLE I
Grafting of Poly(ethylene Oxide) on Poly(methyl Methacrylate)
(Metallation by Potassium Metal[a])

Expt. no.[b]	PEO, g	PMMA, g	[EO]/[Ester groups] %	Reaction time, hr	Yield of crude graft, %
1	12.50	5.0	25.0	6.0	99[c]
2	12.50	5.0	25.0	20.0	79[c]
3	5.62	2.5	22.5	5.0	69
4	11.25	2.5	45.0	5.0	100
5	11.25	2.5	45.0	2.5	81
6	12.01	2.5	48.0	6.0	90
7	24.02	2.5	96.0	6.0	79
8	0.27	5.0	0.5	5.5	99
9	0.56	5.0	1.1	5.5	99
10	1.12	5.0	2.6	5.5	98
11	4.45	5.0	8.9	5.5	—
12[d]	9.02	5.0	4.2	8.0	89
13[d]	9.02	5.0	4.2	8.0	89

[a] Experimental conditions: To the alkoxide, prepared by the reaction of PEO with potassium metal in toluene, PMMA was added and the reaction mixture was heated under reflux as required. In expts. 1 and 2, 75% of the terminal hydroxyl groups were metallated; in all the rest the metallation was 45 ± 5%. In expts. 1–11 PEO of $\bar{M}_n$ = 1000 was used; in the rest $\bar{M}_n$ was 4000.

[b] The graft polymers obtained in expts. 3–7 were soluble in methanol and water. Those obtained in expts. 8–11 were insoluble in methanol or water. The polymers obtained in expts. 8–11 were insoluble in methanol or water. The polymers obtained in expts. 12–13 were soluble in both methanol and hot water.

[c] In expt. 1, 13% and in expt. 2, 48% of the crude polymer was crosslinked and insoluble in chloroform; the rest was soluble even in methanol.

[d] Throughout the reaction, toluene was slowly distilled off the reaction mixture. Methanol was found in the distillate as indicated by gas chromatography.

tions. Whether the alkoxide had been prepared by the reaction of PEO with potassium metal (Table I), with potassium methoxide (Table II), or with potassium naphthalene (Table III), graft polymers of PEO on PMMA were formed.

Proof of the Formation of Graft Polymers

The formation of graft polymers was proved by their solubility properties, by the formation of crosslinked polymers by use of PEO with alkoxide groups at both ends, by the liberation of methanol in the reaction, and by the infrared (Fig. 1) and NMR (Fig. 2) spectra of the various fractions obtained on fractionation of the crude graft polymers.

In all the experiments performed (Tables I–III), proof was obtained for the formation of graft polymers. The experiments made with potassium naphthalene (Table III) gave the more detailed evidence of grafting. It can be seen that, although PMMA is insoluble in methanol or water, all the crude reaction products obtained (excepting experiment 3) were com-

TABLE II
Grafting of Poly(ethylene Oxide) on Poly(methyl Methacrylate)
(Metallation by Methanolic Potassium Methoxide)[a]

Expt. no.[b]	PEO, g	PMMA, g	Terminal OH-group, mmole	$\frac{[\text{PEO}]}{[\text{ester groups}]}$ %	Potassium methoxide, mmole	Yield of crude graft, %
1	1.00	2.5	18.86	37.80	12.50	87
2	0.25	2.5	4.72	9.45	2.50	100
3	0.50	2.5	1.00	2.00	1.25	90
4	0.27	2.5	0.54	1.06	0.50	97
5[c]	9.00	5.0	4.16	4.16	6.75	82
6[c]	9.00	5.0	4.16	4.16	6.75	83
7[c]	9.00	5.0	4.16	4.16	2.25	94
8[c]	9.00	5.0	4.16	4.16	2.25	86
9	0.13	5.0	0.06	0.06	0.25	98
10	0.07	5.0	0.03	0.03	0.25	99

[a] Experimental conditions: PMMA in toluene was added to an alkoxide solution of PEO prepared by reaction with methanolic potassium methoxide, and the reaction mixture was heated under reflux for 8 hr. In expts. 1–2, 3–4, and 5–10, diethylene glycol PEO ($\bar{M}_n$ = 1000), and PEO ($\bar{M}_n$ = 4330), respectively, were used.

[b] The crude graft polymers obtained in expts. 1–4, 9, and 10 were insoluble in methanol or water but soluble in chloroform; in expts. 5–8 they were soluble in methanol but not in water.

[c] The grafting was carried out under slow distillation of the toluene. Methanol (about 2 mmole) was found in the distillate.

pletely soluble in methanol. Part of the graft polymers dissolved in hot or cold water, depending on the composition. This fact points out not only to the formation of graft polymers but also the grafting of all the initial PMMA.

Additional evidence for the formation of graft polymers was obtained from the liberation of methanol, which cannot be due to hydrolysis of the ester groups, as seen from titration of the crude polymers which did not show the presence of acidic groups. Liberation of a quantity of methanol essentially equivalent to the potassium alkoxide derivative of PEO added, points out that all the PEO has participated in the transesterification and was incorporated in the graft polymer. It is interesting to note that even in experiment 3, where part of the PEO (6.06 g, 45% of the starting material) separated in the form of the alkoxide derivative, in the beginning of the reaction, the methanol that was liberated was equivalent to 60% of the starting potassium alkoxide.

In the fractional precipitation of a reaction product, the graft polymers precipitate at nonsolvent:solvent ratios intermediate between those in which the homopolymers precipitate.[22] On this basis the fractionation results (Table IV) give further indication to the incorporation of all the PEO in the graft polymers.

As mentioned, PMMA precipitated first, before the PEO. At the nonsolvent:solvent ratio where the ethylene oxide homopolymer should have

TABLE III

Grafting of Poly(ethylene Oxide) on Poly(methyl Methacrylate) (Metallation by Potassium Naphthalene)[a]

Expt. no.[b]	[Ester groups], mmole/l.	[PEO]/[Ester groups] %	Crude yield, %	Methanol, mmole[c]	Mole methanol/Mole alkoxide %	PEO in crude graft, %		No. of MMA units per grafted PEO chain		Melting range, °C	Solubility[e]		
						Calculated	Found[d]	Calculated	Found[d]		Hot H_2O	Cold H_2O	MeOH
1	360	13.40	—	14.11	94.1	—	—	—	—	—	+	+	+
2	113	42.75	—	16.36	109.1	—	—	—	—	—	+	+	+
3	569	1.85	87.6	1.90	60.4	33.5[f]	29.5[f]	86.0[f]	103.9[f]	65–94	−	−	−
4	284	3.69	86.0	3.54	112.3	61.6	67.8	27.1	20.6	38–41	±	−	−
5	229	5.50	92.5	3.26	103.5	70.4	74.9	18.2	15.4	38–44	+	−	+
6	142	7.39	95.5	2.74	87.6	76.2	78.3	13.5	12.4	39–47	+	+	+
7	114	9.24	100.0	3.14	99.6	80.0	78.0	10.8	12.5	42–45	+	+	+

[a] Experimental conditions: The alkoxide derivative of the PEO was prepared by addition of potassium naphthalene in THF to the PEO in toluene (150 ml). In expts. 1–2, PEO ($\bar{M}_n$ = 1000, 13.5 g, 13.5 mmole) was used, and in expts. 3–7 PEO ($\bar{M}_n$ = 4330, 13.64 g, 3.15 mmole) was used. 50% of the terminal hydroxyl groups were converted to alkoxide; in expts. 1–2 the concentration of the alkoxide was 45 mmole/l, and in expts. 3–7 it was 10.5 mmole/l. The THF was distilled off and a solution of PMMA in toluene was added, and the solution was heated under reflux. The total volume of the reaction mixture was kept constant (300 ml). Reaction time was 6 hr.

[b] In expts. 4, 5, and 7, the amount of hydroxyl groups in the crude polymer, as determined by acetylation,[12] was 3.15, 2.75 and 3.69 mmole, respectively.

[c] Determined by gas chromatography.

[d] Determined by NMR.

[e] + denotes soluble, − insoluble, ± partially soluble.

[f] Part of the PEO (6.06, 45% of the starting material) beside some graft polymer separated from the reaction mixture. These figures are related only to the graft that remained in solution.

precipitated, the fractions (C and D) isolated were very small, and their infrared and NMR spectra showed the characteristic absorptions of both PEO and PMMA. It is interesting to note that these fractions contained a relatively high proportion of PMMA, as seen from NMR.

Furthermore, in experiments 6 and 7, where a high PEO:PMMA ratio was used, i.e., where there was the greatest possibility for the presence of ungrafted PEO in the crude reaction products, these fractions almost disappeared. On increasing the molar ratio of PEO to the ester groups (experiments 4 to 7), both the extreme fractions, A on the one hand and C and D on the other, decreased, while the middle fraction, B, alone increased greatly. This increase in B at the time that the ratio of PEO to PMMA increased once more indicates that essentially all the PEO introduced was grafted.

TABLE IV

Composition and Structure of the Graft Polymers[a, b]

	Expt. 3[c]	Expt. 4	Expt. 5	Expt. 6	Expt. 7
Molar ratio PEO alkoxide/ester groups, %	1.14[c]	3.69	5.50	7.39	9.24
Fraction from crude graft polymer, %					
Fraction A	68.6	39.1	41.6	26.5	20.3
Fraction B	0.0	15.1	18.2	49.4	50.8
Fraction C	11.4	4.6	11.7	4.1	0.0
Fraction D	0.0	9.3	7.4	0.0	0.0
PEO in fraction, %					
Fraction A	20.5	67.4	75.1	68.6	69.6
Fraction B	—	64.5	78.3	81.6	88.8
Fraction C	25.9	69.0	81.0	83.8	—
Fraction D	—	74.2	81.4	—	—
MMA units per grafted chain					
Fraction A	168.6	21.8	15.3	20.4	19.5
Fraction B	—	23.8	12.9	10.4	6.1
Fraction C	124.4	20.4	11.1	9.0	—
Fraction D	—	16.0	10.8	—	—
Melting range, °C					
Fraction A	96–105	37–40	40–42	—	39–42
Fraction B	—	39–41	40–41	36–41	33–39
Fraction C	72–77	38–40	35–39	37–40	—
Fraction D	—	37–39	32–41	—	—

[a] The experiment numbers are those of Table III. The fractionation was performed by addition of ether to a 2% chloroform solution of the crude graft polymer. Fractions A, B, C and D precipitated at the following nonsolvent:solvent ratios: 4.5, 6, 7, and 8.5, respectively. Fraction E was recovered on evaporation of the solvents.

[b] The total PEO contents of all the fractions recovered were about 10–12% less than that of the crude graft polymer fractionated, due to some losses in the fractionation process.

[c] Part of the PEO precipitated from the reaction mixture during the reaction. The figures, including the molar ratio of the reactants, given are those of the fraction of the graft polymer which remained in solution.

Comparison of the Methods Used in the Metallation of PEO

Of the three methods used in converting the terminal hydroxyl groups of PEO to alkoxide, that of potassium naphthalene is the most advantageous.[23-25] The reaction is fast, as seen from the disappearance of the color of the reagent, and does not leave behind any by-products which would interfere in the subsequent grafting process. The reaction is also stoichiometric, and on using excess reagent (equivalent to more than 1 hydroxyl group/mole of PEO) crosslinked graft polymers were formed. This may be compared with the methanolic potassium methoxide method, where the use of even 3.5 equivalents of reagent per mole of poly-E.O. failed to give crosslinked polymers, indicating that the metallation with this reagent is far from being stoichiometric.

Although the metallation by potassium metal should be stoichiometric it is slow and difficult to control.

In the metallation reactions with potassium naphthalene, only one of the two terminal hydroxyl groups of the PEO was metallated to assure complete grafting of the PEO on the one hand and absence of crosslinking on the other. Since in the grafting process, one mole of potassium methoxide is formed for every PEO chain grafted, the absence of crosslinking indicates that no further metallation on the second hydroxyl groups of the PEO took place, probably due to the insolubility of the potassium methoxide in toluene and to the inefficiency of the reagent in metallation.

The formation of soluble graft polymers, free from crosslinking, on metallating 50% of the hydroxyl groups of the PEO by potassium naphthalene, deserves an explanation. The PEO used had a $\overline{DP}_n$ of 25–100, and it is improbable that the formation of an alkoxide group at one end of the chain can effect significantly the metallation of the other hydroxyl group. This means that the metallation with potassium naphthalene should be random, and monometallated, dimetallated and unmetallated PEO should be present in the reaction mixture. The formation of soluble polymers indicates that the dimetallated products do not interact with the ester groups at both reactive ends together. Moreover, the absence of ethylene oxide homopolymer indicates that the unmetallated polymer, initially present, is converted to alkoxide in the course of reaction. Since the amount of potassium naphthalene added was sufficient to metallate an average of only one of the terminal hydroxyl groups of PEO, it follows that there is an exchange reaction between dimetallated and unmetallated PEO in the course of reaction, with formation of a monometallated product. This exchange should be much faster than the reaction of the alkoxide with the ester groups, otherwise crosslinking would have occurred. This behavior may be explained by considering a dimetallated PEO chain. After being attached at one side to the PMMA backbone, its reactivity of attacking an ester group on another backbone chain through its second metallated side is expected to decrease as a consequence of its being now incorporated into a bulky graft polymer molecule and diffusion factors become important. Furthermore, if one takes into account the low dielectric constant of the solvent (toluene), it is very probable that the free hydroxyl groups of the unmetallated PEO solvate the alkoxide group of the grafted side chain and thus can participate in an exchange reaction whereby these hydroxyl groups are metallated. The newly metallated PEO, being relatively a small molecule, is not much affected by diffusion or viscosity of the reaction mixture and can attack an ester group, thus continuing the grafting process.

Structure and Properties of the Graft Polymers

Graft polymers of PEO on PMMA have both hydrophilic and hydrophobic sites and as such are of interest as emulsifiers. Most of the crude graft copolymers were soluble in methanol. Part of them was also soluble in hot or cold water. This is due to their composition and the frequency of grafting of the hydrophilic PEO side chains on the hydrophobic backbone of PMMA. Thus, with increasing ratio of PEO to PMMA, the graft polymers obtained became more soluble in methanol, in hot water, and in cold water. At relatively very low ratios, the crude graft polymers were insoluble in these solvents (Tables I–III).

The solubility of the graft polymers depended also on the $\bar{M}_n$ of the grafted side chains. Thus graft polymers of about the same composition but in which the PEO side chains had $\bar{M}_n = 1000$ were found to be more soluble than those having $\bar{M}_n = 4330$ (compare experiment 1 with experiments 4 and 5, Table III). Actually the former graft polymers had a larger number of grafted side chains than the latter, and this increased their solubility.

The fractionation results showed that the crude graft polymers were not homogeneous in structure (Table IV). Every polymer consisted of several fractions which differed from each other in composition and in the frequency of grafting of the side chains. This indicates that the transesterification is random, as expected.

On increasing the nonsolvent–solvent ratio, the fractions that precipitated contained more and more PEO, particularly in those experiments in which a high ratio of PEO to PMMA was used (experiments 6, 7, Table IV). The crude graft obtained in experiment 7 is especially interesting in that it gave only two fractions A and B; the latter fraction having a much higher PEO content than the former.

The PEO content of the various fractions increased with the increase in the initial ratio of PEO to PMMA. While this increase is small in fraction A, it is large in fraction B. The frequency of grafting of the PEO side chains also increased correspondingly with the increase in the PEO contents. Thus it was possible to obtain fractions of graft polymer containing from about 20% to 90% PEO and having one side chain per about 10–170 methyl methacrylate units.

The melting ranges of the various fractions obtained from the graft polymers were dependent on their PEO contents and on the frequency of grafting of the side chains. The melting ranges decreased continuously with increasing PEO content until graft polymers having melting ranges of about 36–42°C, which is lower than that of the ethylene oxide homopolymer used (~50°C), were obtained.

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Polymers with Quinoxaline Units. V. Polymers with Quinoxaline and Dioxin Units

RAINER WOLF and C. S. MARVEL, *Department of Chemistry, University of Arizona, Tucson, Arizona 85721*

Synopsis

Ladder or partly ladder polymers have been prepared by condensation of tetraphenols with tetrachloroquinoxaline compounds in melt, or in pyridine, naphthalene, and nitrobenzene reaction media. The poymers are dark-colored, powdery materials with good thermal stability. Some of the samples are slightly soluble in sulfuric acid, while others are completely insoluble. No other solvents were found.

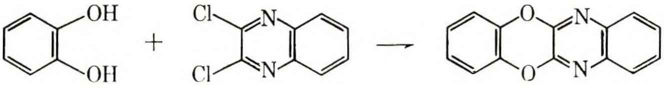
INTRODUCTION

The condensation of tetrachloroquinoxaline derivatives with diamino-dithiophenols[1] or diaminodiphenols[2] is reported to form high molecular weight ladder polymers with quinoxaline and thiazine or oxazine recurring units, respectively. In a further continuation of this work, the condensation of tetrachloroquinoxaline derivatives with tetraphenols has been investigated and will be described in this paper. The replacement of the thiazine or oxazine units by the symmetrical dioxin unit was expected to improve solubility and also to increase oxidative stability of the polymers, since no heterocyclic hydrogens are present.

RESULTS AND DISCUSSION

Model Reactions

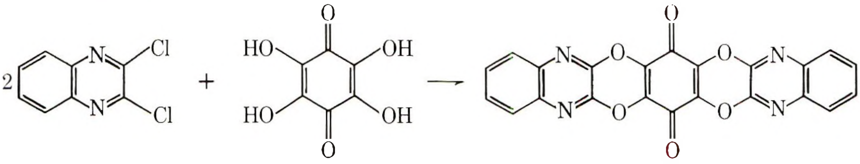
The melt condensation between catechol and 2,3-dichloroquinoxaline is reported[3] to form 9,10-diaza-11,12-dioxatetracene (I) and this can be considered as a model reaction for the preparation of ladder-type polymers with quinoxaline and dioxin recurring units.



I

This reaction has been studied in several solvents in order to find proper conditions for a corresponding polymerization procedure. Compound I was formed in almost quantitative yields in basic solvents, such as pyridine and *N*,*N*-diethylaniline, at the reflux temperature. Some other high-boiling solvents, such as naphthalene or nitrobenzene, were also found to be suitable for the described reaction. Yields are not as high as in the case of basic solvents; however, they can be improved by addition of small amounts of base, as studied in the case of nitrobenzene–pyridine. In other high-boiling solvents, such as dimethylacetamide, hexamethylphosphoramide, or benzonitrile, the reaction could not be accomplished, and even the addition of pyridine did not succeed in a formation of I. Starting materials or unidentified reaction mixtures were obtained.

Model compound II was prepared from 2,3-dichloroquinoxaline and tetrahydroxy-*p*-benzoquinone in both naphthalene and pyridine solution. Structure II was established by analysis; however, in the case of naphthalene as a solvent, a remaining chlorine content of 1.02% indicates an incomplete reaction.



II

Tetrafunctional Monomers

All monomers which have been used in the following investigations are listed in Table I. The compounds were prepared according to the literature. Pyridine is a good solvent for all of the described monomers. Nitrobenzene and *N*,*N*-diethylaniline are sufficient solvents for all monomers except III and VII. All monomers, except V, which is extremely sensitive against oxidation, are stable in air or solution.

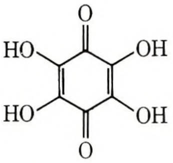
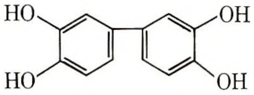
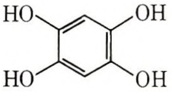
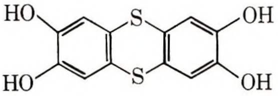
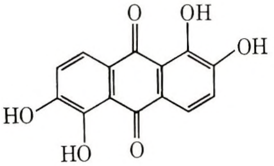
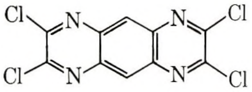
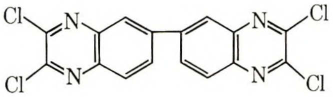
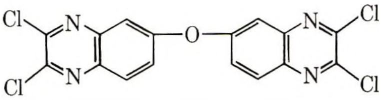
Polymers

Polymers with quinoxaline and dioxin units have been prepared from the various tetraphenols and tetrachloroquinoxaline compounds in pyridine, naphthalene, and nitrobenzene solution, and in melt. The new polymers are summarized in Table II.

The solubility of these polymers was disappointing. Only sulfuric acid was found to be a fairly good solvent for some of the products, while others were only partly soluble or completely insoluble. Solubility in methanesulfonic acid was very poor, and no solubility was found in dimethylacetamide, dimethyl sulfoxide, hexamethylphosphoramide, hexafluoroacetone sesquihydrate, formic acid, or trifluoroacetic acid.

In general, the solution viscosities of the polymers or their soluble portions are rather low, indicating low molecular weights. This is probably due to insufficient solubility of the growing macromolecules with ladder or partly ladder structure in the described solvents. In fact, a precipitation of polymeric material occurs soon after starting the reaction. The highest

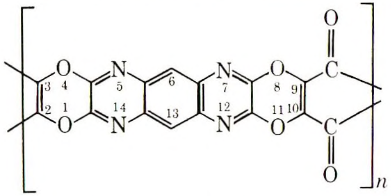
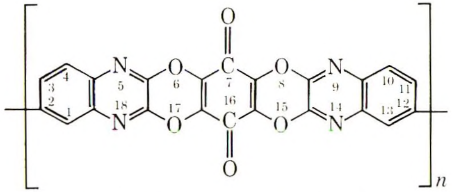
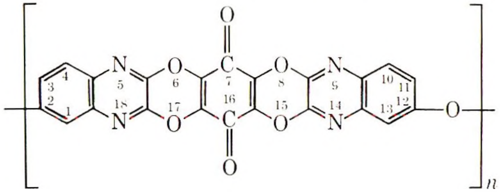
TABLE I
Monomers

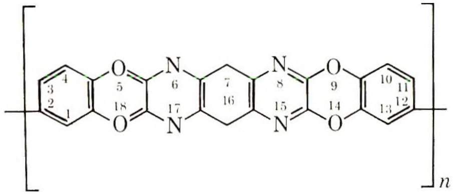
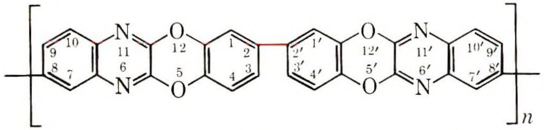
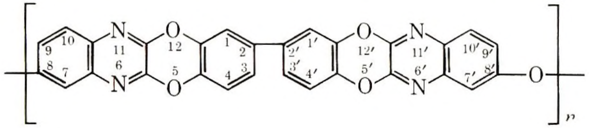
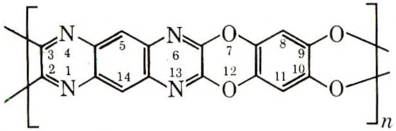
No.	Compound	Formula	Mp, °C
III	Tetrahydroxy-*p*-benzoquinone		>350
IV	3,3′,4,4′-Tetrahydroxydiphenyl		227
V	1,2,4,5-Tetrahydroxybenzene		217–218
VI	2,3,6,7-Tetrahydroxythianthrene		270–275
VII	1,2,5,6-Tetrahydroxyanthraquinone		>350
VIII	2,3,7,8-Tetrachloro-1,4,6,9-tetraazaanthracene		328
IX	2,2′,3,3′-Tetrachloro-6,6′-bisquinoxaline		295
X	2,2′,3,3′-Tetrachloro-6,6′-bisquinoxalyl ether		218

viscosity values were determined on polymers from 3,3′,4,4′-tetrahydroxydiphenyl. Melt polymerizations have been investigated with this monomer, and a light brown polymer with an $[\eta]_{inh}$ of 0.35 was obtained from 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl ether and 3,3′,4,4′-tetrahydroxydiphenyl, both monomers having melting points near 220°C.

Most of the results of the elemental analyses (see Experimental) are in relatively good agreement with the values calculated from the probable formulas. While carbon analyses of some samples are poor, nitrogen is in

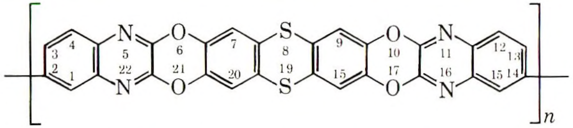
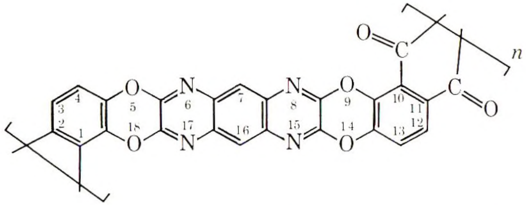
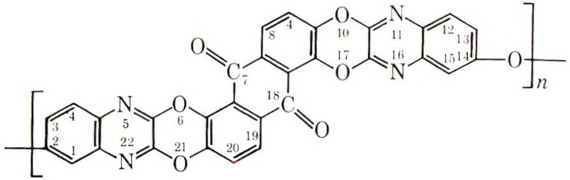
TABLE II
Polymers with Quinoxaline and Dioxin Units

Poly-mer	Monomers	Solvent	Probable formula	$[\eta]_{inh}$[a]	Appearance
XI	III + VIII	Pyridine		0.09	Dark brown
		Naphthalene		0.06	Dark brown
		Nitrobenzene		0.11	Dark brown
			Poly(*p*-dioxino[2,3-*b*]-*p*-dioxino[2′,3′:5,6]pyrazino[2,3-*g*]-quinoxaline-2,3:9,10-tetrayl-9,10-dicarbonyl)		
XII	III + IX	Pyridine		0.6	Dark brown
		Nitrobenzene		0.11	Dark brown
			Poly(7,16-dihydro-7,16-dioxobenzo[1″,2″:5,6;4″,5″:5′,6′]bis-*p*-dioxino[2,3-*b*:2′,3′-*b*′]diquinoxaline-2,12-diyl)		
XIII	III + X	Pyridine		Insoluble	Black
			Poly[(7,16-dihydro-7,16-dioxobenzo[1″,2″:5,6;4″,5″:5′,6′]bis-*p*-dioxino[2,3-*b*:2′,3′-*b*]diquinoxaline-2,12-diyl)-12-oxy]		

XIV	IV + VIII	Pyridine Nitrobenzene	 Poly([1,4]Benzodioxino[2,3-*b*][1,4]benzodioxino[2′,3′:5,6]pyrazino[2,3-*g*]quinoxaline-2,12-diyl)	0.25 0.13	Brown Gold brown
XV	IV + IX	Pyridine	 Poly([2,2′-bi[1,4]benzodioxino[2,3-*b*]quinoxaline]-8,8′-diyl)	0.4	Brown
XVI	IV + X	Pyridine Melt	 Poly([2,2′-bi[1,4]benzodioxino[2,3-*b*]quinoxaline]-8,8′-diyl-8′-oxy)	0.22 0.35	Light brown Light brown
XVII	V + VIII	Pyridine	 Poly([1,4]benzodioxino[2,3-*b*]pyrazino[2,3-*g*]quinoxaline-2,3:9,10-tetrayl-9,10-dioxy)	0.03	Black

(continued)

TABLE II (*continued*)

Poly-mer	Monomers	Solvent	Probable formula	$[\eta]_{\text{inh}}$[a]	Appearance
XVIII	VI + IX	Pyridine	 Poly(*p*-dithiino[2″,3″:6,7;5″,6″:6′,7′]bis[1,4]benzodioxino[2,3-*b*:2′,3′-*b*]diquinoxaline-2,14-diyl)	In-soluble	Brown
XIX	VII + VIII	Pyridine	 Poly([1,4]benzodioxino[2,3-*b*][1,4]benzodioxino[2′,3′:5,6]pyrazino[2,3-*g*]quinoxaline-1,2:10,11-tetrayl-10,11-dicarbonyl)	0.06	Brown
XX	VII + X	Pyridine	 Poly[(7,18-dihydro-7,18-dioxoanthra[1″,2″:5,6;5″,6″:5′,6′]bis-*p*-dioxino[2,3-*b*:2′,3′-*b*]diquinoxaline-2,14-diyl)-14-oxy]	0.09	Dark brown

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[a] Determined for the soluble portions in sulfuric acid at 30°C.

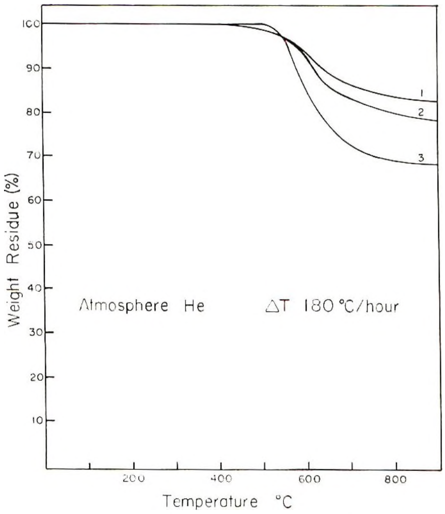

Fig. 1. TGA curves of (*1*) polymer XV, (*2*) polymer XIV, and (*3*) polymer XVI. Polymers XV and XIV were prepared in pyridine solution, XVI in melt.

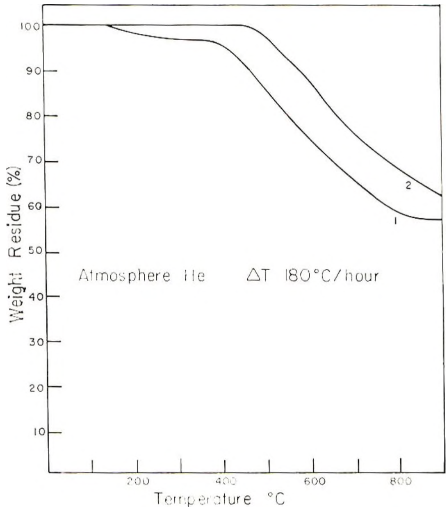

Fig. 2. TGA curves of (*1*) polymer XIII and (*2*) polymer XVIII. Both polymers were prepared in pyridine solution.

better agreement with the calculated values. Polymer XI, prepared in napththalene, has a chlorine content of 5.97%, indicating incomplete ring closure. Polymer XIV, prepared in pyridine or nitrobenzene, also has high chlorine contents of 2.15 and 4.91%, respectively. Chlorine analyses of the other samples are below 1%.

Thermogravimetric analyses on some of the samples, determined in helium at a heating rate of 180°C/hr, are shown in Figures 1 and 2. Initial weight loss occurs at about 500°C.

EXPERIMENTAL

Materials

Catechol was sublimed before use. 2,3-Dichloroquinoxaline was prepared as described in the literature.[4,5]

Tetrahydroxy-*p*-benzoquinone. The dihydrate (Aldrich Chemical Co.) was dissolved in hot dioxane, treated with molecular sieves and crystallized from dioxane.

ANAL. Calcd for $C_6H_4O_6$: C, 41.90%; H, 2.34%. Found: C, 41.95%; H, 2.46%.

3,3′,4,4′-Tetrahydroxydiphenyl. 4-Iodoveratrole was prepared as described.[6] 3,3′,4,4′-Tetramethoxydiphenyl was synthesized by mixing 87 g of iodoveratrole with 90 g sand and heating under nitrogen to 220°C. Then 60 g copper bronze (Crescent Bronze Powder Co.) was added portionwise. After 4 hr further stirring, the mixture was immediately poured into sand and extracted with hot methanol. Pale brown crystals of 3,3′,4,4′-tetramethoxydiphenyl were obtained in 74% yield, mp 132°C (lit.[7] mp 130–132°C). This compound was demethylated as previously described.[8] White crystals of 3,3′,4,4′-tetrahydroxydiphenyl were obtained after sublimation; mp 227°C (lit.[8] mp 229–230°C).

1,2,4,5-Tetrahydroxybenzene. 1,2,4,5-Tetrahydroxybenzene was prepared as described[9] and crystallized from acetic acid; mp 217–218°C (lit.[9] mp 215–220°C).

Other Compounds. 2,3,6,7-Tetrahydroxythianthrene was prepared as described,[10] mp 270–275°C (lit.[10] mp 273°C). Crystallization from acetic acid did not yield a sharp melting material.

1,2,5,6-Tetrahydroxyanthraquinone was prepared as described in the patent literature.[11,12] Orange colored needles were obtained by recrystallization from acetic acid.

ANAL. Calcd for $C_{14}H_8O_6$: C, 61.77%; H, 2.96%. Found: C, 61.47%; H, 3.10%.

2,3,7,8-Tetrachloro-1,4,6,9-tetraazaanthracene,[13] 2,2′,3,3′-tetrachloro-6,-6′-bisquinoxaline,[13] and 2,2′,3,3′-tetrachloro-6,6′-bisquinoxalyl ether[1] were prepared as described in the literature.

Model Reactions

9,10-Diaza-11,12-dioxatetracene. The general procedure was to dissolve (or mix) catechol (1.101 g; 0.01 mole) and 2,3-dichloroquinoxaline (2.011 g; 0.01 mole) with solvent. The concentration of starting materials was 30 wt-% in naphthalene, 5 wt-% in pyridine, and 10 wt-% in *N*,*N*-diethylaniline, nitrobenzene, and nitrobenzene–pyridine mixtures. The solutions were heated under nitrogen atmosphere with stirring to the reflux temperature and kept at this level for 6 hr in the case of pyridine and for 12–22 hr in other solvents. The reaction mixture was cooled, methanol was added, and the product was filtered and washed with methanol. 9,10-Diaza-11,12-dioxatetracene was recrystallized from 95% ethanol. The yield in naphthalene was 75%; mp 265°C (lit.[3] mp 264–265°C).

Anal. Calcd. for: $C_{14}H_8O_2N_2$: C, 71.18%; H, 3.41%; N, 11.86%. Found: C, 71.46%; H, 3.61%; N, 11.71%.

In pyridine the yield was 97%; mp and mixed mp, 265°C. In *N,N*-diethylaniline the yield was 96%; mp and mixed mp, 265°C. In nitrobenzene the yield was 87%; mp and mixed mp, 265°C. In nitrobenzene–pyridine mixture (6:1); the yield was 95%; mp and mixed mp, 265°C.

The procedure in pyridine hydrochloride was as follows. Veratrole (2.763 g, 0.02 mole), 2,3-dichloroquinoxaline (4.021 g; 0.02 mole) and pyridine hydrochloride (15 g, 0.13 mole) were mixed and heated under nitrogen and stirring to 200°C for 12 hrs. After cooling, a dark-colored solid was precipitated in water, filtered, and washed with hot water. After extraction with hot ethanol, 9,10-diaza-11,12-dioxatetracene was obtained in a 6% yield, mp 264°C; mixed mp 261–263°C.

Model Compound II. Tetrahydroxy-*p*-benzoquinone (0.5163 g, 0.003 mole) and 2,3-dichloroquinoxaline (1.327 g, 0.0066 mole) were mixed with naphthalene (10 g) or dissolved in pyridine (50 ml). The mixtures were heated under nitrogen atmosphere and stirring to the reflux temperature for 16 hr. After cooling, the reaction products were precipitated in ethanol, filtered, washed with hot ethanol, and dried. The products were extracted with benzene for one day, then heated in vacuum to 300°C for 6 hr and finally extracted with ethanol for 2 days; mp >360°C. When the reaction was carried out in naphthalene, the yield was 82%.

Anal. Calcd for $C_{22}H_8N_4O_6$: C, 62.27%; H, 1.82%; N, 13.21%. Found: C, 62.00%; H, 2.46%; N, 13.99%; Cl, 1.02%.

When the reaction was carried out in pyridine, the yield was 95%.

Anal. Found: C, 62.18%; H, 2.70%; N, 13.89%; Cl, 0.81%.

Polymers

The general procedure was as follows. Equimolecular amounts of monomers were dissolved or mixed with solvent. The concentration of monomers was 20% in naphthalene, 1–3% in pyridine, and 3% in nitrobenzene. The mixtures were heated under a nitrogen atmosphere with stirring to reflux temperature and kept at this level for 16–24 hr in the case of pyridine and naphthalene as solvents, and for 30–60 hr in nitrobenzene. The mixtures were cooled, methanol was added, and the polymeric materials were filtered, washed with hot methanol, and dried. After Soxhlet extraction with benzene (1 day), the samples were heated to 350°C *in vacuo* for 6 hr and finally extracted with alcohol for 1–2 days. Generally, yields were between 85 and 98%, calculated for a complete ring closure. Viscosities have been determined in sulfuric acid at 30°C. Details for polymers XI–XX are given in Table III.

TABLE III

Polymer	Polymerization solvent	η_{inh} (concn)	Empirical formula	Calculated			Found			
				C, %	H, %	N, %	C, %	H, %	N, %	Cl, %
XI	Pyridine	0.09 (0.5%)[a]	$(C_{16}H_2O_4N_6)_n$	55.51	0.58	16.18	54.46	2.30	17.87	
	Naphthalene	0.06 (0.30%)[b]					54.59	1.78	16.45	5.97
	Nitrobenzene	0.11 (0.5%)[a]					54.20	1.36	16.84	
XII	Pyridine	0.6 (0.03%)[c]	$(C_{22}H_6O_6N_4)_n$	62.55	1.42	13.21	68.30	3.10	15.16	
	Nitrobenzene	0.11 (0.5%)[a]					64.62	2.50	14.61	
XIII	Pyridine	d	$(C_{22}H_6O_7N_4)_n$	60.29	1.38	12.78	64.84	2.70	14.72	
XIV	Pyridine	0.25 (0.40%)[e]	$(C_{22}H_8O_4N_4)_n$	67.35	2.06	14.28	65.74	2.19	14.72	2.15
	Nitrobenzene	0.13 (0.5%)[a]					63.58	2.33	14.18	4.91
XV	Pyridine	0.4 (0.02%)[f]	$(C_{28}N_{12}O_4N_4)_n$	71.79	2.58	11.96	70.42	2.90	12.59	
XVI	Pyridine	0.22 (0.28%)[g]	$(C_{28}H_{12}N_4O_5)_n$	69.42	2.50	11.57	68.11	2.84	11.89	
	Melt	0.35 (0.35%)[h]					68.42	2.69	11.25	
XVII	Pyridine	0.03 (0.04%)[i]	$(C_{16}H_4O_4N_4)_n$	60.75	1.26	17.72	61.45	2.22	17.15	
XVIII	Pyridine	d	$(C_{28}H_{10}O_4N_4S_2)_n$	63.39[j]	1.90	10.56	62.70	2.34	10.81	
XIX	Pyridine	0.06 (0.5%)[a]	$(C_{24}H_6O_6N_4)_n$	64.58	1.36	12.55	62.81	1.96	12.96	
XX	Pyridine	0.09 (0.41%)[k]	$(C_{30}H_{10}O_7N_4)_n$	66.92	1.87	10.41	65.67	2.47	10.66	

[a] Completely soluble.
[b] 40% of sample insoluble.
[c] 94% of sample insoluble.
[d] Insoluble in sulfuric acid and other solvents.
[e] 20% of sample insoluble.
[f] 96% of sample insoluble.
[g] 44% of sample insoluble.
[h] 30% of sample insoluble.
[i] 92% of sample insoluble.
[j] Also: calculated S, 12.09%; found S, 11.09%.
[k] 18% of sample insoluble.

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Polymers from 1,3-Dipole Addition Reactions. The Nitrilimine Dipole from Tetrazoles*

J. K. STILLE and L. D. GOTTER, *Department of Chemistry, University of Iowa, Iowa City, Iowa 52240*

Synopsis

Polymers containing pyrazole and triazole units in the polymer chain were obtained through the 1,3-dipolar addition reaction of bisnitrilimines generated from tetrazoles with diynes and dinitrile dipolarophiles. The reaction of 2,2′-diphenyl-5,5′-*m*- and *p*-phenyleneditetrazole with the dipolarophiles *m*- and *p*-diethynylbenzene, terephthalonitrile, tetrafluoroterephthalonitrile, perfluoroglutarylnitrile, and 4,4′-dicyanobiphenyl gave a series of thermally stable polymers of high molecular weight. The polypyrazoles were soluble in acid and in some cases in chlorobenzene or 1,2,4-trichlorobenzene and had intrinsic viscosities as high as 1.67, while the polytriazoles were soluble in 1,2,4-trichlorobenzene and chlorobenzene, but not in acid, and had viscosities ranging up to 0.40. The thermogravimetric analyses of the finely powdered polymers showed breaks near 500°C in air and nitrogen atmospheres.

Although it was demonstrated that the nitrilimine dipole generated from the corresponding hydrazide chloride did not afford a high molecular weight polymer,[1] preliminary results[2] indicated that high molecular weight polymers could indeed be formed from a 1,3-dipole addition to suitable dipolarophiles if the nitrilimine dipole were generated from a tetrazole at temperatures of about 150°C. Since one of the objectives of this work was to obtain thermally stable polymers containing the aromatic and highly polar pyrazole or triazole units, the bis-1,3-dipole and bisdipolarophile monomers were synthesized such that the connecting linkages could also be expected to be thermally stable.

DISCUSSION

Nitrilimines may be generated by the action of base on acid hydrazide chlorides, or by the thermal decomposition of tetrazoles.[3–8] Nitrilimines react very rapidly with alkynes to form pyrazoles, and, although the dipolarophile activity of the nitrile group is much less, triazoles are obtained from them. Only one pyrazole or triazole isomer has been obtained from these reactions even when two are possible, and, the yield of pyrazole or triazole is increased by the presence of electron-withdrawing groups attached to the dipolarophile.

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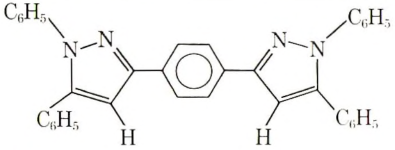
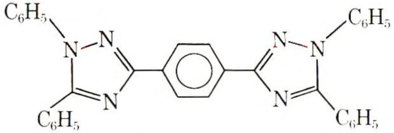
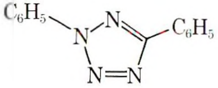
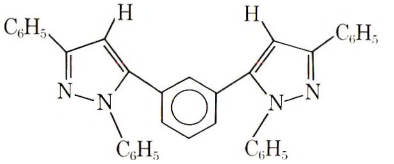
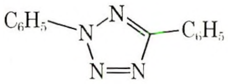
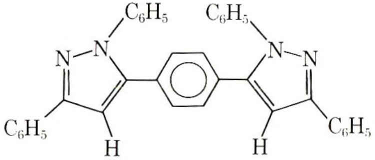
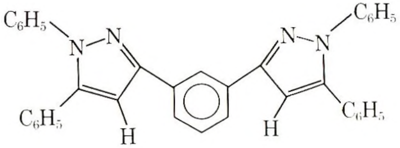
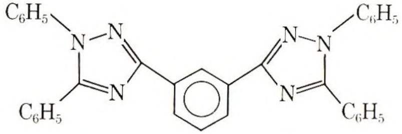
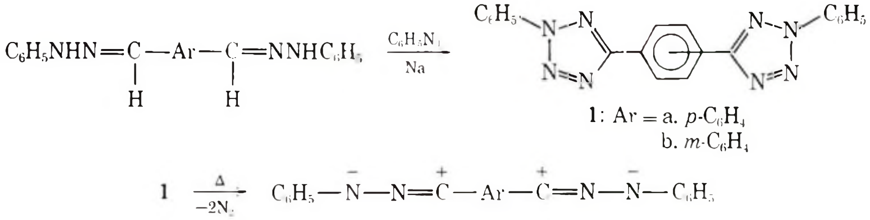
TABLE I
Model Compounds

Tetrazole	Dipolarophile	Model compound No.	Model compound Structure	Mp, °C	Analysis Calcd C, %	Analysis Calcd H, %	Analysis Calcd N, %	Analysis Found C, %	Analysis Found H, %	Analysis Found N, %
1a	C_6H_5—C≡CH	**7**		269–270	84.01	5.09	10.89	84.08	5.04	10.55
1a	C_6H_5—C≡N	**8**		318–320	79.04	4.61	16.29	79.10	4.82	16.35
 **2a**		**9a**		233–235	84.01	5.09	10.89	84.36	5.07	10.77

	 **2b**	**9b**		246–247	84.01	5.09	10.89	84.23	5.19	11.15
1b	$C_6H_5—C{\equiv}CH$	**10**		210–211	84.01	5.09	10.89	83.99	5.21	10.91
1b	$C_6H_5—C{\equiv}N$	**11**		258–259	79.04	4.61	16.29	79.00	4.75	16.14

Monomers

The bistetrazoles, 2,2′-diphenyl-5,5′-*p*-phenyleneditetrazole (**1a**) and 2,2′-diphenyl-5,5′-*m*-phenyleneditetrazole (**1b**), were prepared by the base-catalyzed condensation (sodium in 2-methoxyethanol) of terephthaloylphenylhydrazone and isophthaloylphenylhydrazone with phenyl azide.



These bistetrazoles thermally eliminate nitrogen to give the intermediate nitrilimine dipole. The bistetrazoles, 2,2′-diphenyl-5,5′-*p*-phenyleneditetrazole (**1a**) and 2,2′-diphenyl-5,5′-*m*-phenyleneditetrazole (**1b**) were obtained in 47 and 67% yields, respectively.

The diacetylenes, *m*- and *p*-diethynylbenzene (**2a, 2b**),[9] and the dinitriles, perfluoroglutarylnitrile (**3**)[10] and 4,4′-dicyanobiphenyl (**4**)[11] were synthesized for use as double dipolarophile monomers. In addition, terephthalonitrile (**5**) and tetrafluoroterephthalonitrile (**6**) were employed as double dipolarophiles.

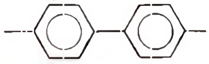
$HC{\equiv}C{-}Ar{-}C{\equiv}CH$

2a: *m*-C_6H_4
2b: *p*-C_6H_4

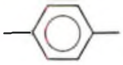
$N{\equiv}C{-}R{-}C{\equiv}N$

3: R = $-(CF_2)_3-$

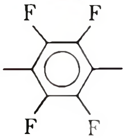
4: R =



5: R =



6: R =

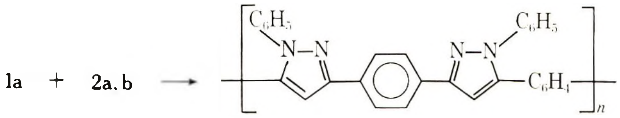


Model Compounds

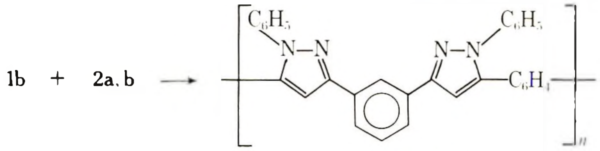
In order to provide standards for the interpretation of polymer structure by infrared analyses, a series of model compounds containing pyrazole, triazole, and phenylene units were prepared. The reactions of 2,2′-diphenyl-5,5′-*p*-phenyleneditetrazole (**1a**) with phenylacetylene and benzonitrile and the reactions of *m*- and *p*-diethynylbenzene (**2a,b**) with 2,5-diphenyltetrazole afford 1,1′-5,5′-tetraphenyl-3,3′-*p*-phenylenedipyrazole (**7**), 1,1′,5,5′-tetraphenyl-3,3′-*p*-phenyleneditriazole (**8**), and 1,1′,3,3′-tetraphenyl-5,5′-*p*- and *m*-phenylenedipyrazole (**9a,b**) respectively (Table I). The reactions of **1a** with phenylacetylene and benzonitrile were carried out in tetralin within sealed tubes and gave products in 28 and 10% yields, respectively. The reactions of **2a,b** with 2,5-diphenyltetrazole were run in diglyme at 170°C and gave 60 and 70% yields of products, respectively. In addition, the analogous reactions of **1b** with phenylacetylene and benzonitrile gave 1,1′,5,5′-tetraphenyl-3,3′-*m*-phenylenedipyrazole (**10**) and 1,1′,5,5′-tetraphenyl-3,3′-*m*-phenyleneditriazole (**11**) in 58 and 20% yields, respectively.

Polymers

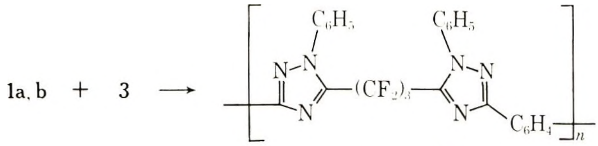
The reactions of the bistetrazole monomers **1a,b** with *m*- and *p*-diethynylbenzene (**2a,b**) within sealed tubes in the presence of tetralin or 1,2,4-trichlorobenzene solvent afforded polypyrazoles **12**–**13** in high yields (Table II). Similarly, the polymerizations of **1a,b** with perfluoroglutaronitrile (**3**), 4,4′-dicyanobiphenyl (**4**), terephthalonitrile (**5**), and tetrafluoroterephthalonitrile (**6**) afforded a series of polytriazoles (**14**–**17**) on good conversion.



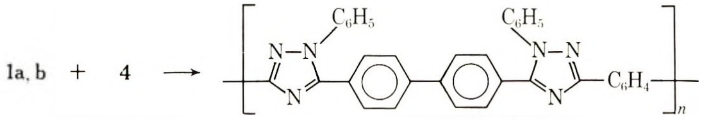
12a: *m*-C_6H_4
12b: *p*-C_6H_4



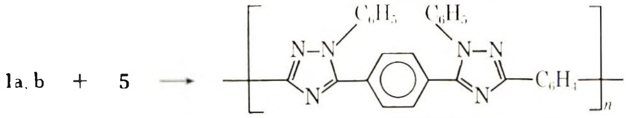
13a: *m*-C_6H_4
13b: *p*-C_6H_4



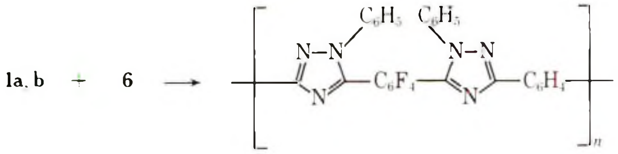
14a: *p*-C_6H_4
14b: *m*-C_6H_4



15a: *p*-C_6H_4
15b: *m*-C_6H_4



16a: *p*-C_6H_4
16b: *m*-C_6H_4



17a: $p\text{-}C_6H_4$
17b: $m\text{-}C_6H_4$

Previous attempts to polymerize dinitriles with bisnitrilimine dipoles derived from acid hydrazide chlorides did not produce high molecular weight polymers. Only oligomeric materials were obtained instead, with the exception that a polymer was formed from perfluoroglutarylnitrile and the nitrilimine dipole.[1] Electron-withdrawing groups attached to the cyano function increase the yields of the resulting triazoles,[6] and this effect probably accounts for the difference in this case. Success in obtaining triazole polymers from tetrazoles may be due to greater reactivity of the nitrilimine dipole when produced at the temperature required for tetrazole decomposition.

The relatively low molecular weight (intrinsic viscosity, Table II) of the triazole polymers may be due to the lower reactivity of the nitrile group, compared to ethynyl monomers. A head-to-tail self-dimerization of the nitrilimine dipole could account for the lower molecular weight since monomer balance would be destroyed, even though a link in the chain would be formed by this reaction. Nitrilimines are known to undergo the head-to-tail self-dimerization reaction in the absence of a suitable dipolarophile.[12] Dihydrotetrazine polymers have been obtained from the bisnitrilimine dipoles derived from iso- and terephthaloylphenylhydrazide chloride.[1] This dimerization reaction along with the relatively high thermal stability of the triazole system (Table II, Fig. 1) could explain the difficulties encountered

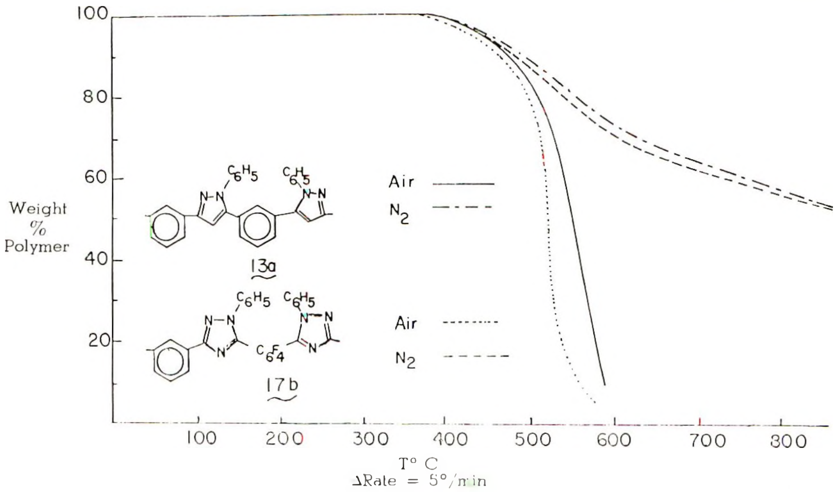


Fig. 1. Thermogravimetric analyses of Polypyrazole **13a** and Polytriazole **17b**.

TABLE II
Polymers

Polymer	Conversion %	TGA (air)[c] [η]	TGA (air)[c] Temp, °C	Analysis Calcd C, %	Analysis Calcd H, %	Analysis Calcd N, %	Analysis Found C, %	Analysis Found H, %	Analysis Found N, %
12a	92	0.41[a]	470	82.57	4.59	12.84	82.13	5.14	11.86
12b	89	1.67[a]	450	82.57	4.59	12.84	82.94	4.84	11.94
13a	92	0.35[a]	470	82.57	4.59	12.84	83.11	4.13	12.06
13b	91	1.03[a]	500	82.57	4.59	12.84	82.73	4.90	12.02
14a	89	0.18[b]	460	58.60	2.74	16.40	58.67	2.78	15.66
14b	94	0.10[b]	370	58.60	2.74	16.40	58.46	2.82	16.12
15a	80	0.05[b]	440	78.37	4.49	17.14	79.05	4.29	15.46
15b	70	0.15[b]	450	78.37	4.49	17.14	77.62	4.49	18.18
16a	65	0.11[b]	480	76.71	4.11	19.18	77.57	4.18	18.16
16b	80	0.16[b]	450	76.71	4.11	19.18	76.14	4.14	17.93
17a	81	0.40	470	65.88	2.75	16.47	66.93	2.71	16.20
17b	91	0.14[b]	470	65.88	2.75	16.47	66.20	2.72	16.11

[a] In 98% formic acid at a concentration of 0.30 g/100 ml.

[b] In 1,2,4-trichlorobenzene at a concentration of 0.30 g/100 ml.

[c] The polymers exhibited no significant difference in thermal stability in nitrogen atmosphere (Fig. 1).

in obtaining satisfactory elemental analyses. In an attempt to detect any monomer imbalance due to side reactions, the monomer balance ratio of dipole to dipolarophile was varied over a wide range in several of the monomer systems; however, no increase in molecular weight was achieved.

Molecular weight data were obtained on several of the more readily soluble pyrazole and triazole polymers (Table III). The molecular weight of the polymers ranged from 6900 to 28000. The infrared spectrum of each polymer sample showed maxima characteristic of the heterocyclic system that it contained and could be compared directly with the spectrum of the corresponding model compound.

TABLE III
Molecular Weights and Intrinsic Viscosities

Polymer	$[\eta]$	$\bar{M}_n$[a]
12a	0.41[b]	12000
13b	0.80[b]	14750, 28400[c]
17b	0.40[d]	6900

[a] Obtained with a Hewlett-Packard high-speed membrane osmometer using a superdense membrane at 29.5°C in chlorobenzene.

[b] In formic acid at 30°C.

[c] After extraction with toluene in which 20% of the material was soluble.

[d] In nitrobenzene at 30°C.

Although problems of polypyrazole solubility were encountered especially when tetralin was used as a solvent, samples of all the polypyrazoles were eventually obtained which were completely soluble in 98% formic acid. Treatment of the tetralin to remove peroxides gave polymers having inincreased viscosity and solubility. Thus the insoluble samples probably contained some crosslinking due to the presence of peroxides during polymerization. Generally, the solubility of the polypyrazoles increased and the viscosity decreased as the percentage of *m*-phenylene linkages was increased. Most of the polytriazoles **14–17** were insoluble in formic or sulfuric acid, but were completely soluble in such organic solvents as chlorobenzene or 1,2,4-trichlorobenzene.

The thermal stabilities of the polypyrazoles **12–13** derived from bistetrazoles were comparable to the stabilities of the corresponding polymers derived from acid hydrazide chlorides.[1] Both the polypyrazoles and polytriazoles underwent only partial decomposition when heated in nitrogen to 800°C (Fig. 1).

The differential thermal analyses (DTA) of the polymers gave poorly resolved curves showing several changes in slope of ΔT versus T lines. The polypyrazoles **12–13** had transitions at 240–255°C with the transition temperature increasing as the number of *para* linkages increased. Second-order transitions were also found for polytriazoles **14–17** (Table IV). Transitions were 25–120°C higher for the polymer derived from the *p*-bistetrazole than for the corresponding one derived from the *meta* isomer.

TABLE IV
Second-Order Transition Temperatures

Polymer	Transition temperature, °C
12a	245
12b	255
13a	240
13b	250
14a	250, 365[a]
14b	130, 340[a]
15a	210, 255
15b	140, 270
16a	225, 320[a]
16b	200, 300[a]
17a	225
17b	125, 265

[a] Polymer appeared to melt at this point.

EXPERIMENTAL

Monomers

2,2′-Diphenyl-5,5′-*p*-phenyleneditetrazole (1a). To a solution of 14.4 g (0.045 mole) terephthaloylphenylhydrazone[13] and 10.0 g (0.430 mole) of sodium in 160 ml of 2-methoxyethanol was added 9.0 g (0.089 mole) of phenyl azide. The solution was heated at the reflux temperature for 16 hr, then cooled to room temperature and filtered. The yellow precipitate was recrystallized several times from benzene to yield 6.8 g (47%) of white product, mp (with decomposition) 220–225°C.

ANAL. Calcd for $C_{20}H_{14}N_8$: C, 65.58%; H, 3.83%; N, 30.60%. Found: C, 65.72%; H, 4.06%; N, 30.54%.

2,2′-Diphenyl-5,5′-*m*-phenyleneditetrazole (1b). To a solution of 14.4 g (0.045 mole) of isophthaloylphenylhydrazone[14] and 10.0 g (0.430 mole) of sodium in 160 ml of 2-methoxyethanol was added 18.0 g (0.178 mole) of phenyl azide over a 4-hr period. The solution was heated at the reflux temperature for 16 hr, then cooled to room temperature and filtered. The tan precipitate was dissolved in benzene, chromatographed on a 20-in. Florisil (100–200 mesh) column, then recrystallized from isopropanol to yield 9.7 g (67%) of white product, mp (with decomposition) 162–165°C.

ANAL. Calcd for $C_{20}H_{14}N_8$: C, 65.58%; H, 3.83%; N, 30.60%. Found: C, 65.41%; H, 4.01%; N, 30.41%.

***m*-Diethynylbenzene (2a).** This was prepared from tetrabromo-*m*-divinylbenzene.[9] Distillation of the crude product under reduced pressure yielded a clear liquid; bp 76–78°C/0.25 mm (lit.[9] bp 78°C/14 mm).

***p*-Diethynylbenzene (2b).** The *para* compound was prepared from a commercial divinylbenzene mixture.[9] Sublimation of the crude product afforded colorless crystals; mp 95–96°C (lit.[9] mp 96.5°C).

Perfluoroglutaronitrile (3). This was obtained by the dehydration of perfluoroglutaramide with benzotrichloride.[10] Distillation of the product afforded the dinitrile; bp 38–39°C (lit.[10] 38°C).

4,4′-Dicyanobiphenyl (4).[11] Sublimation of the crude product followed by recrystallization from ethanol yielded colorless crystals; mp 233–235°C (lit.[11] mp 233°C).

Model Compounds

The three dipyrazole model compounds 1,1′, 5,5′-tetraphenyl-3,3′-*p*-phenylenedipyrazole (**7**) and 1,1′,3,3′-tetraphenyl 5,5′-*m*- and *p*-phenylenedipyrazole (**9a,b**) and the one ditriazole model compound 1,1′, 5,5′-tetraphenyl-3,3′-*p*-phenyleneditriazole (**8**) were prepared as previously described.[2]

1,1′,5,5′-Tetraphenyl-3,3′-*m*-phenylenedipyrazole (10). To a solution of 0.732 g (2.00 mmole) of 2,2′-diphenyl-5,5′-*m*-phenyleneditetrazole (**1b**) in 10 ml of anisole was added 0.612 g (6.00 mmole) of phenylacetylene. The mixture was heated at 160°C for 8 hr. The solvent was then removed under reduced pressure, leaving a tan residue. This tan residue was chromatographed on Merck alumina with benzene as the eluent. Evaporation of the benzene and recrystallization of the resulting solid from benzene-Skelly C gave 0.610 g (58%) of white crystals; mp 210–211°C (lit.[1] mp 210–211°C).

ANAL. Calcd for $C_{36}H_{26}N_4$: C, 84.01%; H, 5.09%; N, 10.89%. Found: C, 83.99%; H, 5.21%; N, 10.91%.

1,1′,5,5′-Tetraphenyl-3,3′-phenyleneditriazole (11). A solution of 1.098 g (3.00 mmole) of 2,2′-diphenyl-5,5′-*m*-phenyleneditetrazole (**1b**) in 10 ml of benzonitrile was heated at 170°C for 8 hr. The solvent was then removed under reduced pressure, leaving a black oil. The black oil was treated with boiling methanol, then the black solid which remained was chromatographed on Florisil with benzene as the eluent. Evaporation of the benzene and recrystallization of the solid from acetone yielded 0.315 g (20%) of white crystals; mp 258–259°C.

ANAL. Calcd for $C_{34}H_{24}N_6$: C, 79.04%; H, 4.61%; N, 16.29%. Found: C, 79.00%; H, 4.75%; N, 16.14%.

Polymers

All polymerizations were carried out in the same general manner and produced polymers having the indicated properties (Tables II–IV). A typical polymerization which yielded poly[1,1′-diphenyl-3,3′-*p*-phenylene-5,5′-*p*-phenylenedipyrazole] (**12b**) was run as follows. A mixture of 0.366 g (1.00 mmole) of 2,2′-diphenyl-5,5′-*p*-phenyleneditetrazole (**1a**) and 0.126 g (1.00 mmole) of *p*-diethynylbenzene (**2b**) was placed in a 15-ml polymerization tube with 5.0 ml of 1,2,4-trichlorobenzene. The contents of the tube were degassed by several freeze–thaw cycles at liquid nitrogen temperatures and then sealed *in vacuo*. The tube was placed in a Parr bomb which also contained 1,2,4-trichlorobenzene to equalize external and internal pressure and the bomb was heated at 185°C for 48 hr. After the bomb had cooled to room temperature, the tube was opened and the contents of the tube were poured into 200 ml of methanol. The precipitated polymer was filtered and dried *in vacuo* at 212°C for 24 hr. The light brown polymer, $[\eta] = 1.67$ (30°C in 98% formic acid), was obtained in a yield of 0.391 g (89%).

Physical Determinations

Melting Points. All melting points were measured on a Laboratory Devices MEL-TEMP capillary melting point apparatus and are uncorrected.

Viscosities. All viscosities (intrinsic) were taken on solutions of 0.30 g of polymer/100 ml of solvent at 30°C with a Cannon-Ubbelohde microdilution viscometer No. 100. 98% Formic acid was used as the solvent for all of the polypyrazoles **12–13** and 1,2,4-trichlorobenzene was used for polytriazoles **14–17a**. Nitrobenzene was used as a solvent for the polytriazole **17b**.

Thermal Gravimetric Analysis and Differential Thermal Analysis. The thermal stabilities of the polymers (Table II, Fig. 1) were measured both in air and nitrogen atmosphere on a DuPont 950 thermogravimetric analyzer by heating a continuously weighed polymer sample (5 mg) from 25 to 800°C at a rate of 5°C/min.

The differential thermal analyses of the polymers (Table IV) were carried out on a DuPont 900 differential thermal analyzer. The samples were heated under a nitrogen atmosphere at a rate of 20°C/min.

Molecular Weights. The molecular weights (Table III) were obtained with a Hewlett-Packard high-speed membrane osmometer using a superdense membrane at 29.5°C in chlorobenzene. The concentrations of the solutions ranged from 5 to 0.6 g/l.

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Reaction of Polyepichlorohydrin with Magnesium and Grignard Reagents

YUJI MINOURA, *Research Institute for Atomic Energy, Osaka City University, Osaka, Japan*, and HISASHI HIRONAKA, TOSHIYUKI KASABO, and YUKIO UENO, *Kyowa Rubber Industry Co., Ltd., Osaka, Japan*

Synopsis

The reaction of polyepichlorohydrin with magnesium in tetrahydrofuran at reflux temperature was studied in the hope of obtaining a polymeric Grignard reagent. The polymeric Grignard reagent could not be obtained, but dechlorination occurred. It was confirmed that the Grignard reagent of polyepichlorohydrin was formed as an intermediate during the dechlorination The reactions of polyepichlorohydrin with Grignard reagents were carried out in tetrahydrofuran at reflux temperature. Benzylmagnesium chloride and allylmagnesium chloride were used as Grignard reagents. It was found that the chlorine atom in polyepichlorohydrin can be replaced by benzyl and allyl groups. The extent of the substitution increased with increasing concentration of Grignard reagent. Dechlorination and scission of the ether linkage occurred simultaneously as side reactions.

INTRODUCTION

The reactions of poly(vinyl chloride) with alkali metal,[1] organometallic reagent[2] (e.g., butyllithium and sodium naphthalene) and zinc[3,4] have been investigated. Greber and Egle[5] have shown that the reaction of dimethylsilylmethylmagnesium chloride with styrene–acrylonitrile copolymers yields macromolecular polymerization initiators which make possible graft polymerization of 4-vinylpyridine, acrylonitrile, and methyl methacrylate. However, no detailed data are available on the reactions of polymers with magnesium and Grignard reagent.

In this work, the reaction of polyepichlorohydrin with magnesium in tetrahydrofuran at reflux temperature was studied for the purpose of preparing the polymeric Grignard reagent. It was found that although the Grignard reagent of polyepichlorohydrin was formed during the reaction, the Grignard reagent reacted immediately with another chloromethyl group.

Furthermore, the reactions of poly(epichlorohydrin) with benzylmagnesium chloride and allylmagnesium chloride were investigated; it was found that the chlorine atoms in the polymer were replaced by benzyl and allyl groups.

EXPERIMENTAL

Materials

Polyepichlorohydrin (PECH, molecular weight 5×10^5) was obtained commercially. The polymer was dissolved in benzene, and the solution, after removal of impurities and the gel fraction, was poured into methanol. The precipitated PECH was dried *in vacuo*. The PECH was more completely dried by standing over phosphorus pentoxide in an atmosphere of nitrogen for a week.

Tetrahydrofuran (THF) was refluxed with sodium wire, distilled, and stored in a bottle containing sodium wire. Refluxing with sodium wire and naphthalene just before use yielded completely anhydrous THF.

Benzyl chloride, allyl chloride, and trimethylchlorosilane were purified by the usual methods and distilled over calcium hydride just before use.

Commercial magnesium turnings were dried in the oven before use.

Other reagents such as Michler's ketone and iodine were obtained commercially.

Reaction of PECH with Magnesium

Into a 100-ml three-necked flask equipped with a stirrer, a reflux condenser, and a three-way tap, were placed 0.26 g (0.011 mole) of magnesium, 30 ml of THF and 1.0 g (0.011 mole) of PECH. After PECH was completely dissolved in THF under stirring and flushing with nitrogen, a small amount of iodine as a reaction initiator was added to the mixture. The reaction was carried out at the reflux temperature of THF. Detection of the Grignard reagent of PECH was made according to the method of Gilman and Schulz,[6] as follows. To 1% solution of Michler's ketone in benzene was added a portion of the reaction mixture and iodine. Then to this hydrolyzed mixture, a few drops of a solution of iodine in glacial acetic acid were added. If the Grignard reagent was present, the tested system would become green. After refluxing for 10 hr, the reaction mixture was filtered, and the solution was poured into methanol. The precipitated polymer was washed well with methanol and dried *in vacuo*.

Reaction of PECH with Grignard Reagents

In all the experiments, a 100-ml four-necked flask equipped with a stirrer, a reflux condenser, a dropping funnel, and a three-way tap was used. The Grignard reagent solution in 30 ml of THF was prepared by the usual method in the flask under an atmosphere of nitrogen. After 1.0 g (0.011 mole) of PECH solution in 20 ml of THF was degassed, the solution was added to the Grignard reagent solution through a dropping funnel. After refluxing for 10 hr, the reaction mixture was filtered and the solution was poured into methanol. The precipitated polymer was washed well with methanol and dried *in vacuo*.

Infrared Spectra

The infrared absorption spectra of thin films of the polymers obtained on rock-salt plates were obtained by using an infrared spectrophotometer, model IR-E, of the Japan Spectroscopic Co., Ltd.

Intrinsic Viscosity

The intrinsic viscosity measurements were made in benzene at 30°C with the use of an Ubbelohde viscometer.

Determinations of Chlorine Content and Unsaturation

Chlorine contents of the polymers were determined by the Schöniger method.[7] Unsaturation values of the polymers were calculated from the iodine values, which were determined by the Wijs method.[8]

RESULTS AND DISCUSSION

Reaction of PECH with Magnesium

The reaction of PECH with magnesium to prepare a polymeric Grignard reagent was carried out in THF at reflux temperature, and the detection of

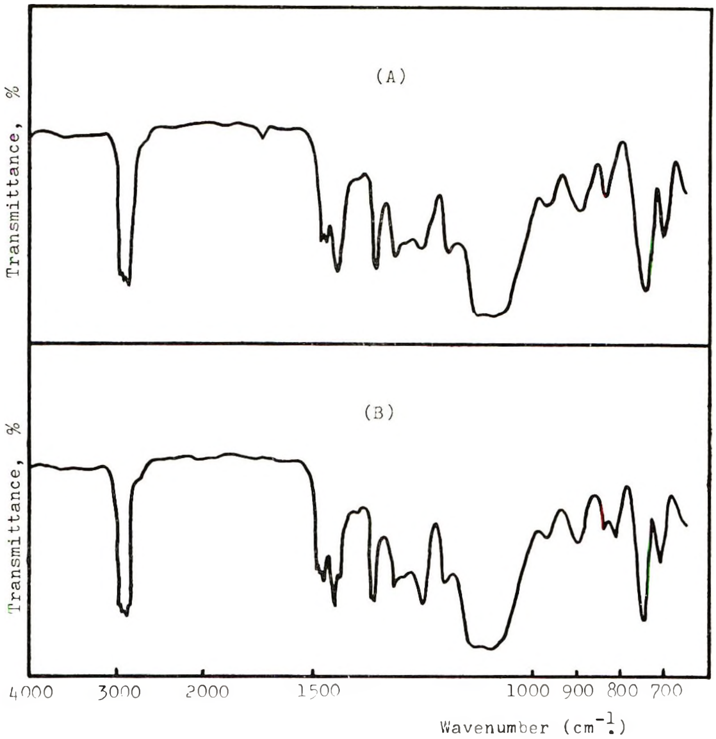


Fig. 1. Infrared spectra of (*A*) PECH and (*B*) product from reaction of PECH with magnesium. PECH 0.011 mole, Mg/PECH = 1.0, THF 30 ml, reflux for 10 hr.

TABLE I
Analysis of PECH and Product from Reaction of PECH with Magnesium[a]

	Composition, %[b]		Found			Calcd from composition			Intrinsic viscosity,
	I	II	C, %	H, %	Cl, %	C, %	H, %	Cl, %	dl/g
PECH	100	0	39.43	5.51	38.86	38.94	5.45	38.32	0.768
Product	95	5	40.20	6.04	35.61	40.3	5.61	36.1	0.795

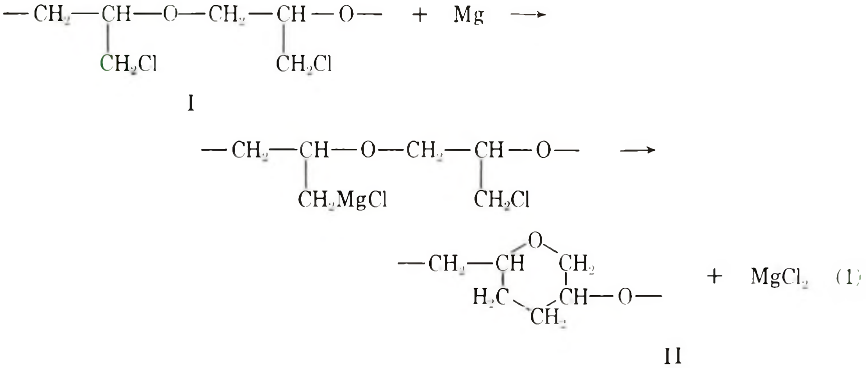
[a] Reaction conditions: PECH 0.011 mole, Mg/PECH = 1.0, THF 30 ml, reflux for 10 hr.

[b] Compounds I and II [see eq. (1)].

the Grignard reagent was made by taking aliquots of the reaction mixture at adequate time intervals. Although the reaction was carried out for 40 hr, Grignard reagent could not be detected by the method of Gilman and Schulz over the reaction period.

The infrared spectra of PECH and the product are shown in Figure 1. The infrared spectrum of the product (Figure 1*B*) showed a new absorption band at 810 cm^{-1} which was not observed in the spectrum of PECH (Figure 1*A*). Moreover, the chlorine content of the product decreased by about 3% from that of PECH. The chlorine content of the product is shown in Table I.

These results suggest that dechlorination takes place in the reaction of PECH with magnesium. It is thought that the dechlorination is due to the coupling reaction of the Grignard reagent of PECH, which is formed as an intermediate, with the adjacent chloromethyl group by elimination of magnesium chloride, and since the formation of the Grignard reagent is followed immediately by the coupling reaction, it can not be detected by the method of Gilman and Schulz.[6]



I

II

(1)

However, the cyclic ether expected [eq. (1)] as the dechlorination product could not be isolated.

Reaction of PECH with Magnesium in the Presence of Trimethylchlorosilane

In the reaction of PECH with magnesium, the formation of the Grignard reagent of PECH as an intermediate was pointed out. Trimethylchlorosilane does not react with magnesium but reacts with Grignard reagents. Therefore, the reaction was carried out under similar conditions but in the presence of trimethylchlorosilane to confirm the formation of the Grignard reagent of PECH. The infrared spectra of the products were measured.

When the mole ratio of trimethylchlorosilane to PECH was equal to 2, the infrared spectrum of the product showed a new absorption band at 810 cm^{-1}, but the absorption bands of the trimethylsilyl group at 1250 and 850 cm^{-1} were not observed. On the other hand, when the mole ratio of trimethylchlorosilane to PECH was 5.0 and the amount of trimethylchlorosilane was increased, the absorption band at 810 cm^{-1} was not observed in the spectrum of the product, as can be seen in Figure 2, and the absorption intensity at 1250 and 850 cm^{-1} assigned to the trimethylsilyl group increased markedly compared to the absorption intensity in the spectrum of PECH (Figure 1*A*) on account of the overlap of the absorptions of PECH and the trimethylsilyl group. These results indicate that the trimethylsilyl group was introduced into PECH.

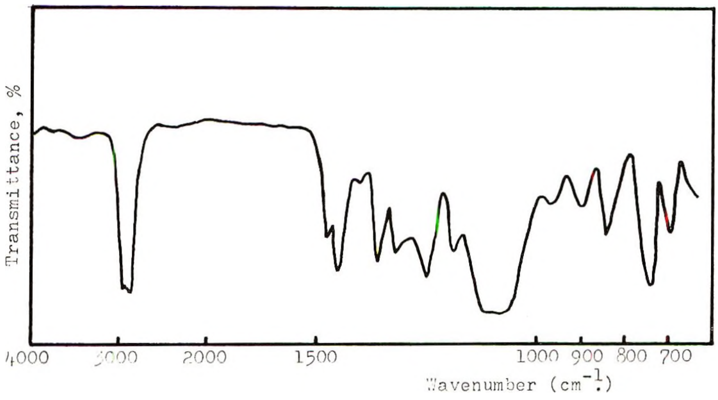
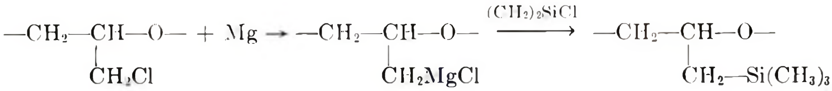


Fig. 2. Infrared spectrum of product from reaction of PECH with magnesium in the presence of trimethylchlorosilane. PECH 0.011 mole, $(CH_3)_3SiCl$/PECH = 5.0, Mg/PECH = 1.0, THF 30 ml, reflux for 10 hr.

It may be concluded that the introduction of the trimethylsilyl group into PECH resulted from the coupling reaction of the Grignard reagent of PECH with trimethylchlorosilane as shown in eq. (2).



$$\underset{\displaystyle CH_2Cl}{—CH_2—CH—O—} + Mg \rightarrow \underset{\displaystyle CH_2MgCl}{—CH_2—CH—O—} \xrightarrow{(CH_3)_3SiCl} \underset{\displaystyle CH_2—Si(CH_3)_3}{—CH_2—CH—O—} \qquad (2)$$

The extent of the substitution in the product, calculated from elemental analysis, was 7.9%.

It may be considered from these results that the Grignard reagent of PECH was not obtained, because the reagent immediately underwent coupling with an adjacent chloromethyl group.

Reaction of PECH with Benzylmagnesium Chloride (BzMgCl)

The reactions of Grignard reagents with low molecular weight compounds having various functional groups have been widely investigated. However, little has been reported about the reactions of polymers with Grignard reagents.

In this study, PECH was reacted with BzMgCl at various concentrations in THF at reflux temperature for 10 hr. The infrared spectrum of the product is shown in Figure 3.

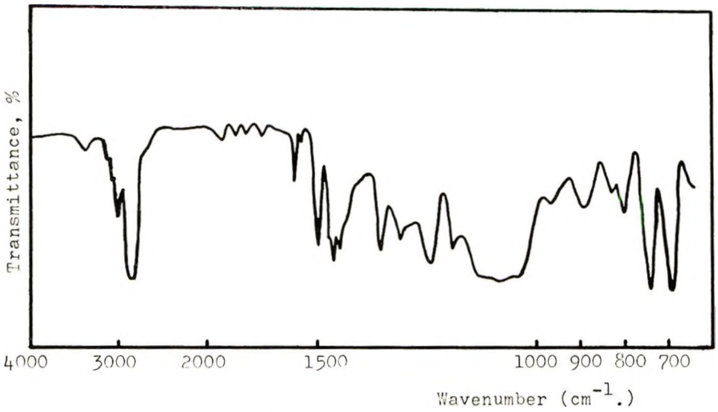


Fig. 3. Infrared spectrum of product from reaction of PECH with BzMgCl. PECH 0.011 mole, BzMgCl/PECH = 4.0, THF 50 ml, reflux for 10 hr.

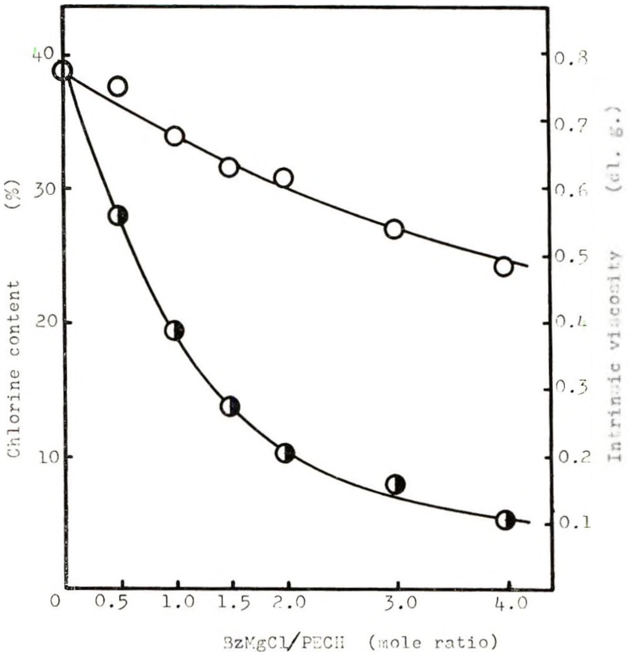
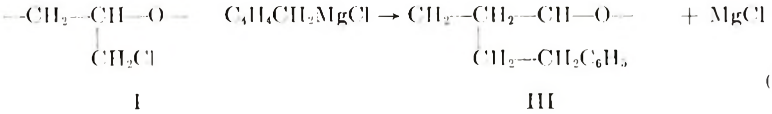


Fig. 4. Relationships between (◐) the chlorine content and (○) intrinsic viscosity of product and the BzMgCl concentration. PECH 0.011 mole, THF 50 ml, reflux for 10 hr.

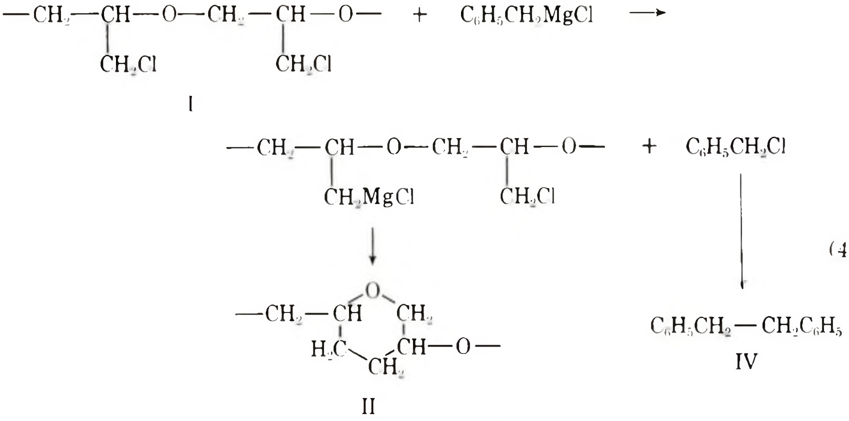
The spectrum showed new absorption bands at 3060, 1603, and 1500 cm^{-1} due to the benzene ring in addition to the bands of PECH. In the range 2000–1700 cm^{-1}, bands due to the monosubstituted benzene ring were observed. These results indicate that chlorine atoms in PECH were replaced with benzyl groups by the coupling reaction between the chloromethyl group and BzMgCl [eq. (3)].



$$-CH_2-\underset{\underset{CH_2Cl}{|}}{CH}-O- \quad C_4H_4CH_2MgCl \rightarrow CH_2-\underset{\underset{CH_2-CH_2C_6H_5}{|}}{CH_2}-CH-O- \quad + MgCl$$

I III (3)

Moreover, a new absorption band at 810 cm^{-1} was observed in the spectrum. This suggests that dechlorination occurs. On the other hand, it has been shown by Reeve and Fine[9] that magnesium–halogen exchange occurs readily between *n*-butylmagnesium compounds and 1,1,1-trichloropropylene oxide. Thus, it may be considered that in this reaction system, dechlorination is caused by the coupling reaction of the Grignard reagent of PECH, which was formed by the exchange between PECH and BzMgCl, with the adjacent chloromethyl group as shown in eq. (4).

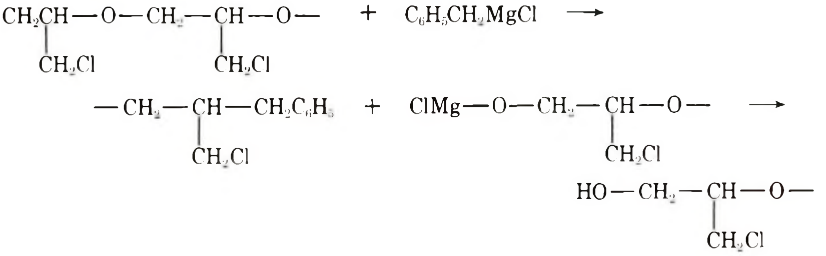


(4)

Dibenzyl (IV) which was isolated from the reaction system, would seem to be formed by the coupling of benzyl chloride, which resulted from the exchange between PECH and BzMgCl, with residual BzMgCl.

The relationships between the chlorine content and intrinsic viscosity of the product and BzMgCl concentration are shown in Figure 4.

The chlorine content of the product decreased with increase in the BzMgCl concentration. This result indicates that the extent of the substitution increases with increase in the BzMgCl concentration. On the other hand, the intrinsic viscosity also decreased with increase in the BzMgCl concentration. The reason for this is considered to be that scission of the ether linkage occurs by attack of BzMgCl on the oxygen in the PECH.



$$CH_2\underset{\underset{CH_2Cl}{|}}{CH}-O-CH_2-\underset{\underset{CH_2Cl}{|}}{CH}-O- \quad + \quad C_6H_5CH_2MgCl \longrightarrow$$

$$-CH_2-\underset{\underset{CH_2Cl}{|}}{CH}-CH_2C_6H_5 \quad + \quad ClMg-O-CH_2-\underset{\underset{CH_2Cl}{|}}{CH}-O- \longrightarrow$$

$$HO-CH_2-\underset{\underset{CH_2Cl}{|}}{CH}-O- \qquad (5)$$

TABLE II
Composition of Products from Reaction of PECH with BzMgCl[a]

BzMgCl/PECH, mole ratio	Composition, %[b]			Found			Calcd from composition		
	I	II	III	C, %	H, %	Cl, %	C, %	H, %	Cl, %
100% PECH	100	—	—	39.43	5.51	38.86	38.94	5.45	38.32
1.0	86.9	11.4	1.7	42.39	5.88	33.90	42.41	5.88	33.30
2.0	76.8	12.4	10.8	46.47	6.14	30.76	46.49	6.16	29.43
4.0	67.0	4.0	29.0	52.11	6.37	24.36	52.12	6.37	25.67

[a] Reaction conditions: PECH 0.011 mole, THF 50 ml, reflux for 10 hr.

[b] Compounds I, II, III, see eqs. (3) and (4).

Furthermore, the product compositions were calculated from the carbon–hydrogen content by assuming the formation of cyclic ether as the dechlorination product. The results are shown in Table II.

These results proved that the extent of the substitution increased with increasing BzMgCl concentration. It can be assumed that the decrease in the dechlorination product II, when the BzMgCl concentration is high, results from the decrease in the number of the chloromethyl groups adjacent to the —CH_2MgCl group formed by the exchange reaction, because the coupling reaction of the chloromethyl group with BzMgCl easily occurs.

Reaction of PECH with Allylmagnesium Chloride (AllylMgCl)

Since the benzyl group was introduced into the PECH by the reaction with BzMgCl, it may be considered that various functional groups can be introduced into a polymer by reaction with Grignard reagents having various functional groups.

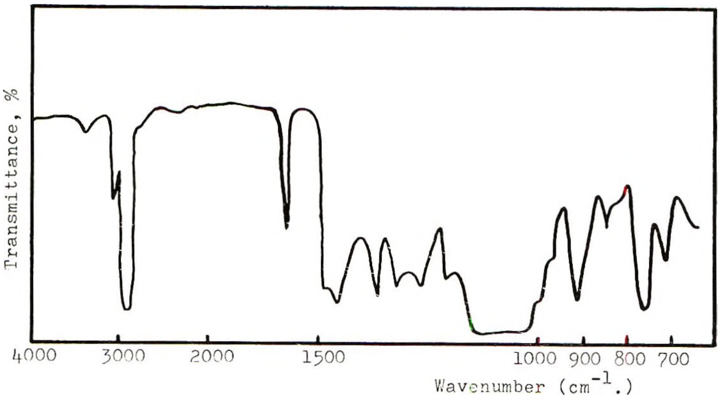


Fig. 5. Infrared spectrum of product from reaction of PECH with AllylMgCl. PECH 0.011 mole, AllylMgCl/PECH = 2.0, THF 50 ml, reflux for 10 hr.

In this study, to introduce unsaturation, the reaction of PECH with AllylMgCl was carried out under similar conditions to these described above.

The infrared spectrum of the product is shown in Figure 5.

The spectrum showed new absorption bands at 3100 and 1650 cm^{-1} due to a carbon–carbon double bond. This result indicates that chlorine atoms in the PECH are replaced by allyl groups. The band at 810 cm^{-1} in the infrared spectrum was very weak.

As shown in Figure 6, the chlorine content and intrinsic viscosity decreased with increasing AllylMgCl concentration as observed in the case of BzMgCl.

It may be concluded from these results that in the reaction of PECH with Grignard reagent, scission of the ether linkage and dechlorination occur simultaneously as side reactions, in addition to the coupling reaction be-

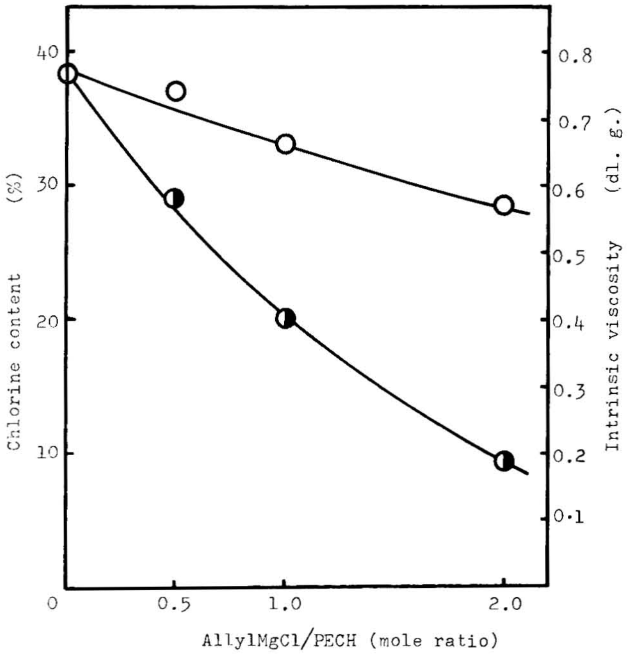


Fig. 6. Relationships between (◐) the chlorine content and (○) intrinsic viscosity of product and the AllylMgCl concentration. PECH 0.011 mole, THF 50 ml, reflux for 10 hr.

tween PECH and Grignard reagent. Unsaturation and the extent of reaction calculated from the chlorine content of the product are shown in Table III.

Unsaturation in the product increased with increasing AllylMgCl concentration; that is, it was found that the extent of substitution increases with increasing concentration of Grignard reagent. Since the value of the unsaturation nearly agrees with the extent of reaction, and the intensity of the band at 810 cm^{-1} is weaker, it may be considered that the dechlorination is slight in the reaction of PECH and AllylMgCl.

Purified PECH degraded on standing at room temperature in the atmosphere. The product having 12.5% unsaturation crosslinked on stand-

TABLE III

Unsaturation of Product from Reaction of PECH with AllylMgCl[a]

AllylMgCl/PECH, mole ratio	Unsaturation, %	Extent of reaction, %[b]
0.5	1.8	2.6
1.0	12.5	13.6
2.0	23.1	25.1

[a] Reaction conditions: PECH 0.011 mole, THF 50 ml, reflux for 10 hr.

[b] The extent of reaction was calculated from the chlorine content of the products.

ing at room temperature for a week in the atmosphere, and the crosslinked product was insoluble in solvents such as THF and benzene. Two products having unsaturation values of 1.8 and 23.1% did not crosslink under the conditions mentioned above. The reason for this is considered to be that the unsaturation is too low in the former and the degree of polymerization is too low in the latter. When two products having unsaturations of 12.5 and 23.1% were heated at 150°C for 15 min in the atmosphere, both became insoluble in solvents. 10% (w/v) polymer solution in benzene were reacted at 80°C for 10 hr in the presence of 1% (w/w) benzoyl peroxide or azobisisobutyronitrile under a nitrogen atmosphere. Only the product having an unsaturation of 12.5% crosslinked in the presence of benzoyl peroxide after 5 hr.

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Accessibility of Cotton and Chemically Swollen Cottons to Methylating Reagents

FRANK S. H. HEAD and GLADYS E. HADFIELD, *Cotton Silk and Man-made Fibres Research Association, Shirley Institute, Manchester, England*

Synopsis

Standard Acala cotton, and modified cottons obtained from it by swelling in 5*N* sodium hydroxide, 62% sulfuric acid, or 81% phosphoric acid, have been methylated with moist ethereal diazomethane or with a toluene solution of dimethyl sulfate in the presence of 2*N* sodium hydroxide. The accessibility of cotton to either reagent is increased by swelling in the order sulfuric acid <phosphoric acid <5*N* sodium hydroxide. Each fiber is more accessible to the alkaline methylating agent than to diazomethane. The results confirm the view of Roberts et al. that a more rapid methylation of accessible hydroxyl groups in the surfaces of crystalline aggregates is followed by a slower penetration of the ordered material. Analysis of the methylated products and interpretation of the results on similar lines suggests that aggregates of approximately two elementary fibrils (found in cotton methylated with moist diazomethane) are split into single fibrils by 81% phosphoric acid or 2*N* sodium hydroxide and that mercerization transforms the elementary fibrils into smaller units, but an alternative explanation is possible. Progressive penetration of the elementary fibrils by swelling agents may increase the amount of accessible material without decreasing the size of the fibrils.

INTRODUCTION

From studies of the reaction between a solution of dimethyl sulfate in dimethyl sulfoxide and cotton cloth impregnated with 2*N* sodium hydroxide followed by hydrolysis of the products and analysis of the hydrolyzates, Haworth, Roberts, and Robinson[1,2] deduced a model for the elementary structural unit in cotton cellulose having a surface of anhydroglucose units (a.g.u.) with accessible 2, 3, and 6-hydroxyl groups in the proportions indicated by methoxyl distribution measurements. According to this model, which is based on the crystalline fibril theory 3, alternate a.g.u. in one pair of parallel surfaces of a unit of rectangular cross section would, on methylation and hydrolysis, give rise to 2- and 6-*O*-methyl-D-glucose, respectively, while those on the other pair would yield 2,6-di-*O*-methyl- and 2,3,6-tri-*O*-methyl-D-glucose. The occurrence of intramolecular hydrogen bonding between the C-3 hydroxyl and the C-5′ oxygen atom[4] was assumed, and this made it possible to explain the occurrence of roughly equal quantities of 2- and 6-*O*-methyl-D-glucose, and of 2,6-di-*O*-methyl- and 2,3,6-tri-*O*-methyl-D-glucose, respectively, with very little 3-*O*-methyl-, 2,3-di-*O*-

methyl-, or 3,6-di-*O*-methyl-D-glucose. Since all four products occurred in nearly equal amounts it was concluded[5] that the cross section was nearly square.

The structural unit finally deduced on this basis[5] was a bundle of 80 cellulose chains in a block of 8 × 10 a.g.u. cross section such that the eight units in each short side (corners included) would give rise to 2,6-di- and 2,3,6-tri-*O*-methyl-D-glucose and the eight units remaining from the longer sides would give 2- and 6-*O*-methyl-D-glucose. Complete methylation of the outside of such a bundle containing 32 accessible units on the surface and 48 inaccessible units inside would give an overall degree of substitution (DS) of 0.70. Complete hydrolysis of the product would give 60 mole-% of D-glucose and 10 mole-% each of 2- and 6-*O*-methyl-D-glucose, 2,6-di-*O*-methyl-, and 2,3,6-tri-*O*-methyl-D-glucose. The observed results agreed well with these figures; the products contained only 4% of other 3-*O*-methylated glucoses. The suggested units, having a cross section of ca. 40 × 50 Å, would be about the same size as the smallest elementary fibrils observed by electron microscopy (diameter 30–60 Å[6]).

A similar examination of methoxyl distribution in cotton cloth methylated with diazomethane in ether saturated with water[1,2,5] indicated the presence of rather larger units and suggested that the elementary fibrils are aggregated. Since dry cotton is scarcely methylated at all by dry ethereal diazomethane,[7] the authors[5] suggest that it is almost completely aggregated in the natural state. The reported figures[7] for methoxyl content correspond to fibrillar units containing about 10^6 a.g.u. in the cross section.

On this view, the presence of water must lead to extensive disaggregation, but complete breakdown to elementary fibrillar size does not occur unless alkali is present.

The present work, primarily planned as a study of the effect of swelling with various reagents upon the accessibility of cotton, has taken the form of an extension of the earlier work of Roberts et al.[1,2,5] and largely confirms the results. Diazomethane was chosen as a suitable reagent for examining the accessibility of preswollen cottons because the reaction in ethereal solution takes place with little or no swelling and appears to be largely confined to the accessible regions.[8] For comparison, the four fibers used were also methylated with dimethyl sulfate in toluene, after soaking in 2*N* sodium hydroxide. The distribution of methoxyl groups in the methylated products was determined by the procedures of hydrolysis, trimethylsilylation and gas liquid chromatographic analysis evolved in the earlier work.[9]

EXPERIMENTAL

Materials

The fibers used in this work were scoured standard Acala 4-42 cotton (Found: S, 0.07%; P, 0.12%). These were (*a*) unmodified; (*b*) mercerized for 1 hr in 5*N* sodium hydroxide at 25°C, washed with 0.1*N* acetic acid and with water and air-dried; (*c*) swollen with 62% sulfuric acid for 30 min at 25°C, washed and dried (Found: S, 0.07%; cuprammonium fluidity, 35.8 poise^{-1});[10] and (*d*) swollen with 81% phosphoric acid for 30 min at 25°C, washed, and dried. (Found: P, 0.16%; cuprammonium fluidity 4.6 poise^{-1}.)

Methylation Procedure

Diazomethane. Ethereal diazomethane (ca. 0.4*M*) was prepared by De Boer's method[11] and its concentration was determined by adding aliquots to known weights of benzoic acid in ether and titrating the excess of acid with sodium hydroxide. Before use it was diluted to 0.25*M*, mixed with water (25 g/l. of ethereal solution), shaken at intervals during $^1/_2$–1 hr, and separated from surplus water. A quantity of the cotton or modified cotton fiber, previously conditioned for at least 3 days in a room at 65% RH was steeped in the moist 0.25*M* ethereal diazomethane (100 cc/g) for the required time in a refrigerator at about 6–7°C, collected, washed well with ether, air-dried, washed, steeped in water for ca. 2 hr, and air-dried. For times of less than 24 hr individual 1-g specimens of fiber were used. For times of 24 hr and upwards a bulk specimen was methylated and small portions (0.5 or 1 g) removed at suitable intervals when the reagent was being changed i.e., after 1, 2, 3, and 4 days and then at 3-day intervals. The bulk was well washed with ether, and air-dried briefly each time before fresh reagent was added; the small portions removed for analysis were washed with water and air-dried.

Dimethyl Sulfate. Portions of fiber (6 g) were steeped for 0.5 hr in a mixture of 2*N* sodium hydroxide (300 cc) and 3% aqueous sodium dodecylsulfate solution (6 cc), collected in a slitted sieve glass funnel, and pressed to remove liquid as far as possible. The soaked fiber was shaken with toluene (300 cc) for $^1/_2$ hr and dimethyl sulfate (30 cc) added. The whole was well shaken by hand and shaken mechanically for a further 3 hr at room temperature (ca. 22°C). The fiber was then collected, well washed with methanol and with water, heated in boiling water containing a slight excess of sodium hydroxide, collected again, washed with water, steeped in 2% acetic acid, washed thoroughly with water and finally with methanol, and air-dried over-night. The process was repeated on the following day. At suitable intervals 0.5-g portions of the air-dried fiber were removed, steeped in water for 1 hr, and air-dried for analysis. After each removal the remaining fiber was remethylated with proportionally reduced quantities of reagents. The good agreement obtained in duplicate methoxyl determinations indicated that methylation was reasonably uniform.

Determination of Methoxyl Content. The modified Zeisel method of Samsel and McHard was used[12] but ca. 0.2 g red phosphorus was added to the hydriodic acid and the time of heating was extended to 1 hr.[7] Fiber samples (usually 0.1 g, but sometimes 0.05 g) were dried *in vacuo* over phosphorus pentoxide for at least 4 days before weighing. The results were corrected to allow for the apparent methoxyl content of the original cotton; the mean figure for four 0.1 g samples (0.35 cc of 0.1*N* sodium thiosulfate) corresponded to about 0.2% methoxyl. Determinations were carried out in duplicate and seldom differed by as much as 0.2%. The linear portions of the graphs plotted in Figures 1 and 3 were obtained by applying the method of least squares to the results for 13 days or ten methylations and upwards, respectively.

Hydrolysis of Methylated Fiber Samples and Analysis of Hydrolyzates

The procedure used was that described by Haworth, Roberts, and Sagar.[9] Individual values for α- and β-anomers were summed to give the figures for the respective sugars.

RESULTS AND DISCUSSION

In the earlier work[1,2,5] it was suggested that in the methylation of cotton, a relatively rapid initial reaction of the accessible hydroxyl groups on the surface of the elementary structural unit is followed by a much slower attack at constant rate consistent with an advancing zone of methylation passing through ordered material. In the hope of obtaining rate curves to distinguish between these reactions, the procedure with diazomethane was designed so that the cellulose was always exposed to a large excess of the reagent during methylation. In trial methylations it was found that the

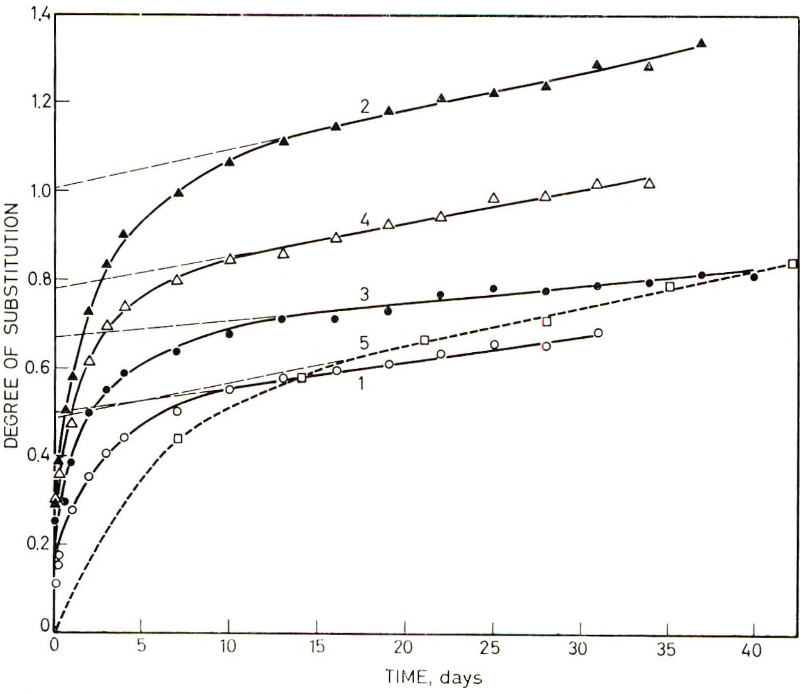

Fig. 1. Methylation of fibers with 0.25M diazomethane: (*1*) cotton; (*2*) mercerized cotton; (*3*) cotton swollen with 62% sulfuric acid; (*4*) cotton swollen with 81% phosphoric acid; (*5*) cotton with 0.5M diazomethane.

concentration of diazomethane fell from 0.25M to 0.11M during the first 24 hr and to ca. 0.17M in subsequent methylations.

Results for the diazomethane methylation of standard Acala cotton, mercerized cotton (MC), and cotton swollen with 62% sulfuric acid (SC),

TABLE I

Analysis of Hydrolyzate from Fibers Methylated with Diazomethane

Fiber	Reaction time, days	Overall DS of fiber (Zeisel)	Composition of hydrolyzate, mole-%[a]							
			G	G_2	G_3	G_6	G_{23}	G_{26}	G_{36}	G_{236}
Cotton	0		98.8[b]	0	0	0	0	0	0	0
	1	0.28	81.1	6.3	1.4	7.3	1.1	2.8	1.1	0.7
	2	0.35	75.1	6.3	2.0	8.3	1.3	6.1	1.2	2.1
	3	0.41	65.7	6.0	3.3	6.9	4.4	4.5	2.6	6.6
	4	0.44	69.6	4.8	1.6	6.3	2.8	3.7	2.1	4.5
	10	0.55	67.6	8.2	0.8	8.8	3.4	4.4	1.0	7.0
	16	0.59	66.0	5.6	1.0	6.3	2.5	5.3	1.9	8.5
	22	0.64	62.7	9.8	2.7	9.3	1.7	6.9	1.5	9.9
	31	0.69	60.0	6.9	3.6	10.3	4.4	6.5	2.0	11.4
Mercerized cotton	1	0.58	61.0	14.3	5.3	10.0	3.5	5.2	3.1	2.3
	2	0.73	51.4	17.4	4.4	9.2	3.5	9.0	3.5	4.7
	3	0.84	44.4	15.9	3.0	9.1	5.7	9.1	4.3	9.7
	4	0.90	43.3	18.2	2.6	9.6	5.6	9.9	3.7	11.0
	10	1.07	39.4	15.8	2.6	7.2	3.5	13.2	4.1	15.1
	16	1.15	37.0	13.4	2.4	7.6	5.5	11.2	3.1	18.4
	22	1.21	33.3	15.0	1.8	8.0	2.9	13.1	3.4	23.2
	31	1.29	31.8	15.2	1.0	8.7	4.2	13.5	3.7	23.2
	37	1.34	30.8	14.7	2.0	7.2	4.3	14.5	2.8	27.1
Cotton swollen in sulfuric acid	1	0.39	73.8	5.3	4.5	4.5	1.9	4.9	3.4	3.6
	2	0.50	71.1	3.5	1.2	4.9	1.9	5.0	2.8	5.8
	3	0.55	66.8	6.7	3.8	8.6	2.8	6.9	2.1	8.7
	4	0.59	67.9	4.0	1.8	6.1	2.5	4.6	2.6	7.9
	10	0.68	63.8	4.5	1.5	6.7	5.0	5.0	2.3	11.2
	16	0.71	63.5	4.0	0.8	7.2	2.1	4.8	1.9	13.7
	22	0.77	61.8	5.3	4.4	8.7	2.8	6.5	1.5	15.9
	31	0.80	62.0	3.3	1.1	6.9	1.6	3.4	1.4	15.8
	40	0.81	58.7	2.9	1.4	7.4	1.5	3.8	1.4	19.0
Cotton swollen in phosphoric acid	1	0.47	70.9	6.8	2.7	6.3	2.2	4.0	2.4	2.7
	2	0.62	63.9	7.6	1.4	6.3	2.9	5.7	3.2	6.9
	3	0.69	62.4	7.0	2.3	7.3	3.0	7.7	2.7	7.3
	4	0.74	61.2	6.5	3.5	7.1	2.0	9.2	3.2	9.8
	10	0.85	57.1	5.6	2.3	6.7	3.1	9.4	3.0	13.6
	16	0.90	54.3	5.6	1.1	6.5	3.4	8.7	2.7	17.6
	22	0.95	53.0	3.5	5.9	4.2	9.2	6.6	2.5	19.5
	28	0.99	47.7	5.3	2.5	7.3	1.5	9.5	2.2	24.4
	34	1.02	50.4	5.4	0.4	7.5	2.9	4.6	1.8	22.1

[a] G = D-glucose, G_2 = 2-*O*-methyl-D-glucose, etc.

[b] The other three fibers gave figures of 98.7, 98.9, and 98.7.

or 81% phosphoric acid (PC) are given in Figure 1. Figure 1 also contains points (curve *5*) for an earlier methylation of a Texas cotton with $0.5M$ diazomethane (renewed every seven days).[7] Although the rate of the slow reaction was greater than with $0.25M$ diazomethane, the intercept on the DS axis for zero time was the same, the figures obtained by the least-square method being 0.49 and 0.50, respectively.

The three modified cottons all reacted much more extensively than cotton itself, the effect being most marked with MC, somewhat less with PC, and least with SC. The curves obtained were all of the same type, and in all cases the reaction could be considered to have reached a constant rate after 13 days (if not before). The results for the extrapolated DS at zero time are included in Table II. Mercerization doubled the DS attributable to the initial reaction and the acid treatments gave intermediate values. These figures can be taken as an indication of the extent to which the various treatments increase the accessibility of the cellulose.

Results for the analyses of the hydrolyzates derived from the methylated fibers are given in Table I and derived figures corresponding to completion of the first stage of the methylation are summarized in Table II. In agreement with Roberts et al.[1,2] it was found that the amounts of glucose from each material fell quite rapidly during the first stage of the reaction but the reduction in glucose content finally attained a slow constant rate, while the yields of 2,3,6-tri-*O*-methyl-D-glucose rose rapidly at first before achieving a similar slow constant rate of increase. The amounts of glucose and trimethylglucose corresponding to completion of the first stage could therefore be calculated from the respective results from 10 or 16 days upwards, as

TABLE II

Sugars in Hydrolyzate Derived from Figure 1 and Table I for Fibers Fully Methylated According to the First State of Methylation with Diazomethane

	Sugar content, mole-%							
	Cotton		Sulfuric acid-swollen cotton		Phosphoric acid-swollen cotton		Mercerized cotton	
Sugar	Found	Calcd for 12 × 14 a.g.u.	Found	Calcd for 12 × 9 a.g.u.	Found	Calcd for 9 × 8 a.g.u.	Found	Calcd for 5 × 7 a.g.u.
G	72	71	66	65	58	58	41	43
G_2	7	7	4	6	5	8	15	14
G_3	2	0	2	0	2	0	2	0
G_6	9	7	7	6	7	8	8	14
G_{23}	3	0	2	0	3	0	4	0
G_{26}	6	7	5	11	8	12.5	13	14
G_{36}	2	0	2	0	2	0	3	0
G_{236}	5	7	10	11	11	2.5	12	14
DS (Zeisel)	0.50	0.50	0.67	0.68	0.78	0.79	1.01	1.00

seemed appropriate. The results for the other partially methylated glucoses were more scattered and the figures given for them in Table II are usually the means of the observed values for 10 days and more.

On the assumption that the figures in Table II refer to hypothetical materials in which all surfaces accessible to moist diazomethane have been methylated, it is possible to form an idea of the cross-sectional area of the associated bundles of polymer chains, whether these be regarded as elementary fibrils or as aggregates or subdivisions thereof. Calculations make it clear that figures fairly close to those observed will usually be given by a number of similar units. This is shown graphically in Figure 2, which gives separate lines joining all the rectangles with sides up to 20 a.g.u. corresponding to each observed experimental result for cotton on the basis of the model.[1,2] For a unique solution all the lines should intersect at the same point. In fact, units in which sides A and B equalled 12 × 14, 13 × 14, and 11 × 15 a.g.u. would all give figures very close to those observed for cotton, and several others are almost as good. With this reservation, the

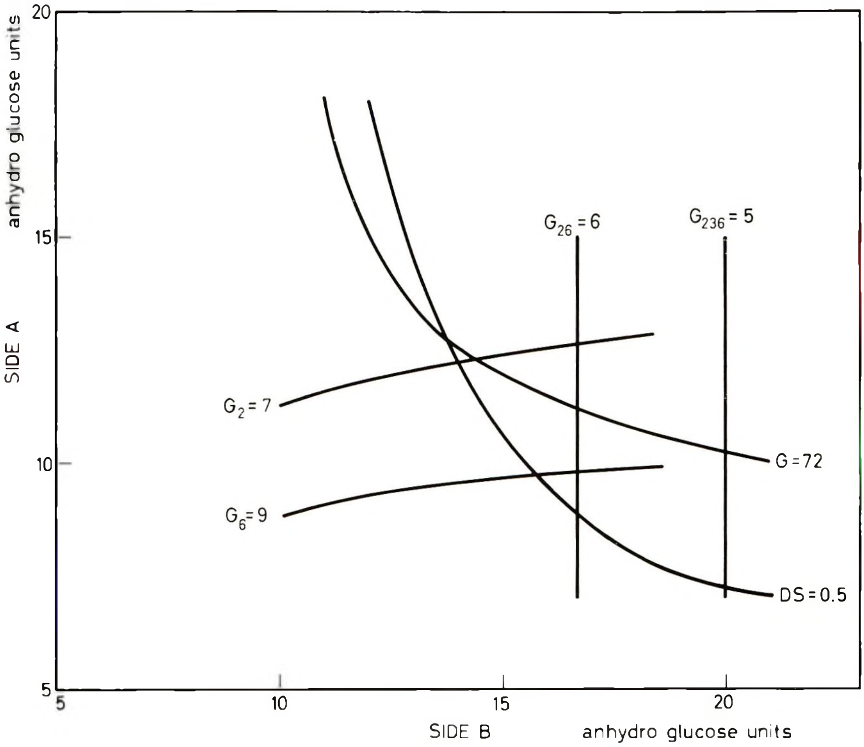

Fig. 2. Lines indicating rectangles which would give the results observed in diazomethane methylation of cotton. Side A is assumed to contain the corner units and to give rise to G_{26} and G_{236}, and side B to give G_2 and G_6. For the assumed model. $DS = (5A + 2B - 4)/AB$; $G = 100[AB - 2(A + B) + 4]/AB$; $G_2 = G_6 = 100(B - 2)/AB$; $G_{26} = G_{236} = 100/B$.

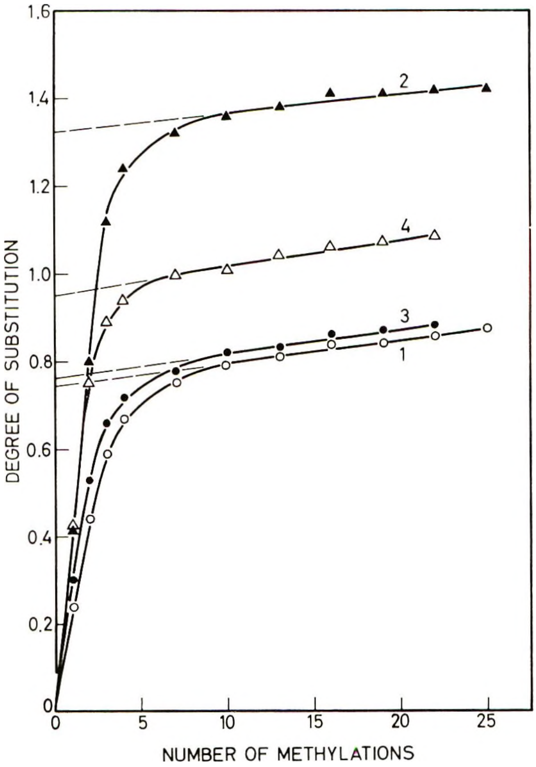

Fig. 3. Methylation of fibers soaked in 2*N* sodium hydroxide with dimethyl sulfate in toluene; (*1*) cotton; (*2*) mercerized cotton; (*3*) cotton swollen with 62% sulfuric acid; (*4*) cotton swollen with 81% phosphoric acid.

units whose calculated figures agree best with the observed values for the various fibers are listed in Table II.

Results for the methylation of cotton, SC, PC, and MC with dimethyl sulfate and 2*N* sodium hydroxide are given in Figure 3, which is generally similar to Figure 1 for diazomethane. The accessibility to either reagent is increased by swelling in the order 62% sulfuric acid <81% phosphoric acid <5*N* sodium hydroxide. The intercept figures on the DS axis (Table III) indicate further that each fiber is more accessible to dimethyl sulfate/2*N* sodium hydroxide than to diazomethane, but the increase in DS is markedly smaller with SC than with the other fibers.

The closeness of curves *1* and *3* (Fig. 3) for cotton and SC suggests that the combined interfibrillar swelling effects[13] of 62% sulfuric acid and 2*N*

TABLE III

	Cotton	SC	PC	MC
DS intercept (diazomethane)	0.50	0.67	0.78	1.01
DS intercept (dimethyl sulfate)	0.75	0.76	0.95	1.33

TABLE IV

Analysis of Hydrolyzate from Fibers Methylated with Dimethyl Sulfate

Fiber	Number of methylations	Overall DS (Zeisel)	Composition of hydrolyzate, mole-%							
			G	G_2	G_3	G_6	G_{25}	G_{26}	G_{36}	G_{236}
Cotton	10	0.79	56.8	6.4	0.0	6.6	2.3	7.9	0.9	17.0
	13	0.81	56.1	6.9	1.4	8.5	3.3	8.8	0.5	17.6
	16	0.84	54.9	7.1	0.3	9.3	2.0	9.5	0.9	18.1
	19	0.84	55.1	6.0	1.1	9.7	2.7	7.2	1.2	21.9
	22	0.86	53.8	7.5	1.6	10.0	1.8	9.7	0.8	21.4
Mercerized cotton	10	1.36	30.2	10.3	1.6	5.9	7.0	13.3	1.2	34.1
	13	1.38	29.5	10.4	3.8	9.3	1.8	14.2	1.7	32.8
	16	1.41	28.5	11.4	0.8	7.1	3.9	14.0	2.5	34.5
	19	1.41	28.1	11.3	(9.8)	7.9	9.4	10.9	2.4	35.9
	22	1.42	31.0	11.2	0.6	7.4	6.8	13.3	2.9	30.7
	25	1.42	29.8	11.0	1.0	8.9	4.1	13.1	0.8	35.9
Cotton swollen in sulfuric acid	10	0.81	60.0	8.2	1.7	9.7	1.8	8.5	0.6	16.4
	13	0.83	56.9	6.4	0.7	9.9	2.5	6.5	0.8	18.5
	16	0.86	55.7	7.4	2.5	8.9	3.8	6.4	0.6	21.6
	19	0.87	56.2	9.6	0.1	8.4	1.1	6.8	0.7	20.6
	22	0.88	57.1	5.0	1.2	7.4	2.7	6.7	1.3	20.6
Cotton swollen in phosphoric acid	10	1.01	50.9	5.5	1.1	6.4	2.7	9.1	0.9	25.2
	13	1.04	49.3	5.8	2.2	6.7	5.0	9.4	1.0	26.0
	16	1.06	49.0	5.4	2.3	6.5	2.7	8.3	0.8	28.3
	19	1.07	49.2	5.2	0.9	7.0	3.7	8.4	1.6	25.8

sodium hydroxide are but little greater than that of 2*N* sodium hydroxide alone, but the rather lower DS attained by SC methylated with diazomethane indicates that the swelling effect of the acid is not as great as that of the 2*N* alkali. Methylation of PC with diazomethane also gives a DS similar to those obtained when cotton and SC are methylated with dimethyl sulfate, but methylation of PC with dimethyl sulfate/2*N* sodium hydroxide leads to a further considerable increase in DS to 0.95, a figure approaching that for MC (diazomethane). This effect might be connected with the occurrence of some degree of intrafibrillar swelling in the preparation of the fiber or under the influence of the 2*N* alkali. While it is known that 2*N* sodium hydroxide gives only interfibrillar swelling with cotton,[13] its effect upon highly preswollen fibers may be more extensive especially in the presence of dimethyl sulfate; its effect upon the DS attained with MC may be significant here.

Hydrolyzates from several of the methylated products have been analyzed, and the results (given in Table IV) interpreted as described before. The DS values derived from the individual molar percentages of methylated glucoses did not agree as well as usual with the Zeisel figures and were uniformly about 20% higher. This discrepancy was associated with the occurrence of an abnormal disparity in the amounts of α- and β-G_{236}, up to about 50% more of the α-anomer being obtained. If the results were recalculated taking 2β instead of $(\alpha + \beta)$, the differences would largely disappear. It is therefore possible that the G_{236} figures are about 25% too high.

Table V summarizes the findings and includes calculated figures for the best-fitting cross sections for each material in terms of the model.[1,2] The GLC values, generally, are not inconsistent with the above view that methylation of cotton and SC with dimethyl sulfate and dilute alkali gives very similar products, and that those obtained by methylating SC and PC with diazomethane are also rather similar to them. The results as a whole can be interpreted in terms of the crystalline fibril theory of cellulose structure and the related concepts of inter- and intrafibrillar swelling.[13] The extremely slow rate of methylation of cotton by diazomethane under dry conditions suggests a high degree of aggregation of the elementary fibrils in dried cotton,[5] but when water is present, a considerable degree of disaggregation and methylation occurs. With reagents such as 62% sulfuric acid and 2*N* sodium hydroxide, which promote interfibrillar swelling, the aggregates will be progressively broken up into bundles of smaller average cross section. The effect seems to be increased when these acid and alkaline treatments are used successively. In concentrated alkali rapid and complete interfibrillar swelling (which should give the smallest units) will be followed by intrafibrillar swelling. The model so far used to explain the results may not apply, and it is perhaps significant that hydrolyzates from PC and MC methylated with dimethyl sulfate/2*N* sodium hydroxide con-

TABLE V
Sugars in Hydrolyzate Derived from Figure 3 and Table IV for Fibers Fully Methylated According to the First Stage of Methylation with Dimethyl Sulfate/2*N* Sodium Hydroxide

	Sugar content, mole-%							
	Cotton		Sulfuric acid-swollen cotton		Phosphoric acid swollen cotton		Mercerized cotton	
Sugar	Found	Calcd for 8 × 9 a.g.u.	Found	Calcd for 11 × 8 a.g.u.	Found	Calcd for 10 × 6 a.g.u.	Found	Calcd for 4 × 5 a.g.u.
G	59	58	61	61	52	53	29	30
G_2	7	10	7	7	5	7	11	15
G_3	1	0	1	0	1	0	2	0
G_6	9	10	9	7	6	7	8	15
G_{23}	2	0	2	0	3	0	6	0
G_{26}	9	11	7	12.5	9	17	13	20
G_{36}	1	0	1	0	2	0	2	0
G_{236}	12	11	14	12.5	24	17	33	20
DS (Zeisel)	0.75	0.75	0.76	0.76	0.95	0.97	1.33	1.30

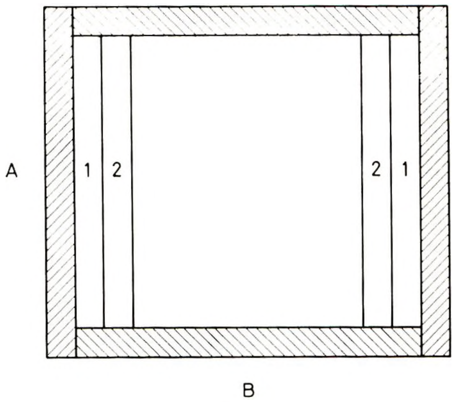

Fig. 4. Cross section of elementary fibril showing additional layers (1 and 2) penetrated by swelling agents. Side *A* (8 a.g.u.) gives G_{26} and G_{236}; side *B* (10 a.g.u.) gives G_2 and G_6 (from 8 a.g.u.).

tain much higher molar percentages of 2,3,6-tri-*O*-methyl-D-glucose than of 2,6-di-*O*-methyl-D-glucose and that there is a significant rise in the amount of 2,3-di-*O*-methyl-D-glucose in the latter case. On the other hand, no such discrepancy arises with diazomethane methylation. If mercerization resulted in breaking of the C-3(OH) – C-5′(O) hydrogen bonds, increases in the amounts of 2,3-di-*O*-methyl-D-glucose and trimethyl glucose would occur.

The aggregates observed in cotton methylated with moist diazomethane contain about 170 a.g.u. in the cross section, and are therefore about twice as thick as the units of elementary fibrillar size observed by Roberts et al.[5] and by ourselves in cotton methylated with dimethyl sulfate. The units observed with PC methylated with diazomethane and with SC methylated with dimethyl sulfate are also of this smaller thickness, but those found in MC methylated with diazomethane or with dimethyl sulfate are only about one half and one quarter, respectively, of this size.

The general conclusion, therefore, is that aggregates of approximately two elementary fibrils, found in cotton methylated with diazomethane, are split into elementary fibrils by 81% phosphoric acid, or by 2*N* sodium hydroxide, but that the process is incomplete in 62% sulfuric acid. Mercerization transforms the elementary fibrils of Cellulose I into smaller units of cellulose II; this is in agreement with x-ray evidence[14] which indicates that the elementary fibrils in MC have only about half the cross-sectional area of those in cotton.

It might appear that the best fitting unit sizes reported in Tables II and V for the various fibers do not lend themselves to a unified interpretation of the results, e.g., a 12 × 14 unit could not be simply subdivided to give one of 8 × 9 or 11 × 8 a.g.u. On the other hand, if either of the smaller units were doubled to give 8 × 18 or 11 × 16 units, the calculated figures for DS and hydrolyzate content would not differ very greatly from the observed values. The results are reconcilable if the various sizes are regarded as very approximate averages.

An alternative explanation[15] is that the elementary fibrils are not further subdivided but suffer progressive penetration of the outer layers by swelling agents. This would increase the amount of accessible material capable of taking part in the initial fast reaction. If it is assumed that swelling agents penetrate only through side *A* (Fig. 4) in a direction parallel with side *B* (the 101 crystallographic plane)[3] and that the C—3(OH)—C—5′(O) hydrogen bonds remain intact; it can be shown that, with increasing penetration, the composition of the corresponding hydrolyzates should change progressively from figures similar to those for cotton with diazomethane in the direction of those for MC with dimethyl sulfate. The figures given in Table VI illustrate this point.

TABLE VI
Sugars Calculated on the Basis of Methylation of Successive A layers in a Unit of 8 × 10 a.g.u. (Fig. 4)

	Composition, mole-%, for 0, 1, and 2 layers methylated (in addition to outside layers A and B)		
	0	1	2
G	60	45	30
G_2	10	10	10
G_6	10	10	10
G_{26}	10	17.5	25
G_{236}	10	17.5	25
DS	0.70	1.08	1.45

It can be seen that the calculated figures for one extra layer methylated resemble those for MC methylated with diazomethane (Table II) and the figures for two extra layers also bear some resemblance to those for MC methylated with dimethyl sulfate (Table V), though the agreement is poor.

The available evidence does not permit a definite choice between the alternative explanations put forward, but on the whole, the second seems more satisfactory.

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Phase Diagram and X-Ray Diffraction Analysis of the Acrylic Acid–Acrylamide System

C. F. PARRISH, *Chemistry Department, Indiana State University, Terre Haute, Indiana 47809* and G. L. KOCHANNY JR. and H. W. RINN, *Dow Chemical Company, Midland, Michigan 48640*

Synopsis

The phase diagram of the acrylic acid–acrylamide system as determined by DTA and the supporting x-ray diffraction data are presented. This diagram shows that the system forms a 1:1 addition compound which decomposes above 0°C. There is also one eutectic point at a 67 mole-% acrylic acid composition.

INTRODUCTION

The phase diagram of the acrylic acid–acrylamide system along with the copolymerization of this system in the solid phase has recently been reported.[1] Copolymers formed from this system are of considerable interest both from their potential commercial applications and as a fundamental system in solid-state copolymerizations. In our efforts to obtain a soluble copolymer of this system, we undertook an investigation of the copolymerization in the solid phase at various compositions. To select effectively the areas of interest, a phase diagram was constructed for the system, and great care was taken to assure the purity of the monomers. Our resulting phase diagram was noticeably different from the one which has been recently reported for this system.[1] Therefore, it was decided to look at the x-ray diffraction pattern of the various compositions in order to determine if an addition compound exists and, if so, what its composition is. Results of DTA and the x-ray diffraction data are given.

EXPERIMENTAL

Monomers

The acrylic acid was distilled under reduced pressure in a dry nitrogen atmosphere to exclude the presence of water vapor. After distillation the samples were never exposed to atmospheric moisture. The acrylamide was sublimed several times and after sublimation and before use the monomer was stored in a dry box.

Differential Thermal Analysis

A phase diagram was constructed with the aid of a DuPont model 900 DTA instrument equipped with a remote cell attachment. This remote cell attachment made it possible to prepare all samples in the dry box to assure the exclusion of atmospheric moisture.

X-Ray Diffraction

A Norelco diffractometer with Ni-filtered Cu radiation and a scanning rate of $2\theta = 2°$/min was used. The samples were maintained at approximately −50°C with the aid of a modified sample holder.[2] The compositions used for x-ray analysis were mixed at room temperature and allowed to slowly crystallize, thus producing small, needlelike crystals which were powdered before use.

RESULTS AND DISCUSSION

The phase diagram obtained by DTA is shown in Figure 1. Here a 1:1 addition compound which has an incongruent melting point at 0°C can be seen. There is one eutectic which is formed between the 1:1 addition compound and acrylic acid at 67 mole-% acrylic acid which has a melting point of −8°C. Although there is some scatter in the data, there is little doubt as to the structure of the phase diagram. Several compositions are worth noting. Pure acrylic acid and pure acrylamide show no endotherm at 0°C, which indicates the absence of trace amounts of water in the starting materials. This then means that the endotherm at 0°C corresponds to a change which results from the mixing of acrylic acid and acrylamide and not from

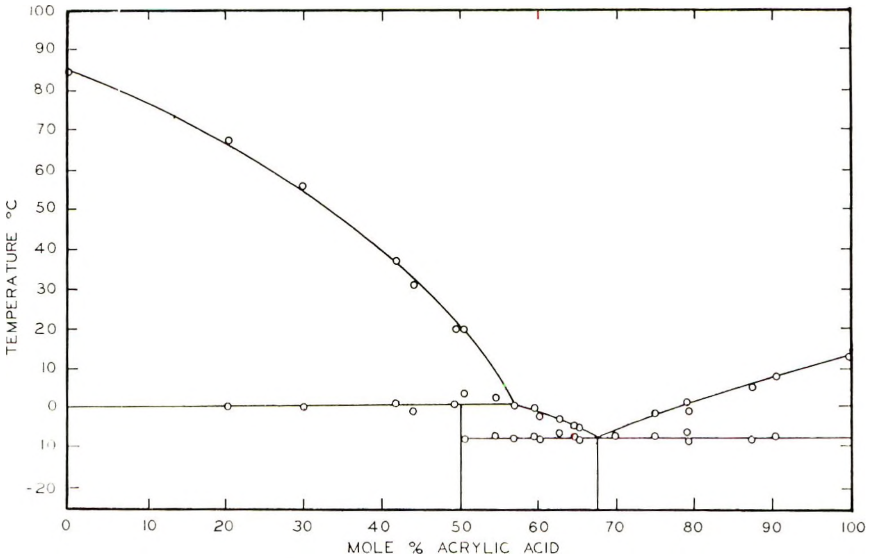

Fig. 1. Phase diagram of the acrylic acid–acrylamide system.

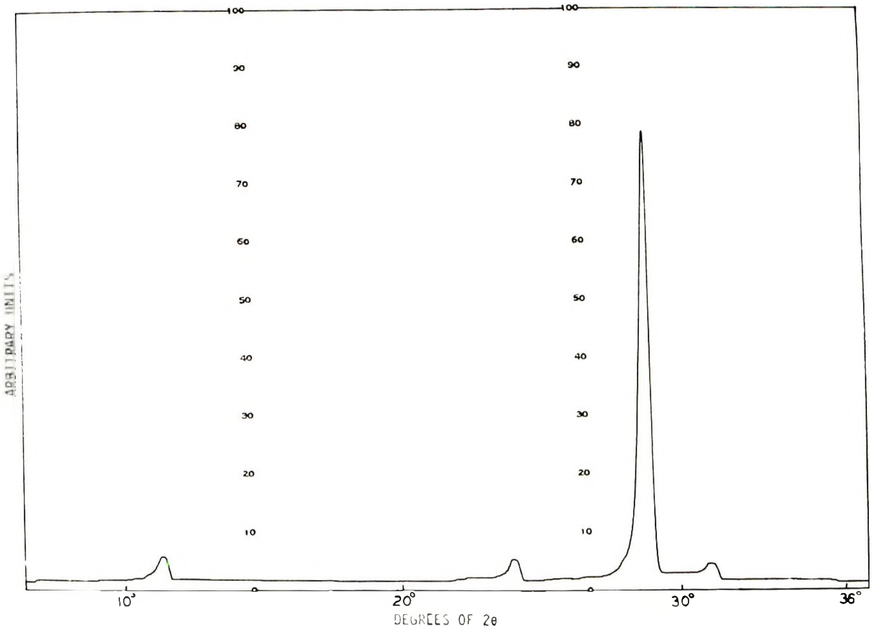

Fig. 2. X-Ray diffraction pattern of pure acrylic acid.

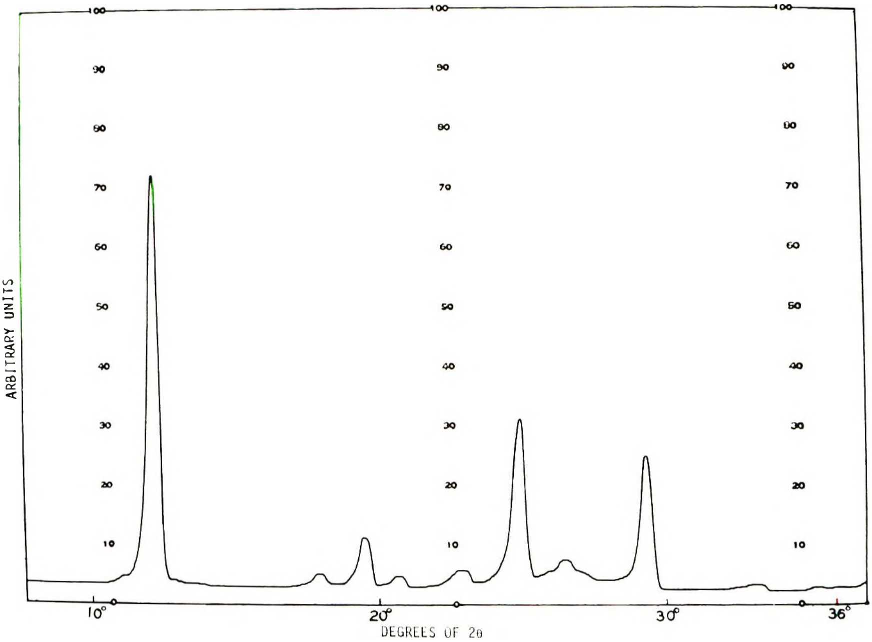

Fig. 3. X-Ray diffraction pattern of pure acrylamide.

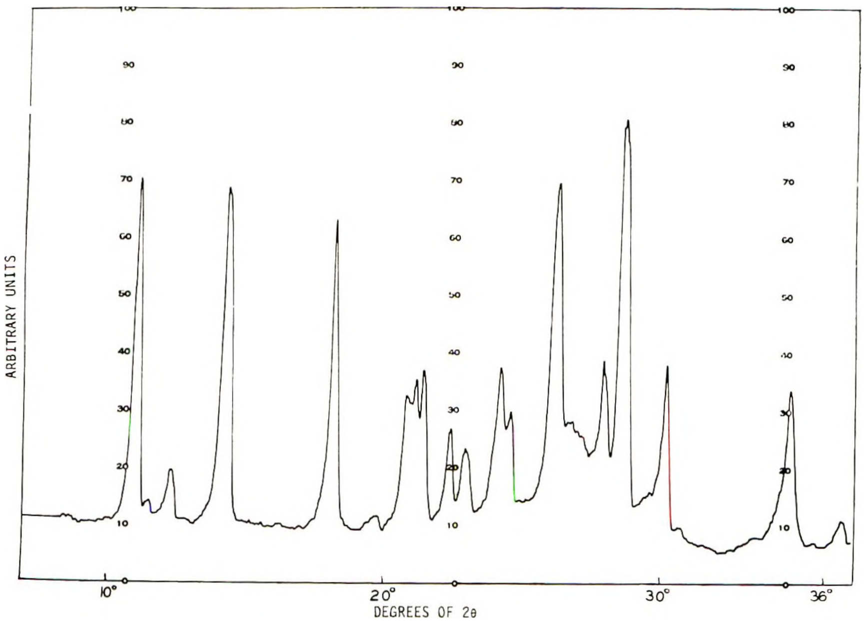

Fig. 4. X-Ray diffraction pattern of the 1:1 acrylic acid–acrylamide addition compound.

condensed water. The transitions to either side of the 50 mole-% composition show on one side the melting of the acrylamide and the peritectic reaction at 0°C, while on the other side the melting of acrylamide, the peritectic reaction, and the melting of the eutectic are shown.

The x-ray diffraction patterns for the pure acrylic acid and acrylamide are shown in Figures 2 and 3. Due to the magnitude of the reflection at $d = 3.1$ Å for the acrylic acid, the gain had to be lower to keep this peak on scale; therefore, most of the fine structure was lost. The existence of a 1:1 addition compound is supported by the x-ray diffraction data shown in Table I and by comparison of Figures 2, 3, and 4. Table I lists the predominate *d* spacing and the relative intensities for the pure acrylic acid and acrylamide and a 1:1 mole mixture of the two. A comparison of the diffraction patterns of Figures 2, 3, and 4 indicates that the 1:1 acrylic acid–

TABLE I

Predominate *d* Spacings for Acrylic Acid, Acrylamide, and the 1:1 Mixture of Acrylic Acid and Acrylamide

Acrylamide			1:1 mixture			Acrylic acid		
2θ	*d*, Å	I/I_0	2θ	*d*, Å	I/I_0	2θ	*d*, Å	I/I_0
12.3°	7.2	100	11.1°	8.0	81	11.4°	7.7	6.3
19.5°	4.55	12	14.3°	6.2	78	24.1°	3.7	6.3
24.9°	3.6	40	18.2°	4.9	72	28.8°	3.1	100
29.3°	3.05	32	26.3°	3.4	84	31.3°	2.86	4.4
			28.8°	3.1	100			

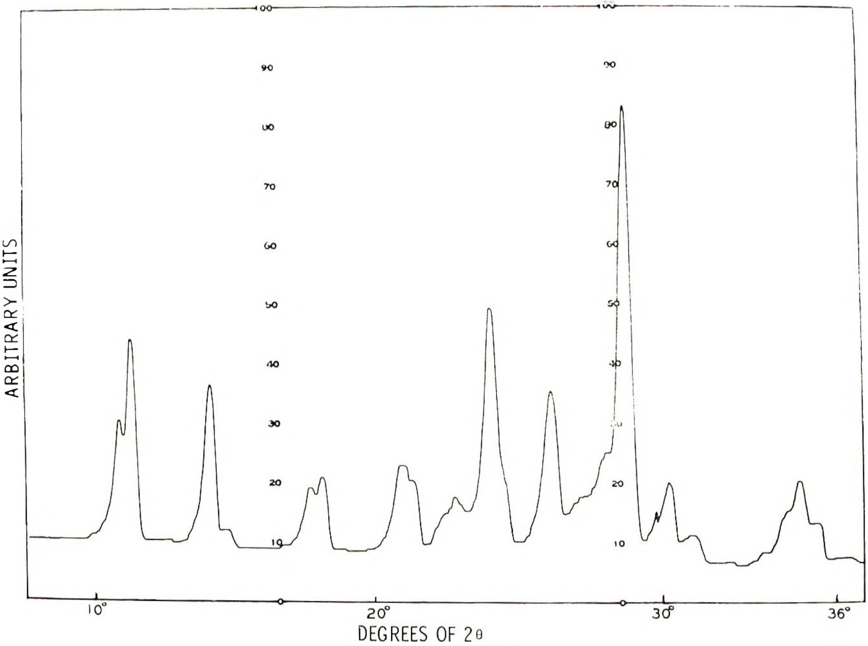

Fig. 5. X-Ray diffraction pattern of the 33–67% acrylamide–acrylic acid eutectic mixture.

acrylamide mixture is predominately a single phase. The small reflection at 2θ = 12.3° appears to be due to acrylamide. Since this is a strong reflection in the acrylamide pattern this would indicate that the quantity of acrylamide as a separate phase is quite small. Therefore, the pattern represented by Figure 4 shows predominately a single phase of the 1:1 addition compound.

The 33–67 mole-% acrylamide–acrylic acid sample shows a mixture of the 1:1 phase and acrylic acid. The reflections at 2θ = 11.5°, 17.7°, 24.1°, 31.2°, and 34.2° are due to the acrylic acid with the strongest reflection of acrylic acid at 2θ = 28.8° superimposed on the strongest reflection of the 1:1 phase (See Figs. 2 and 5).

When the x-ray data are combined with the DTA phase diagram data, there appears to be little doubt that the correct phase diagram for this system is the one shown in Figure 1. This would then say that there is a 1:1 addition compound formed in the acrylic acid–acrylamide system which decomposes at 0°C and also there is only one eutectic point at a 67–33 mole-% acrylic acid–acrylamide composition.

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Anionic Graft Polymerization of Lithiated Poly(2,6-dimethyl-1,4-phenylene Ether)

A. J. CHALK and T. J. HOOGEBOOM, *General Electric Research and Development Center, Schenectady, New York 12301*

Synopsis

Lithiated poly(2,6-dimethyl-1,4-phenylene ether) has been used as an initiator for the graft polymerization of isoprene, methyl methacrylate, hexamethylcyclotrisiloxane, and phenyl isocyanate with the use of toluene and tetrahydrofuran as solvents. The products were examined by gel-permeation chromatography for evidence of homopolymerization and graft polymerization. The composition of the graft copolymers was determined by NMR, and for isoprene and hexamethylcyclotrisiloxane, termination by trialkylchlorosilanes enabled chain lengths to be determined by NMR. The use of toluene gave rise to some homopolymerization, but with tetrahydrofuran, only hexamethylcyclotrisiloxane gave homopolymer. In all cases, graft copolymers were formed. With isoprene and methyl methacrylate, soluble graft copolymers were formed in good yield. In the former case approximately 60% 3,4 and 40% 1,4 addition was found. In the latter case 1,1-diphenylethylene was used to reduce crosslinking, in its absence, methyl methacrylate gave only crosslinked gels in tetrahydrofuran. Hexamethylcyclotrisiloxane added only one molecule per lithium on the polymer, the remainder giving homopolymer. Phenyl isocyanate gave some soluble graft copolymer in toluene, but only crosslinked products were obtained when tetrahydrofuran was used as reaction solvent.

INTRODUCTION

Earlier papers describe the direct metalation of poly(2,6-dimethyl-1,4-phenylene ether) (I) with alkali metals and its use for the synthesis of graft copolymers.[1-3] This paper in the series reports the results obtained in further investigating the graft polymerization of isoprene, methyl methacrylate, hexamethylcyclotrisiloxane, and phenyl isocyanate onto lithiated poly(2,6-dimethyl-1,4-phenylene ether).

Conditions under which the present work was carried out were determined to a considerable extent by the work on styrene polymerization.[3] Thus it was shown earlier that when the ratio of lithiated sites to polymer units (1 polymer unit = 1 polymer oxygen) exceeds ~0.2, all lithiated sites did not react with styrene. For this reason the amount of added butyllithium was generally varied in the range [BuLi]/[I] = 0–0.2 or kept constant at 0.2 or 0.1.

In some cases reaction of the "living" graft polymers with a trialkylchlorosilane was used to indicate their average chain length. Both toluene and tetrahydrofuran were used as solvents, the latter having been shown to obviate the formation of homopolymer.

A wide variety of monomers may be polymerized anionically.[4] In addition to the more familiar examples, hexamethylcyclotrisiloxane[5] and phenyl isocyanate were chosen. The latter polymerizes to a 1-nylon soluble only in concentrated sulfuric acid in which it degrades.[6] By initiating polymerization with lithiated poly(2,6-dimethyl-1,4-phenylene ether), however, it was hoped that soluble grafts would be obtained.

EXPERIMENTAL

Materials

Methyl methacrylate was stirred over calcium hydride for 48 hr and distilled on a vacuum transfer line prior to use.

Phenyl isocyanate was distilled under vacuum prior to use.

Isoprene was dried over calcium hydride for 1 hr and distilled under vacuum into a flask coated internally with a sodium mirror. After 30 min it was distilled into a further similarly coated flask before a final distillation 30 min later.

Hexamethylcyclotrisiloxane, obtained from G.E. Silicone Products Department, was distilled at an atmospheric pressure of nitrogen from calcium hydride and sublimed in vacuum prior to use.

1,1-Diphenylethylene was obtained from Eastman and used without purification.

Graft Polymerizations

Lithiation of 2% solutions of I in toluene (in the presence of tetramethylethylenediamine) or in tetrahydrofuran was carried out as previously described.[2] The solutions were allowed to stand for approximately 1 hr at room temperature prior to the addition of monomer. Monomer addition was made with stirring at a temperature which would result in a conveniently fast rate of polymerization. The samples were then left until such time as observation of viscosity, etc. indicated the reaction was complete, whereupon the reaction was terminated with an appropriate reagent. Polymer was recovered by precipitation into methanol after filtration from any insoluble materials such as crosslinked gel and lithium salts.

Products were examined by NMR, gel-permeation chromatography, osmometry, and differential scanning calorimetry.[2,3]

RESULTS AND DISCUSSION

Isoprene Grafts

In tetrahydrofuran, addition of monomer at 25°C resulted in a rapid deepening of color from yellow to dark orange-yellow. Viscosity increases were noticeable after 15 min with sample 2. Similar effects were noticed

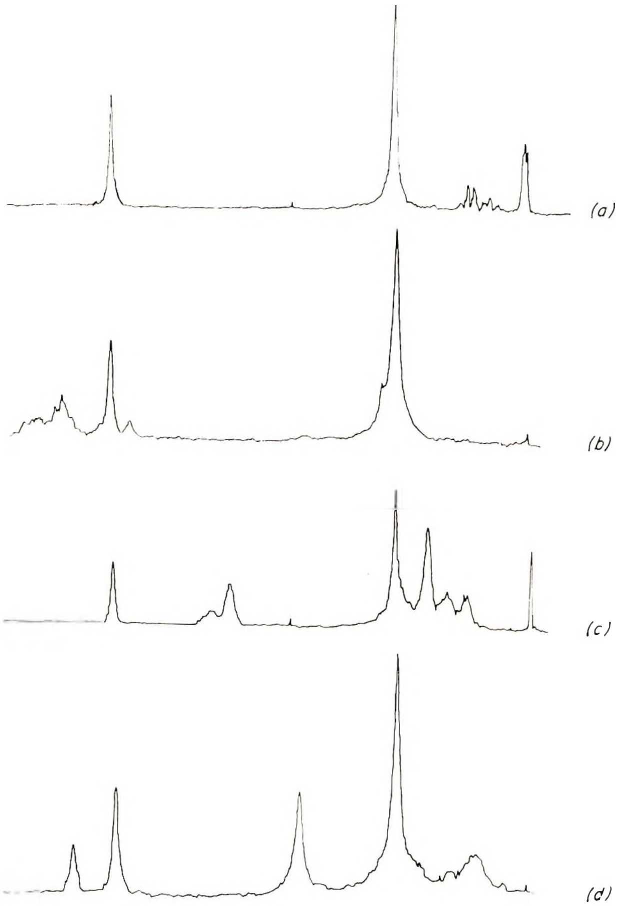

Fig. 1. NMR spectra of graft copolymers.

when benzene was used as solvent, but the changes were somewhat slower. Samples were allowed to stand overnight at room temperature before termination with trimethylchlorosilane, which rapidly decolorized them to give somewhat viscous, clear, water-white solutions. Precipitation with methanol tended to give gummy rubbery materials. No crosslinked material was evident.

The NMR spectrum of sample 1 is shown in Figure 1*c*. The ratio of the two polymers was calculated from the area of the 3.5τ absorption due to the aromatic protons on I and the remaining absorptions due to vinyl and aliphatic protons on I and polyisoprene (II). Absorptions in the vinyl region occurred at 4.95τ, indicating 1,4 addition and 5.3τ indicating 3,4 addition.[6] The ratio of the two areas indicated approximately 60% 3,4 and 40% 1,4 addition for all samples. No vinyl absorption at 4.7τ corresponding to 1,2 addition[7] was found. The low extent of 1,2 addition was also indicated by the lack of any significant absorption at 9τ $(\mathrm{CH_3{-}C{-}C})$ compared to the strong absorption at 8.4τ $(\mathrm{CH_3{-}C{=}C})$. Infrared spectra

TABLE I
Poly(2,6-Dimethyl-1,4-phenylene Ether) (I)–Polyisoprene (II) Graft Copolymers

Sample	Solvent	II/I[a]		Li, (Found) %[c]	Chain length[d]	Molecular wt[e]		[η][f]
		Added	Found[b]			Homo-polymer	Graft	
1	Tetrahydrofuran	2.0	2.7	77	17.5	None	100000	0.47
2	"	10.0	12			None	140000	0.73
3	Benzene	2.0	2.1	80	13	4000	100000	0.51[g]
4	"	10.00	12			14000	140000	0.44[g]

[a] Equivalent of II (68 g) per equivalent of I (120 g).

[b] By NMR.

[c] % of added Li found by NMR on $ClSiMe_3$-terminated polymer. Added ratio Li/I = 0.2 for this series.

[d] Chain length of grafted isoprene (from NMR).

[e] Molecular weight corresponding to maximum in gel permeation chromatograph. These compare to a value of 40000 found for initial I. The significance of these values is discussed elsewhere.[3]

[f] Intrinsic viscosity in chloroform at 25°C ([η] for initial I = 0.52).

[g] Polyisoprene homopolymer.

were also consistent with partial 3,4 and partial 1,4 addition (vinyl C—H stretch, 3070 cm^{-1}; C=C stretch 1645 cm^{-1}; vinyl C—H deformation, 885 cm^{-1}). NMR adsorptions due to $Si(CH_3)_3$ were only significant for samples 1 and 3 and occurred at approximately 10.04τ as expected for silicon at the end of a polyisoprene chain. No adsorption was found at 9.53τ corresponding to $Si(CH_3)_3$ on the ring position of I. It therefore seems reasonable to assume that all the silicon is in fact terminating polyisoprene chains, and this assumption was used in calculating chain lengths in Table I.

Gel-permeation chromatography revealed isoprene homopolymer only for the samples prepared in benzene solution (approximately 10–20% homopolymer for 3 and 30–40% homopolymer for 4). The graft polymers showed molecular weight increases of about the expected magnitude (Table I). Yields were in the range 85–100%.

Methyl Methacrylate Grafts

Initial experiments gave only crosslinked products. The polymerization of methyl methacrylate by butyllithium and other monoanions has been reported to result in branched polymers.[7,8] With a polyanion, crosslinking should result. The crosslinking has been attributed to the attack of the carbanion on the carbonyl group of poly(methyl methacrylate)[8,9] and has been reduced by reacting the initiator (e.g., butyllithium) with 1,1-diphenylethylene to produce a less reactive carbanion which favors vinyl over carbonyl addition.[8,9]

Accordingly, the lithiated I poly(phenylene ether) was reacted with a slight excess of 1,1-diphenylethylene over lithium. A deep red color was immediately formed at room temperature. Subsequently the temperature was lowered to −40°C for solutions in toluene and −90°C for solutions in tetrahydrofuran before reacting with monomer. In both cases the color was rapidly discharged and the solutions set up to a thick gel which was

TABLE II
Poly(2,6-Dimethyl-1,4-phenylene Ether) (I)–Poly(methyl Methacrylate) (III) (Graft Copolymers)

Sample	Solvent	Diphenylethylene/I (found)[a]	III/I (found)[b]	Molecular wt[c]
5	Toluene	0	0.67	90 000
6	"	<0.01	0.62	90 000
7	"	<0.01	0.67	80 000
8	Tetrahydrofuran	0.08	0.9	90 000
9	"	0.10	1.1	100 000

[a] From NMR. Added ratio ≥Li/I = 0.1 mole/120 g (I). Sample 5 had no added diphenylethylene (see text).

[b] From NMR. Added ratio III/I = 1.0 (100 g III per 120 g I).

[c] Molecular weight corresponding to maxima in gel-permeation chromatograph.

then dispersed by addition of a little methanol (1 ml) to give viscous solutions. At this stage, experiments carried out in tetrahydrofuran without 1,1-diphenylethylene gave insoluble crosslinked gels. In toluene, however, the absence of 1,1-diphenylethylene had little effect. In this case (sample 5, Table II) and in all cases where 1,1-diphenylethylene was used, (samples 6–9, Table II), graft polymers soluble in chloroform and benzene were recovered.

Yields were in the range 75–85% for samples prepared in toluene and 95–98% for those prepared in tetrahydrofuran. This suggests the formation of poly(methyl methacrylate) homopolymer in the former case and its loss following precipitation into methanol.

The NMR spectrum of sample 8 is shown in Figure 1*d*. The amount of diphenylethylene was calculated from the area of the adsorption at 2.7τ, the poly(dimethylphenylene ether) from the area at 3.5τ and the poly(methyl methacrylate) from the area at 6.6τ (OCH_3). The resulting ratios were approximately the same as the added proportions, for samples 8 and and 9. Samples 5–7, however, contained less poly(methyl methacrylate), again indicating the formation and loss of homopolymer. Gel-permeation chromatograms also showed no evidence of homopolymer, and the molecular weights of the grafts showed the expected increase over initial poly(dimethylphenylene ether). Samples 6 and 7 showed only traces of 1,1-diphenylethylene. This was attributed to insufficient reaction time (45 min at 25°C). Accordingly, in samples 8 and 9 a longer time was allowed (18 hr at 25°C).

Infrared spectra showed strong carbonyl ester bands at 1730 cm^{-1}. Intrinsic viscosities were similar to those of original poly(2,6-dimethyl-1,4-phenylene ether).

Siloxane Grafts

Addition of hexamethylcyclotrisiloxane to lithiated poly(dimethylphenylene ether) at 25°C resulted in a slow discharge of color. The solutions increased in viscosity sometimes leading to precipitation. On terminating the reaction with trialkylchlorosilane, clear colorless solutions were obtained with no evidence of crosslinking.

Precipitation of the graft copolymer was made by slow addition to excess methanol containing a little pyridine to neutralize any hydrochloric acid from hydrolysis of the excess trialkylchlorosilane used. (The presence of acid was found to result in crosslinking when the samples were later dried at 60°C. Presumably this resulted from acid cleavage of siloxane bonds followed by random condensation on heating.)

Hexamethylcyclotrisiloxane was the only monomer to form homopolymer when tetrahydrofuran was used as solvent. Unlike the other polymers, polydimethylsiloxane has a lower refractive index than the solvent (benzene) used for molecular weight determinations by gel-permeation chromatography. Thus homopolymer was revealed by a negative peak at lower molecular weights than expected for the graft.

TABLE III
Poly(2,6-Dimethyl-1,4-Phenylene Ether) (I)–Polydimethylsiloxane (IV) Graft Copolymers[a]

Sample	I/Li[b]	IV/Li[c]		Yield[d]	
		Added	Found[d]	Li, %	IV, %
10	5	0.5	0.6	75	89
11	10	1.0	0.9	80	74
12	20	2.0	0.9	83	38
13	50	5.0	1.7	88	29
14	100	10.0	—	—	44

[a] Lithiated I reacted with hexamethylcyclotrisiloxane for 18 hr before terminating with triethylchlorosilane.

[b] Added ratio in equivalents of (I) (one equivalent = 120 g) per mole of butyllithium.

[c] Equivalents of (IV) (one equivalent = 222 g) per mole of lithium. (i.e., added ratio of I/IV = 10 throughout).

[d] From NMR measurements (see text).

Figure 1*a* shows the NMR spectrum of a graft copolymer terminated by triethychlorosilane (sample 11, Table III). In addition to absorptions typical of the poly(dimethylphenylene ether),[2] methyl protons typical of polydimethylsiloxane show up as a broad peak at 9.92–10.02τ while the triethylsilyl group showed up at 9.25–9.65τ (methylene α to Si) and 8.9–9.25τ (methyl β to Si). From the former area it was possible to obtain the amount of polydimethylsiloxane in the graft and from the latter it was possible to calculate the amount of lithium effective in initiating graft polymerization (fifth column, Table III). The experimental error for both the fourth and fifth columns increases as the amount of lithium on the polymer decreases. For the last two samples, the absorptions due to $Si(C_2H_5)_3$ were very small and were measured by a computer average of transients. Similar experiments in which trimethylchlorosilane was used to terminate the polymerization established that all the lithium on I reacted with monomer (absence of absorptions at 9.53 and 10.05τ[2]). From Table III it can be seen that the yield of polydimethylsiloxane (IV) in the graft copolymer was good only for the first two samples where IV/Li $\leqslant$ 1.0. For the remaining samples, siloxane homopolymer was formed and remained in solution when the graft copolymer was precipitated into methanol. Homopolymer was presumably initiated by a lithium alkoxide formed by metalation of tetrahydrofuran. Since little homopolymer is formed when IV/Li $\leqslant$ 1, it seems that hexamethylcyclotrisiloxane reacts with lithiated I in preference, but that subsequently there is a competition for monomer between lithium alkoxide and the silanolate anions of the graft copolymer. At the higher IV/Li ratios the polydimethylsiloxane homopolymer may be high enough in molecular weight to coprecipitate with the graft. This was found to be the case only for sample 14. Extraction with hexane gave a small amount of polymer which was found by gel-permeation chromatography to be a mixture of siloxane homopolymer and siloxane-rich graft.

Molecular weights of the graft copolymers were not significantly different from that of starting I. Thus gel-permeation maxima were around 50000 compared to a value of 40000 for I. Intrinsic viscosities were also in the same range as for I (0.48–0.54).

The effect of the siloxane graft on the T_g of (I) was very marked, thus a sample identical to sample 11 in Table III but having $-\mathrm{Si(CH_3)_3}$ end-groups was found to have a T_g of 160°C compared to a value of 220°C for I. By pressing the graft copolymer at 200°C and 200 psi for 1 min, optically clear films were obtained. These were readily soluble in benzene unless pressed in the presence of a little acid or base (e.g., 1% lauric acid or a trace of pyridine). In this case crosslinked films were obtained, presumably due to random Si-O cleavage and condensation reactions.

Phenyl Isocyanate Grafts

Phenyl isocyanate was added to the lithiated poly(dimethylphenylene ether) at −40°C. The yellow color rapidly faded and the solution became more viscous. After 1 hr further at 10°C (toluene) or at −40°C (tetrahydrofuran), the reactions were terminated with methyl iodide. A precipitate resulted in the toluene samples which was found to be soluble in chloroform. Gel, insoluble in chloroform, was found only when tetrahydrofuran was used as solvent. Recovered graft polymer was soluble in chloroform, but was only very sparingly soluble in benzene.

Figure 1*b* shows the NMR spectrum of one of the resulting polymers (sample 19, Table IV). In addition to the usual phenyl absorption for unsubstituted I at 3.5τ and monosubstituted I at 3.8τ, there was an absorption from 2.2–3.0τ due to the phenyl isocyanate. This allowed the determination of the ratio of the components (Table IV). Extraction of samples with benzene gave only materials with identical infrared and NMR spectra so that they can be presumed to be free of homopolymer.

From Table IV it can be seen that the amount of phenyl isocyanate graft on I is not greatly different from the amount of butyllithium used.

TABLE IV

Poly(2,6-Dimethyl-1,4-Phenylene Ether) (I)–Poly(phenyl Isocyanate) (V) Graft Copolymers[a]

Sample	Li/I[b]	V/I (found)[c]
15	0.05	0.06
16	0.10	0.19
17	0.20	0.11
18	0.50	0.38
19	1.00	0.37

[a] All samples were run in toluene as solvent at a constant ratio of 1 mole phenylisocyanate per 120 g I.

[b] Moles butyllithium per 120 g I.

[c] Equivalents of V (one equivalent = 119 g) per 120 g I from NMR.

Since approximately 40–70% of the butyllithium is known to lithiate I,[2] the average chain length for the 1-nylon grafts must be only 2 or 3 units. Yields were accordingly depressed by loss of homopolymer (phenyl isocyanate) as they were for the siloxane grafts. Recovery of I was good, however, in both these cases. The infrared spectrum of sample 19 showed a strong band at 1675 cm^{-1}, typical of amides, as expected for a 1-nylon graft. It also showed distinctly less solubility in benzene than I and greater craze resistance to hexane. Intrinsic viscosities were not significantly different (0.49–0.65) from that of starting poly(2,6-dimethyl-1,4-phenylene ether) (0.52).

The authors wish to thank Drs. A. S. Hay and E. E. Bostick for their helpful advice and Dr. J. B. Bush, Jr., for his help in interpreting NMR spectra.

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Block Copolymerization with Trapped Radicals

YUJI MINOURA and YAYOI OGATA, *Department of Chemistry, Osaka City University, Kitaku, Osaka, Japan*

Synopsis

Acrylonitrile-styrene, vinyl chloride-styrene and vinyl chloride-methyl methacrylate block copolymers were obtained by employing trapped radicals in polyacrylonitrile or poly(vinyl chloride) formed in a heterogeneous system by tri-*n*-butylboron in air as initiator. The trapped polymer radicals were activated on addition of dimethylformamide as solvent. Confirmation of block copolymers was carried out with solvent extractions, elementary analysis, and turbidimetry. In block copolymerization, the polyacrylonitrile trapped radical was more active than the poly(vinyl chloride) radical. Results of kinetic studies were used to consider the mechanism of polymerization.

INTRODUCTION

When polymerization of acrylonitrile (AN) or vinyl chloride (VCl) is carried out in the nonsolvents for the polymer, the polymer precipitates from the reaction system. In such heterogeneous polymerization systems, termination occurs by unimolecular termination. "Trapped radicals" in the polymers obtained by heterogeneous polymerization were first postulated by Bamford and Jenkins[1] and Thomas and Pellon.[2] Bamford[3] found by an ESR method that trapped free radicals were occluded in the precipitated polymers which were formed by the heterogeneous polymerization. G. Smets[4,5] observed that the block copolymer was obtained from polyacrylonitrile trapped radicals prepared by photopolymerization, but not from trapped radicals of polyacrylamide and poly(vinyl chloride). Concerning these phenomena, they considered that the radicals in polyacrylamide and PVC involved resonance stabilization or chain transfer and with a change into nonactive radicals.

In the previous reports in this series,[6] it was found that the degree of polymerization of AN or VCl increased with increasing polymerization time. This was considered to be due to polymerization by trapped radicals in polymer.

In this the present study block copolymerization by trapped radicals in PAN or PVC was studied. The trapped polymer radicals were activated by addition of solvents, and then block copolymer was obtained by addition of the second monomer. Kinetic studies of block copolymerization, with PAN trapped radicals were used to elucidate the mechanism of polymerization.

EXPERIMENTS

Reagents

Tri-*n*-butyl boron (Bu_3B) was prepared by the reaction of *n*-butylmagnesium bromide with boron trifluoride. Details of this reaction were described in previous papers.[6]

Monomer such as AN, styrene (St), VCl, or methyl methacrylate (MMA) and solvents such as tetrahydrofuran (THF), dimethylformamide (DMF), and benzene were purified by common methods.

Method of Polymerization

AN or VCl monomer was polymerized in a nonsolvent such as THF of methanol with the Bu_3B air system as initiator. In this case, a milky suspension was formed under conditions of low monomer and initiator concentration. From this suspension, the same amount of polymer was taken up by pipetting. The reproducibility of this pipetting-out experiment was evaluated in a series of experiments.

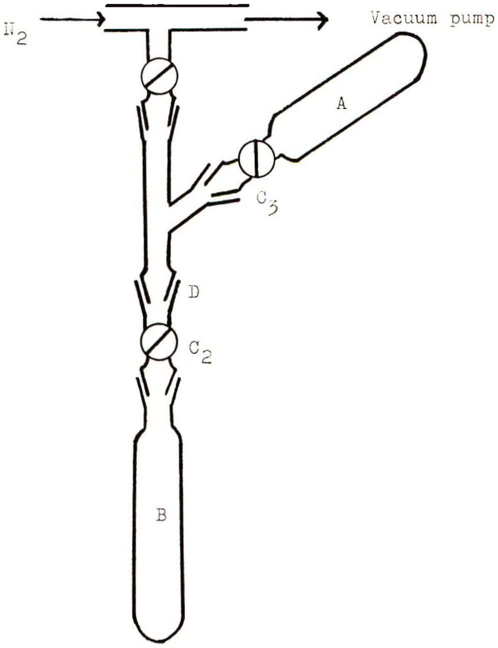

Fig. 1. Polymerization apparatus.

Example A. The heterogeneous polymerization of AN (10 ml) in THF (10 ml) was carried out in the presence of Bu_3B (0.5 ml) at 0°C for 20 hr. When 5 ml of suspension was pipetted out, weight of dried PAN polymer in four separate experiments was 0.3738, 0.3720, 0.3704, and 0.3719 g.

Example B. The heterogeneous polymerization of VCl (10 g) in methanol (100 ml) with Bu_3B (1 ml) was carried out at −78°C for 24 hr. The dried weight of PVC polymer in 10 ml suspension was 0.1883, 0.1883, and 0.1892 g in three consecutive runs.

The polymer suspension was put into an ampoule (B in Fig. 1). The solvent and the second monomer were put into ampoule A, and dissolved gas was removed by a freeze–thaw technique with liquid N_2 and was attached to the apparatus according to Figure 1. First, C_3 was closed, C_1 and C_2 were opened. The solvent, residual monomer, and catalyst in B were removed by distillation. Temperature of B was held at less than 0°C. After nearly complete drying, B was heated at about 50°C for 10 min. Then C_1 was closed, C_3 was opened and the contents of ampoule A were transferred into ampoule B. After closing C_2, ampoule B was cut off at D and block copolymerization was carried out at the defined conditions. After the predetermined time, polymer was precipitated with methanol, isolated, and dried.

Fractional Extraction

Extraction of polymer with benzene yielded two fractions: an extract and a residue. It was suggested that the residue consisted of homopolymer with trapped polymer radicals and the extract was block copolymer. This was confirmed by elementary analysis and turbidimetry. In turbidimetry, the solvent pairs used were DMF–methanol for the PAN–St pair and cyclohexanone–methanol for the PVC–MMA system.

RESULTS AND DISCUSSION

Solvent Effect in Polymerization by Trapped Radicals

The second monomer was copolymerized by the trapped radicals, and the rate of polymerization in good solvent was compared to the rate in nonsolvent. These results are shown as follows.

Example 1. In the first polymerization step, 10 ml AN, 20 ml petroleum ether, and 0.2 ml Bu_3B were used. The polymerization was carried out at 25°C for 25 min. The concentration of PAN suspension in the polymerization system was 0.282 g/10 ml. in the second polymerization step, 10

TABLE 1
Polymerization of Various Monomers by Polyacrylonitrile Trapped Radicals (Second-Step Polymerization)

Second monomer		Solvent		Wt monomer polymerized, g
Type	Vol, ml.	Type	Vol, ml	
MMA	9	DMF	8	0.489
MMA	9	Benzene	8	0.211
Vinyl acetate	9	DMF	8	0.300
Vinyl acetate	9	Benzene	8	0.179

ml PAN suspension (0.282 g PAN), 10 ml AN monomer, and 10 ml DMF were used. The second polymerization was carried out at room temperature for 18.5 hr and 0.643 g PAN was obtained. Therefore, the amount of monomer which was polymerized in the second step was 0.643–0.282 = 0.361 g.

Example 2. PAN suspension having a polymer concentration of 0.194 g/10 ml was used. Polymerizations of various monomers were carried out at 60°C for 4 hr. The results are shown in Table I. A 10-ml portion of PAN suspension (0.194 g PAN) was used for each experiment.

These results, indicate that the polymerization of the second monomer by the trapped radicals proceeded easily on addition of solvent for the polymer including trapped radicals.

Formation of Block Copolymers by Trapped Radicals in Polymer

AN–St and VCl–MMA block copolymers were obtained by two-step polymerization with the use of PAN and PVC suspensions which contained trapped radicals. The yield of crude copolymer was increased by addition of good solvent for the original polymer suspension. The formation of block copolymer was confirmed by turbidimetry, i.e., crude copolymer was dissolved in good solvent, and then, nonsolvent was added to the polymer solution and the change of turbidity during addition of nonsolvent was measured. Cyclohexanone–methanol was used as the solvent–nonsolvent pair for VCl–St and VCl–MMA systems and DMF–methanol was used for the AN–St system.

VCl–St System. VCl (10 g) was polymerized in 200 ml methanol with the use of 2 ml Bu_3B as initiator at 0°C for 20 hr. The PVC suspension

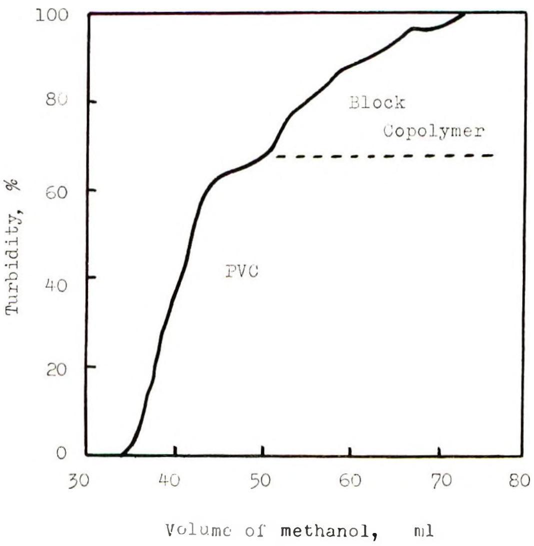

Fig. 2. Turbidimetry for poly(vinyl chloride)–styrene system; unfractionated polymer. Precipitant, methanol.

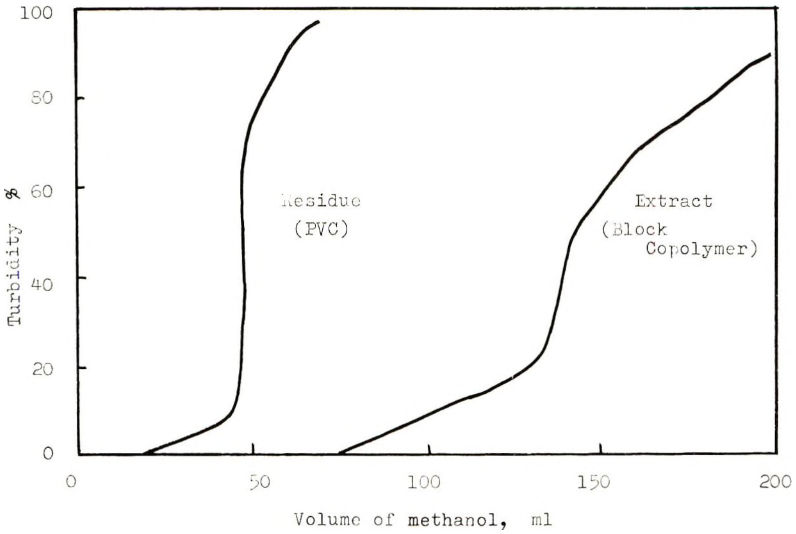

Fig. 3. Turbidimetry for poly(vinyl chloride)-methyl methacrylate system; polymers fractionated by benzene. Solvent, cyclohexanone; precipitant, methanol.

obtained contained 0.207 g of PVC in 10 ml. The second-step polymerization in which 5.7 ml St and 9.3 ml DMF were added was carried out at 80°C for 240 min. The total polymer yield was 0.341 g. The result of turbidometry is shown in Figure 2. It was found that the crude copolymer consisted of a mixture of PVC and VCl–St block copolymer.

VCl–MMA system. The first polymerization step was carried out at −78°C for 48 hr with the use of a reactant mixture which contained VCl (15 ml at −78°C), petroleum ether (15 ml at 15°C) and Bu_3B (2 ml at 15°C). After this suspension was dried by vacuum distillation, then the second polymerization step was carried out at 15°C for 30 min and then at 15°C for 20 hr. The yield of crude copolymer obtained was 13.5 g. This crude polymer was extracted with benzene. Elemental analysis and turbidimetry were carried out for each fraction. Consequently, it was suggested that the residue of benzene extraction was PVC homopolymer and the extract contained PVC–MMA block copolymer. The results of turbidometry are shown in Figure 3 and the elementary analyses are summarized in Table II.

TABLE II
Results of Benzene Extraction and Elementary Analysis on Poly(vinyl Chloride)–Methyl Methacrylate Block Copolymer

	Wt-%	C, %	H, %	MMA/VCL mole ratio
Crude polymer	100	53.80	7.19	1.55
Extract	65	57.39	7.89	4.48
Residue	35	41.36	5.41	0.04

TABLE III
Results of Benzene Extraction and Elementary Analysis of Polyacrylonitrile–styrene System

	Wt-%	N, %	C, %	H, %	St/AN mole ratio
Crude polymer	100	19.18	73.35	6.63	0.19
Extract	27	11.22	81.45	7.17	0.71
Residue	73	23.55	68.73	5.92	0.06

Elementary analysis showed that the benzene extract was block copolymer which consisted of one mole of PVC and 4.48 moles of MMA. Block copolymer can thus be synthesized by using PVC trapped radicals.

AN–St System. Block copolymer was obtained from PAN suspension by the two-step polymerization method. The first polymerization step was carried out at 0°C for 73 min with 30 ml AN and 2 ml Bu_3B in bulk. The PAN suspension was dried *in vacuo*, then 10 ml St and 8 ml DMF were added to dried PAN. The second polymerization step was carried out at 0°C for 44 hr. The yield of crude copolymer was 4.8 g. The composition of this crude copolymer was found by extraction with benzene and elementary analysis. These results are shown in Table III.

As shown in Table III, the crude polymer consisted of 27% benzene-extractable material and 73% residue polymer. The St/AN mole ratios of extract and residue polymer were 0.71 and 0.07, respectively, and it was considered that the former was a block copolymer and the latter was a free PAN. And from the relationship between turbidity and the amount of

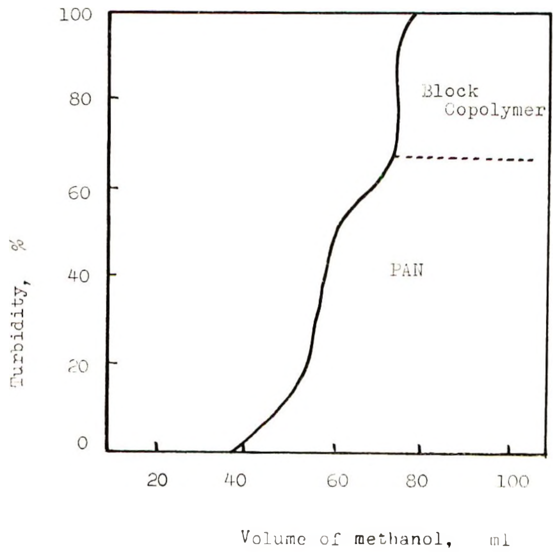

Fig. 4. Turbidimetry for polyacrylonitrile–styrene system; polymer unfractionated. Solvent, DMF; precipitant, methanol.

methanol (Fig. 4), it was obvious that the crude polymer contained 70% free PAN and 30% block copolymer. These results indicate that block copolymer could be obtained easily by using together trapped radical and good solvent.

Kinetic Considerations

In the copolymerization by trapped radicals, the effect of concentration of monomer and trapped radicals on the rate of polymerization was studied. In the PAN–St system, the first polymerization step was carried out in THF at 0°C and the second step in DMF at 80°C. In the PVC–St system, the first step was carried out in methanol at 0°C and the second step in DMF at 80°C. Figures 5 and 6 show the time–conversion curves for copolymerization of the PAN–St and PVC–St systems.

The rate of polymerization was obtained at the initial stage. It was suggested that the decrease of rate of polymerization corresponded to a decrease of the concentration of trapped radicals. The change of initial rate of the second step of copolymerization with the variation of monomer concentration was studied. In the PAN–St system, the second copolymerization step was carried out at 80°C for 3 hr on a PAN suspension having a concentration of 0.3773 g/10 ml. In the PVC–St system, the second copolymerization step was carried out at 80°C for 2 hr with the use of a PVC suspension having a concentration of 0.1883 g/10 ml. The initial

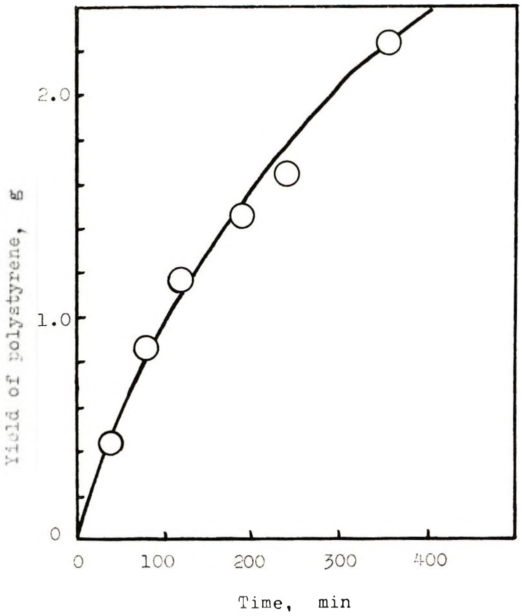

Fig. 5. Time–conversion curve of polyacrylonitrile–styrene system. First polymerization: AN, 35 ml; THF, 75 ml; $B(Bu)_3$, 1 ml; 0°C; 22 hr.; concn. of polymer suspension: 0.4264 g PAN/10 ml. Second polymerization: PAN, 0.4264 g; St, 9.5 ml. DMF, 9.5 ml; 80°C.

rate was calculated from the conversion of previous experiments. The relationships between the concentration of St and the rate of polymerization by trapped radicals of PVC and PAN are shown in Figures 7 and 8.

Consequently, in the PAN and PVC series, the rate of copolymerization was proportional to the square of monomer concentration. Figures 9 and

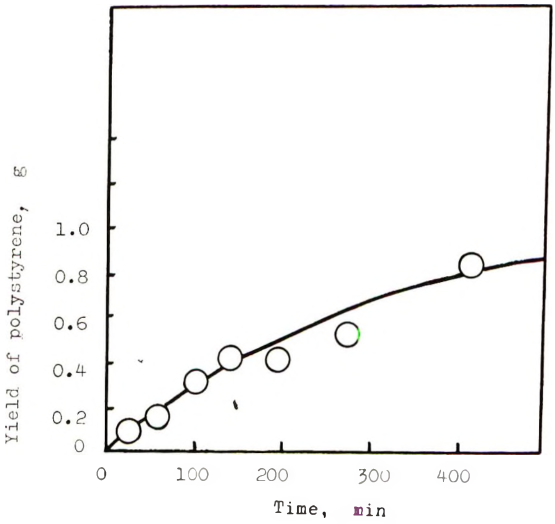

Fig. 6. Time–conversion curve of poly(vinyl chloride)–styrene system. First polymerization: VC, 10 g; methanol, 100 ml; $B(Bu)_3$, 2 ml; 0°C 24 hr.; Second polymerization: PVC, 0.1645 g; St, 5.7 ml; DMF, 9.3 ml; 80°C.

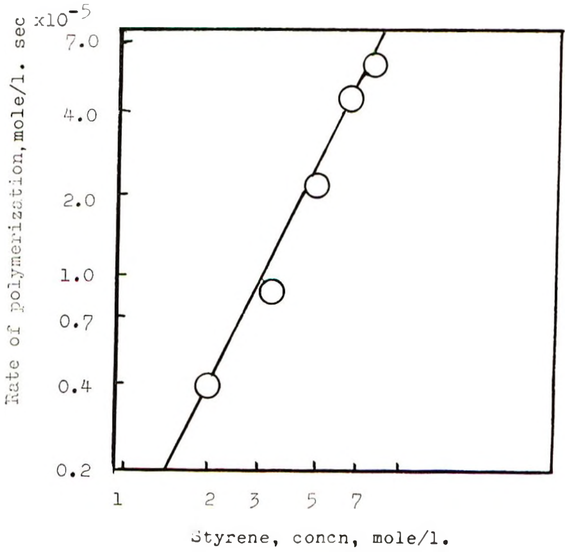

Fig. 7. Rate of polymerization for poly(vinyl chloride)–styrene system vs. concentration of monomer. PVC, 0.1883 g; solvent, THF; 80°C; 2 hr.

10 show the relation between the rate of polymerization and concentration of the suspension.

The rate of polymerization R_p was proportional to concentration of trapped radicals.

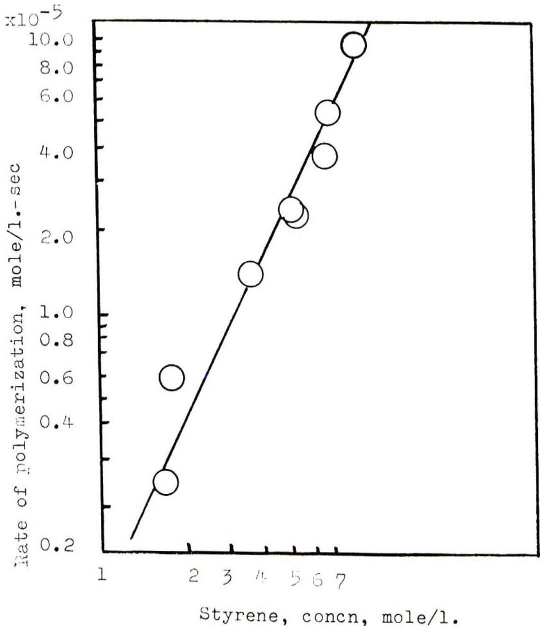

Fig. 8. Rate of polymerization for polyacrylonitrile–styrene system vs. concentration of monomer. PAN, 0.3773 g; solvent, DMF; 80°C; 3 hr.

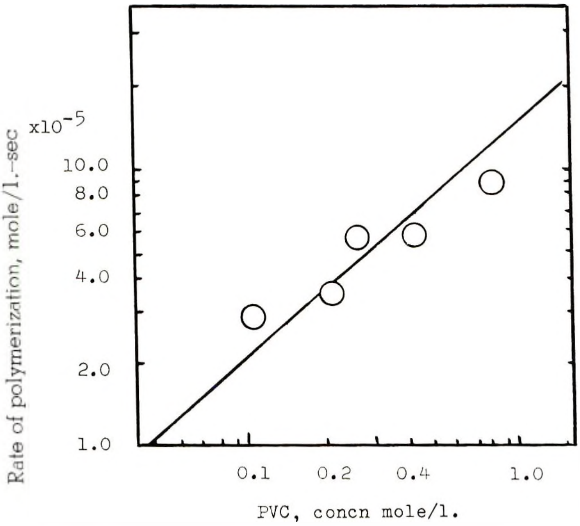

Fig. 9. Rate of polymerization for poly(vinyl chloride)–styrene system vs. concentration of poly(vinyl chloride). St, 5.56 mole/l.; solvent, DMF; 80°C; 3 hr.

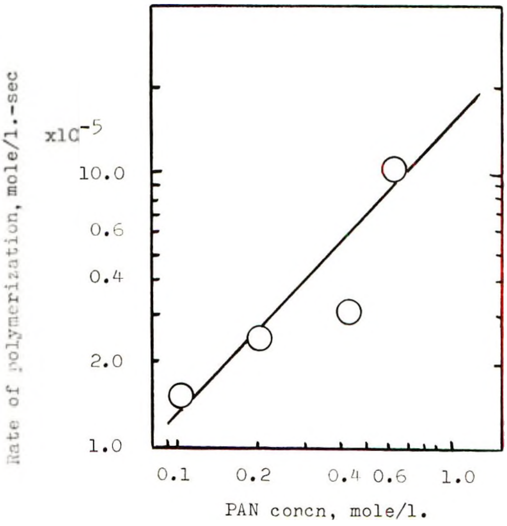

Fig. 10. Rate of polymerization for polyacrylonitrile–styrene system vs. concentration of polyacrylonitrile. St, 7.04 mole/l.; solvent, DMF; 80°C; 4 hr.

From these results, the relation (1) was formulated

$$R_p = K[M]^2[P] \tag{1}$$

where [M] and [P] are the concentration of monomer and the trapped radicals, respectively, and K is the overall rate constant.

In considering the above results, the reaction scheme (2)–(4) was suggested.

Reinitiation:

$$P_0\cdot + M \xrightarrow[k_i]{} P\cdot \tag{2}$$

Propagation:

$$P\cdot + M \xrightarrow[k_p]{} P\cdot \tag{3}$$

Unimolecular termination:

$$P\cdot \xrightarrow[k_3]{} \text{dead polymer} \tag{4}$$

Here P_0. denotes trapped radical in polymer which is proportional to the concentration of polymer suspension and P· denotes propagating radicals. P· is terminated in a unimolecular termination mechanism, because these systems are in a viscous and swollen state. Equation (5) is nonformulated:

$$d[P\cdot]/dt = k_i f[P_0\cdot][M] - k_t[P\cdot] \tag{5}$$

where f is the reinitiating factor. A steady state for [P·] is assumed.

$$k_i f[P_0\cdot][M] = k_t[P\cdot] \tag{6}$$

$$[P\cdot] = k_i/k_t f[P_0\cdot][M] \tag{7}$$

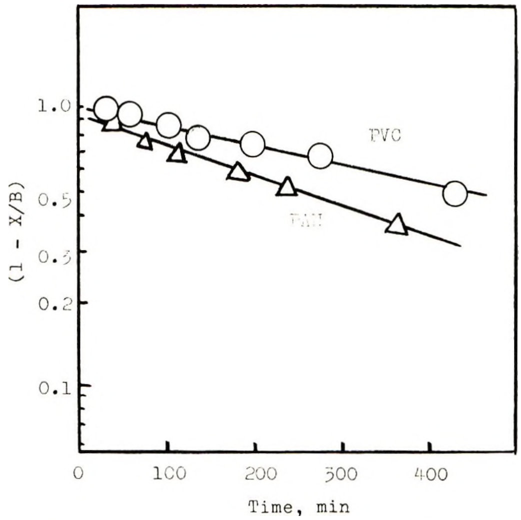

Fig. 11. [1-(X/B)] vs. polymerization time for PVC (B = 1.6) and PAN (B = 3.6).

Therefore,

$$R_p = k_p[\mathrm{P}\cdot][\mathrm{M}] = (k_i/k_t)\, k_p\, [\mathrm{P}_0\cdot][\mathrm{M}]^2 \tag{8}$$

And, for $[\mathrm{P}_0\cdot]$, eq. (9) is formulated.

$$-d[\mathrm{P}_0\cdot]/dt = k_i[\mathrm{P}_0\cdot][\mathrm{M}] \tag{9}$$

Integration yields eq. (10):

$$[\mathrm{P}_0\cdot] = [\mathrm{P}_0\cdot]_0\, e^{-k_i[\mathrm{M}]t} \tag{10}$$

where $[\mathrm{P}_0\cdot]_0$ is the initial concentration of trapped radicals.
Therefore,

$$\begin{aligned} R_p &= (k_i/k_t)\, k_p\, [\mathrm{P}_0\cdot][\mathrm{M}]^2 \\ &= k_i/k_t\, k_p\, [\mathrm{P}_0\cdot]_0[\mathrm{M}]^2\, e^{-k_i[\mathrm{M}]t} \end{aligned} \tag{11}$$

Equation (11) is successful in explaining the experimental results in the initial state. The amount of polymerized styrene is denoted by X.

$$R_p = dX/dt = Ae^{-k_i[\mathrm{M}]t} \tag{12}$$

where

$$A \equiv k_i\, k_p/k_t\, [\mathrm{P}_0\cdot]_0[\mathrm{M}]^2 \tag{13}$$

By integration we have:

$$X = A/k_i[\mathrm{M}]\,(1 - e^{-k_i[\mathrm{M}]t}) \tag{14}$$

$$X = (k_p/k_t)\, [\mathrm{P}_0\cdot]_0\, [\mathrm{M}]\, (1 - e^{-k_i[\mathrm{M}]t}) \tag{15}$$

On substituting with $k_p/k_t\, [\mathrm{P}_0\cdot]_0\, [\mathrm{M}] = B$, we have

$$X = B\,(1 - e^{-k_i[\mathrm{M}]t}) \tag{16}$$

where

$$\lim_{t \to \infty} X = B.$$

Therefore,

$$\ln [1 - (X/B)] = -k_i[M]t \tag{17}$$

The value of B is obtained from Figures 5 and 6 by extrapolation. A plot of $\ln [1 - (X/B)]$ versus time is linear, as shown in Figure 11. These results agreed with the above explanation. In the case of PVC a value of $B = 1.6$ was used; for PAN, B was taken as 3.6.

Viscosity of Crude PVC–St Copolymer

The viscosity of crude copolymer containing PVC–St block copolymer was measured in DMF at 30°C with an Ubbelohde viscometer. The intrinsic viscosity of the polymer increased slightly with increasing conversion. The results are shown in Figure 12.

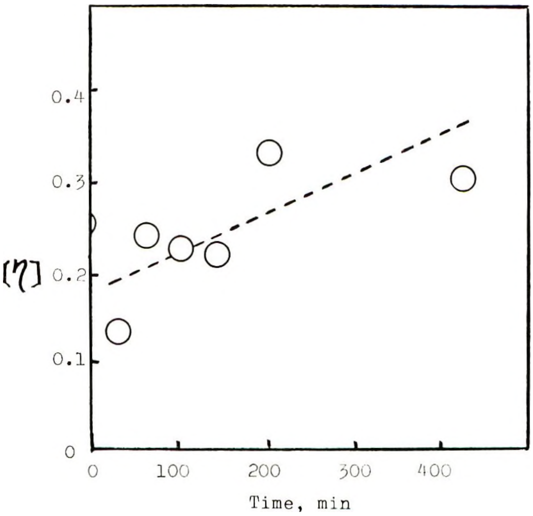

Fig. 12. [η] of poly(vinyl chloride)–styrene system polymer in DMF at 30°C vs. polymerization time.

CONCLUSION

These experimental results indicate that the trapped radicals were activated by addition of solvent and the block copolymer was obtained in the presence of a second monomer. By use of this method, block copolymers such as PVC–St, PVC–MMA, and PAN–St were prepared. The kinetics of the polymerization were considered.

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Calorimetric Investigation of Polymerization Reactions. II. Copolymerization of Diethyl Fumarate with Styrene

KAZUYUKI HORIE, ITARU MITA, and HIROTARO KAMBE,
Institute of Space and Aeronautical Science, University of Tokyo, Komaba, Tokyo, Japan

Synopsis

The bulk copolymerization of diethyl fumarate with styrene initiated by benzoyl peroxide or azobisisobutyronitrile was investigated with a differential scanning calorimeter (DSC) operated isothermally. The heat of copolymerization decreased almost linearly with the increase in diethyl fumarate content in the copolymer. The heat of homopolymerization for diethyl fumarate was equal to 15.5 ± 0.3 kcal/mole. Monomer reactivity ratios at 100°C were also determined. The rate of copolymerization was followed over the whole range of conversion. A gel effect was noticed in copolymerizations at lower but not at higher temperatures. The initial rate of copolymerization exhibited a maximum at an intermediate monomer feed composition, differing from the previously reported tendency. The difference was found to be due to the method used for determining the rate of copolymerization, and the superiority of the DSC method was proved. The mechanism of the radical-radical termination process was discussed. From the viewpoint of chemically controlled termination, the cross-termination factor ϕ was estimated to be 2.0, which is reasonable considering the steric hindrance; assumption of the predominance of a diffusion-controlled termination reaction was also consistent with the results.

INTRODUCTION

The copolymerization of diethyl fumarate with styrene initiated by radical initiators is investigated in the present paper. The heat of copolymerization and monomer reactivity ratios were determined at 100°C. The rate of copolymerization was followed over the whole range of conversion with a differential scanning calorimeter (DSC), and distinct autoacceleration was noticed in polymerizations at lower but not at higher temperatures. The initial rate of copolymerization is compared with literature values[1] and discussed from the viewpoints of both the classical kinetic equation and diffusion-controlled termination in nonviscous systems.

In a previous paper,[2] it was shown that the change in the rate of diffusion-controlled polymerization of methyl methacrylate and styrene as well as the heat of polymerization can be measured accurately by the isothermal operation of a DSC. The gel effect in crosslinking polymerizations may be caused by the formation of the three-dimensional network which controls the diffusion in both termination and propagation reactions. Our preliminary studies on the curing reaction of unsaturated polyester with styrene have proved that this is the case. It is necessary for the kinetic investigation of the curing reaction with DSC to determine the heat of copolymerization at various monomer compositions and the rate of copolymerization in cases where autoacceleration is not taking place.[3]

The copolymerization of diethyl fumarate with styrene is a suitable model for the curing reaction of polyester fumarate with styrene. Monomer reactivity ratios for the copolymerization have been determined by Lewis and his co-workers.[4] Walling and McElhill[1] have determined the initial rates of copolymerization for various compositions of two monomers, but we obtained preliminary data differing appreciably from theirs. The rate of copolymerization over the whole range of conversion is also needed. In addition, the heat of copolymerization for this system has not yet been reported. Thus it was decided to investigate this system by the DSC method.

Another important problem is associated with the cross-termination factor ϕ:

$$\phi = k_{t12}/(k_{t11}k_{t22})^{1/2}$$

which Walling and McElhill have calculated by using the classical kinetic theory of copolymerization.[5] Later it was recognized by North and his co-workers[6-8] as well as by Allen and Patrick[9] that radical–radical termination reactions are often diffusion-controlled, even in nonviscous media. If this should also be the case for copolymerizations, the termination rate would be independent of the chemical nature of the active chain end but dependent mainly on the composition and some solution properties of the whole growing chain. The concept of the ϕ factor in copolymerization reactions, therefore, would lose its significance. It is thus necessary to reexamine the rate of polymerization from the standpoint of diffusion-controlled termination. In fact, Atherton and North[10] have shown the viscosity dependence of the rate of copolymerization of methyl methacrylate with vinyl acetate and proposed a kinetic equation for the rate of copolymerization with a diffusion-controlled termination reaction. The ϕ factor for this system was reported to have abnormally large values varying with monomer feed compositions (100–800).[11] The ϕ factor for the copolymerization of diethyl fumarate with styrene was reexamined here from this point of view. To distinguish this type of diffusion-controlled reaction in termination from the previously mentioned one during or after the autoacceleration stage, the latter is called autoacceleration or gel effect in this report.

EXPERIMENTAL

Materials

Diethyl fumarate was freed from inhibitor, dried, and purified by distillation under nitrogen at a reduced pressure. The middle fraction was collected and stored in an icebox. Styrene was purified and stored in the same way.

Benzoyl peroxide (BPO) and 2,2′-azobisisobutyronitrile (AIBN) were recrystallized in the usual manner.

Procedure

Diethyl fumarate and styrene were homopolymerized and copolymerized in bulk with 0.09 mole/l. BPO at 100°C and with 0.05 mole/l. AIBN at 90°C. Polymerization was carried out in a modified closed sample pan of a Perkin-Elmer differential scanning calorimeter (DSC-1), operated isothermally. Details of the procedure with the DSC are similar to those described previously.[2] The enclosed area of the DSC curve with the baseline represents the total heat evolved by the copolymerization reaction. The deflection of the curve from the baseline expresses the rate of heat evolution and is proportional to the rate of copolymerization at every instant.

A factor converting the peak area to the thermal energy was obtained from heats of fusion of eight nonvolatile compounds measured between 40 and 150°C, and was found to be constant in this range of temperatures.[12]

Residual Monomer Content

The content of residual monomers was determined by ultraviolet spectrophotometry. A Shimadzu IV-50A type spectrophotometer was used for the determination of the absorbances at 214 mμ for diethyl fumarate monomer and at 248 mμ for styrene monomer in an ethanol–acetone (199:1) mixture. The influence of the absorbance at 214 mμ due to styrene monomer was corrected.

Molecular Weight Measurements

The number-average molecular weights were measured with a Mechrolab vapor-pressure osmometer (VPO) at 37°C in benzene.

Viscosity Measurements

The viscosity of the monomer mixture or solution was measured at 90°C with an Ubbelohde capillary viscometer calibrated with the literature value for toluene.[13]

RESULTS AND DISCUSSION

Heat of Copolymerization

Typical DSC curves for the isothermal copolymerization of diethyl fumarate with styrene at 100°C with BPO are shown in Figure 1. In the homopolymerization of styrene a marked gel effect is observed, while the copolymerization and homopolymerization of diethyl fumarate do not show any autoacceleration. The spectrophotometrically determined monomer

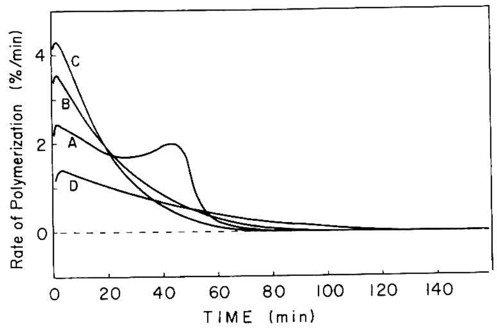

Fig. 1. DSC curves for polymerization and copolymerization of styrene (St) and diethyl fumarate (DEF) at 100°C with BPO at various monomer compositions: (*A*) St 100%; (*B*) St 75%, DEF 25%; (*C*) St 50%, DEF 50%; (*D*) DEF 100%.

feed composition and residual monomer content, as well as the final conversion, are summarized in Table I. About 10–40% of the diethyl fumarate monomer remains unpolymerized, and the final conversion decreases with the increase in the fraction of diethyl fumarate in the feed. A temperature scan to 200°C on the isothermally copolymerized sample showed no further copolymerization of residual monomers, which is different from the case of methyl methacrylate polymerization.[2] Thus, the cessation of polymerization before complete conversion cannot be attributed to a gel effect. This fact agrees with the so-called dead-end theory of Tobolsky et al.,[14] which predicts the end of polymerization for the limiting conversion due to the complete consumption of initiator at comparatively high temperatures.

TABLE I
Copolymerization of Diethyl Fumarate (DEF) with Styrene (St) at 100°C with 0.09 mole/l. BPO Followed by DSC

DEF in feed, mole-%	Residual monomer, % for each monomer feed		DEF in copolymer, mole-%	Final conversion, %	Heat of copolymerization, kcal/mole
	DEF	St			
0	—	2.4	0	97.6	16.4
0	—	2.5	0	97.5	16.2
24.8	10.9	1.5	22.9	96.2	15.9
25.8	17.6	2.6	22.8	93.6	16.7
34.7	18.5	2.0	30.7	92.1	15.9
34.9	17.8	1.6	31.9	90.0	16.1
39.2	21.0	2.0	34.2	90.6	16.0
40.2	18.3	2.0	35.9	91.4	16.2
50.4	23.5	0	43.8	88.1	16.1
58.9	22.9	0	52.6	86.5	16.4
80.7	32.0	0	74.1	74.3	16.0
86.6	32.8	0	81.2	71.7	15.7
100.0	38.6	—	100.0	61.4	15.8
100.0	35.9	—	100.0	64.1	15.3

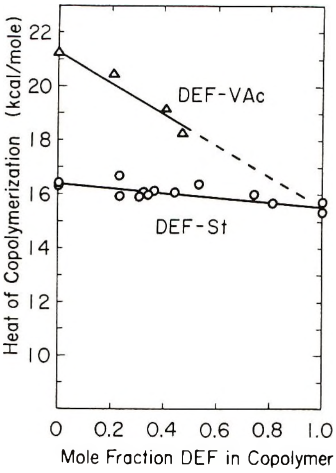

Fig. 2. Heat of copolymerization of diethyl fumarate with styrene against mole fraction of diethyl fumarate in copolymer. Data for diethyl fumarate with vinyl acetate[16] are indicated for reference.

The heats of copolymerization of diethyl fumarate with styrene were determined by comparison of total heat evolved with monomer consumption. They are also listed in Table I and plotted against the composition of monomers in the copolymer in Figure 2.

The heat of polymerization for styrene obtained with DSC agrees with literature values (16.1–16.8 kcal/mole).[15] The heat of polymerization for diethyl fumarate was determined to be 15.5 ± 0.3 kcal/mole, which shows a good agreement with the value extrapolated from the data of Tong and Kenyon[16] for the copolymerization of diethyl fumarate with vinyl acetate also shown in Figure 2. The heat of copolymerization decreases almost linearly with an increase in mole fraction of diethyl fumarate in the copolymer.

As diethyl fumarate has two substituent groups in the *trans*-1,2 position, steric hindrance in the polymer is assumed to be small and to have little effect on the heat of polymerization, in comparison with the case of a 1,1-disubstituted monomer such as methyl methacrylate. Thus, the release of steric strain presumed in the case of copolymerization of methyl methacrylate with styrene and the resulting curvature observed in the plots of heat of copolymerization against monomer composition[17] did not appear for the copolymerization of diethyl fumarate with styrene. In this case the resonance effect of three substituents belonging to two monomers will be regarded as the main factor affecting the heat of copolymerization.

Monomer Reactivity Ratios at 100°C

Monomer reactivity ratios for the copolymerization of diethyl fumarate with styrene at 60 and 131°C have been reported by Lewis and his coworkers.[4] In our experiments monomer reactivity ratios were determined at 100°C.

Copolymerizations with monomer feeds containing 25–75% of diethyl fumarate were carried out up to 20–30% conversion. Construction of r_1–r_2 plots according to the integrated equation of Mayo and Lewis[18] yielded $r_1 = 0.36 \pm 0.04$ and $r_2 = 0.10 \pm 0.02$, where monomer 1 was styrene. These values are in accord with the reported values ($r_1 = 0.30$, $r_2 = 0.07$ for 60°C and $r_1 = 0.40$, $r_2 = 0.09$ for 131°C).[4]

Rate of Copolymerization

The rate of copolymerization R_p can be followed over the whole range of conversion by the use of a DSC. The change in the rate of copolymerization with conversion is shown in Figures 3 and 4 for the copolymerization of diethyl fumarate with styrene at 100°C with BPO and at 90°C with AIBN, respectively.

The rate decreases with conversion because of the consumption of monomers and initiator. In the homopolymerization of styrene the autoacceleration appears at 50–60% conversion. In the homopolymerization

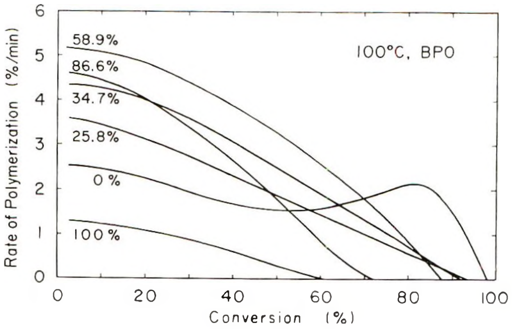

Fig. 3. Change in polymerization rate with conversion for copolymerization of diethyl fumarate with styrene at 100°C with 0.09 mole/l. BPO. Mole-% DEF in feed is as indicated.

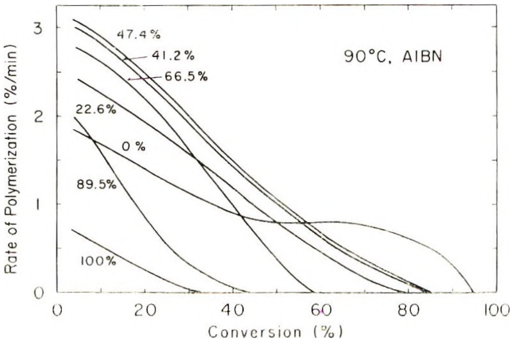

Fig. 4. Change in polymerization rate with conversion for copolymerization of diethyl fumarate with styrene at 90°C with 0.05 mole/l. AIBN. Mole-% DEF in feed is as indicated.

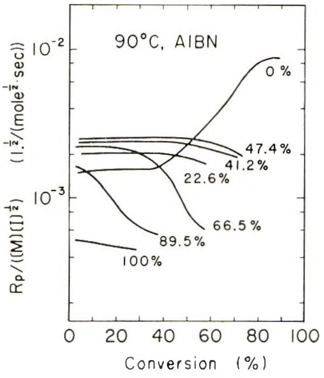

Fig. 5. Reduced rate curves with conversion for copolymerization of diethyl fumarate with styrene at 90°C with AIBN. Mole-% DEF in feed is as indicated.

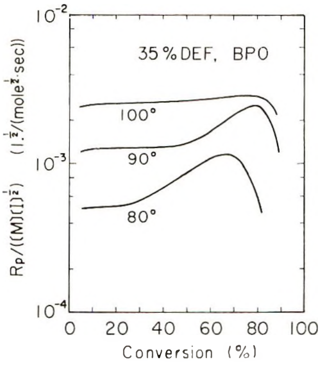

Fig. 6. Temperature dependence of reduced rate curves for copolymerization of 35% diethyl fumarate with 65% styrene with BPO. Polymerization temperatures are as indicated.

and copolymerization of diethyl fumarate no autoacceleration was observed under these conditions.

The rate of copolymerization of diethyl fumarate with styrene was divided by the total concentration of monomers [M] and the square root of the concentration of initiator [I] at each conversion in order to eliminate the effect due to the decrease in their concentrations. The reduced rate of copolymerization against conversion for the case at 90°C with AIBN is illustrated in Figure 5. Reduced rate curves with a similar change against conversion were obtained for the case at 100°C with BPO.

The reduced rate grows up to sixfold to its initial value at the later stage of styrene polymerization. The reduced rate remains constant up to a fairly high conversion for copolymerization with styrene-rich compositions. It can be shown from the r_1 and r_2 values that the monomer composition hardly changes during the course of copolymerization in this range of feed composition. In copolymerization with compositions rich in diethyl fumarate, the reduced rate shows a gradual decrease to the level for the

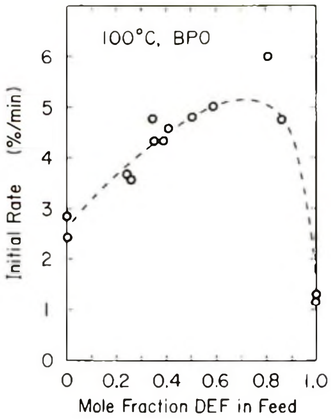

Fig. 7. Initial rate of copolymerization of diethyl fumarate with styrene at 100°C with BPO against monomer composition.

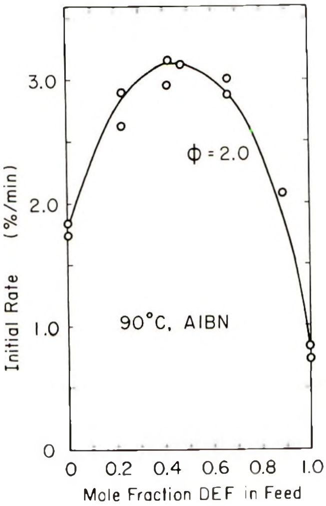

Fig. 8. Initial rate of copolymerization of diethyl fumarate with styrene at 90°C with AIBN against monomer composition: (O) experimental points; (——) calculated rate curve for $\phi = 2.0$.

homopolymerization of diethyl fumarate. As styrene monomer is more reactive than diethyl fumarate monomer, the consumption of the former is faster than the latter, and the monomer composition becomes more and more rich in diethyl fumarate, which results in the decrease in the reduced rate.

The temperature dependence of the reduced rate curves is illustrated in Figure 6 for the copolymerization with a monomer feed containing 35% diethyl fumarate. As the copolymerization temperature decreases, a clear gel effect appears in the later stage of copolymerization which was not apparent at 100°C with the same concentration of initiator. It should be noted that the molecular weights of the resulting copolymers are very low (about a few thousands determined with a VPO) compared with cases in which the gel effect has generally been reported to occur.

The initial rate of copolymerization extrapolated to zero conversion is shown plotted against monomer feed composition in Figures 7 and 8 for the cases with BPO at 100°C and with AIBN at 90°C, respectively.

The initial rate exhibits its maximum at an intermediate composition of the monomer feed in either case. For the copolymerization with AIBN, the maximum value is obtained exactly at the azeotropic composition, i.e., 42% for diethyl fumarate. The initial rate of homopolymerization of diethyl fumarate proves to be two or three times smaller than that of styrene.

These results differ from those reported by Walling and McElhill,[1] in which, as the fraction of diethyl fumarate in the feed increases, the initial rate of copolymerization decreases monotonically to the value for the rate of polymerization of diethyl fumarate, which is one-eighth that of styrene.

It is possible that this difference might be due to the techniques used for the determination of the polymer yields. As the molecular weights of polymers and copolymers of diethyl fumarate were very small, oligomers with low molecular weight may not have been precipitated when petroleum ether was added to benzene solutions of the polymer. So, the rate of polymerization and copolymerization of diethyl fumarate may have been underestimated.

In order to confirm this possibility, the polymerization and copolymerization of diethyl fumarate and styrene were carried out under conditions similar as those used by Walling and McElhill (in evacuated and sealed tubes at 60°C with 1.0 g/l. AIBN), and polymer yields were determined both by spectroscopic measurement of residual monomer contents and by isolating the polymer from benzene–petroleum ether system and weighing. The rates of polymerization and copolymerization are obtained from the polymer yields by dividing by the times of polymerization. The results are summarized in Table II.

The same results were obtained for the rate of polymerization of styrene measured by both methods, whereas the rate of copolymerization and homopolymerization of diethyl fumarate determined by polymer isolation were

TABLE II
Rate of Copolymerization of Diethyl Fumarate with Styrene at 60°C with 1.0 g/l. AIBN

DEF in feed, mole-%	Polymerization time, hr	$R_p \times 10^5$, mole/l.-sec By UV method	By precipitation of polymer	Walling et al.[1]	$\bar{M}_n$ by VPO
0	2.25	6.0	6.3	6.0	~37000
32	3.25	7.5	2.1	4.7	4000
100	24.25	3.0	0.17	0.72	2600

appreciably smaller than those obtained by the spectroscopic method. In the case of the spectroscopic determination of residual monomer, the rate of copolymerization is larger than that of homopolymerization of each monomer, a similar tendency as the results obtained with DSC. In the case of the polymer isolation method, the results were qualitatively similar to those of Walling and McElhill.[1] The number-average molecular weights of the tarlike copolymer and homopolymer of diethyl fumarate were several thousands or so according to vapor-pressure osmometry (Table II). The validity of spectroscopic determination of the residual monomer contents has been confirmed at the previous discussion on the heat of copolymerization.

Thus, it would be reasonable to consider the polymer isolation from benzene–petroleum ether solution not to be adequate for the determination of the rate of copolymerization and homopolymerization of diethyl fumarate, because appreciable amounts of oligomer cannot be precipitated by this method. In contrast, DSC is suitable for the determination of the rate of polymerization resulting in polymers of low molecular weights.

The cross-termination factor ϕ for the copolymerization of styrene (M_1) with diethyl fumarate (M_2) was calculated according to eq. (1),[5]

$$\frac{d([M_1] + [M_2])}{dt} = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)(R_i^{1/2}/\delta_1)}{\{r_1^2[M_1]^2 + 2(\phi r_1 r_2 \delta_2/\delta_1)[M_1][M_2] + (r_2\delta_2/\delta_1)^2[M_2]^2\}^{1/2}} \qquad (1)$$

where R_i is the rate of initiation, r_1 and r_2 are monomer reactivity ratios, values of $r_1 = 0.36$ and $r_2 = 0.10$ being assumed; δ_1 and δ_2 represent the rate-

TABLE III

Cross-Termination Factor ϕ for Copolymerization of Diethyl Fumarate with Styrene

Runs at 100°C with BPO			Runs at 90°C with AIBN		
DEF in feed, mole-%	Initial rate, %/min	ϕ	DEF in feed, mole-%	Initial rate, %/min	ϕ
0	2.40	—	0	1.85	—
0	2.84	—	0	1.73	—
24.8	3.66	3.22	22.6	2.90	1.70
25.8	3.53	3.64	22.6	2.61	2.72
34.7	4.75	1.56	41.2	2.95	2.38
34.9	4.31	2.26	41.2	3.16	1.91
39.2	4.33	2.35	47.4	3.12	2.04
40.2	4.57	1.96			
50.4	4.78	1.83	66.4	3.02	1.74
58.9	5.03	1.55	66.5	2.87	2.03
80.7	5.99	0.16			
86.6	4.74	0.98	89.5	2.08	1.83
100.0	1.32	—	100.0	0.73	—
100.0	1.13	—	100.0	0.84	—

constant ratios $k_{t11}^{1/2}/k_{p11}$ and $k_{t22}^{1/2}/k_{p22}$, respectively. The $R_i^{1/2}/\delta_1$ and δ_2/δ_1 values were obtained from the rates of homopolymerization of styrene and diethyl fumarate. The results are listed in Table III.

The ϕ values for the copolymerization initiated with BPO vary widely with monomer composition. This is presumably due to the change in the rate of decomposition of BPO in the mixed solvent of various compositions.[19] The ϕ values for the copolymerization initiated with AIBN are fairly well reproducible and equal to 2.0 on the average.

It is usually believed that the ϕ value increases as the product r_1r_2 decreases, since these r values reflect polarity effects of polymeric chain ends and monomer. In the case of copolymerization of styrene with 1,2-disubstituted monomer, however, the product r_1r_2 gives zero or very small values independent of polarity of the 1,2-disubstituted monomer. Even for crotonic acid or methyl cinnamate, which has a polarity factor e smaller than 0.5, the product r_1r_2 proves to be zero.[20] This may be mainly due to steric hindrance in the transition state. In termination reactions, the steric hindrance affects not only the termination between two 1,2-disubstituted chain ends (k_{t22}) but also the cross termination (k_{t12}), because the termination is usually a head-to-head reaction. Thus, it is reasonable to assume that k_{t12} is not much larger than the square root of the product $k_{t11}k_{t22}$, and hence the ϕ value becomes close to unity. This concept is consistent with our results.

The above discussion is valid only when the termination reaction is not controlled by the diffusion of polymeric radicals. This may be the case for the copolymerization of diethyl fumarate with styrene, since the resulting copolymers and homopolymers have very low molecular weights and since reasonable values have been obtained.

Alternatively, the initial rate of copolymerization of diethyl fumarate with styrene can be discussed on the assumption that the diffusion-controlled termination reaction might also be predominant in this case.

The rate of copolymerization can be formulated by eq. (2) according to Atherton and North,[10]

$$-\frac{d([\mathrm{M}_1] + [\mathrm{M}_2])}{dt} = \frac{R_i^{1/2}(r_1[\mathrm{M}_1]^2 + 2[\mathrm{M}_1][\mathrm{M}_2] + r_2[\mathrm{M}_2]^2)}{k_{t(12)}^{1/2}(r_1[\mathrm{M}_1]/k_{p11} + r_2[\mathrm{M}_2]/k_{p22})} \qquad (2)$$

where the termination rate coefficient $k_{t(12)}$ is independent of the nature of the terminal group and is a function only of the polymer (and hence monomer feed) composition, while the other notation is similar to that of eq. (1). It may be assumed that the diffusion-controlled termination rate coefficient $k_{t(12)}$ satisfies the molar additivity of termination rate constants of each homopolymerization k_{t1} and k_{t2},

$$k_{t(12)} = k_{t1}x_1 + k_{t2}x_2 \qquad (3)$$

where x_1 and x_2 are the mole fractions of M_1 and M_2 units, respectively, in the copolymer. By substituting eq. (3) into eq. (2) and using $\delta_2 = k_{t2}^{1/2}/k_{p22}$, the rate of copolymerization can also be expressed by eq. (4).

$$-\frac{d([M_1] + [M_2])}{dt} = \frac{R_i^{1/2}(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)}{\{k_{t1}x_1 + k_{t2}(1 - x_1)\}^{1/2}\,(r_1[M_1]/k_{p11} + r_2\delta_2[M_2]/k_{t2}^{1/2})} \qquad (4)$$

The mole fraction x_1 is related to the monomer feed composition by the classical eq. (5).

$$x_1 = \frac{[M_1]([M_2] + r_1[M_1])}{r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2} \qquad (5)$$

For the copolymerization of styrene (M_1) with diethyl fumarate (M_2) at 90°C with AIBN, R_i was evaluated according to the data of Tobolsky et al.,[14] the k_{t1} value was taken to be 9.4×10^7 l./mole-sec,[21] and the k_{t2} value was estimated to be 3.8×10^8 l./mole-sec by the use of eqs. (4) and (5) with a value of the rate of copolymerization for azeotropic composition. The numerical values for k_{p11} and k_{p22} were obtained by using these values with $R_i^{1/2}/\delta_1$ and δ_2/δ_1. The termination rate coefficient $k_{t(12)}$ was then calculated for each monomer feed composition according to eq. (2) and is plotted in Figure 9 against the monomer feed composition.

The $k_{t(12)}$ values increase almost linearly with increase in diethyl fumarate in the monomer feed composition. This is in fairly good agreement with eq. (3), indicated by the solid line in Figure 9.

The termination rate constant of 4×10^8 l./mole-sec is to be expected for polymeric radicals with a diffusivity of about 2×10^{-6} cm^2/sec according to the relationship between the rate constant for diffusion-controlled reaction and the diffusion coefficient derived by Smoluchowski.[22] Such an order of magnitude for the diffusivity is reasonable for polymeric chains with molecular weight of a few thousands;[23] these results support the diffusion-controlled termination mechanism for the copolymerization of diethyl

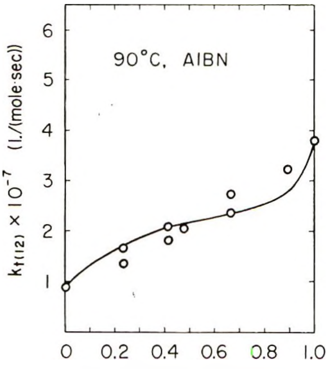

Fig. 9. Dependence of $k_{t(12)}$ on monomer feed composition for copolymerization of diethyl fumarate with styrene at 90°C with AIBN: (O) experimental; (——) curve corresponds to eq. (3).

fumarate with styrene. In fact, the initial rate of copolymerization markedly increased when the copolymerization with 41.2% diethyl fumarate was carried out in solution more viscous than the bulk, i.e., R_{p0} = 4.03%/min in 50% *p*-cresol solution(η = 0.70 cP) in contrast with R_{p0} = 3.16%/min in bulk (η = 0.47 cP), but the change in the initial rate was not realized in less viscous solutions.

From the above results it is difficult to ascertain whether the termination reaction in the copolymerization of diethyl fumarate with styrene at 90°C with AIBN is controlled by diffusion or not. The elucidation of this problem is left to the further investigation about the quantitative dependence of the termination rate coefficient $k_{t(12)}$ on the solution viscosity over a wide range. It can be stated, however, that the copolymerization of diethyl fumarate with styrene is one of the interesting cases where the rates of diffusive and chemical processes are of the same order of magnitude in the radical–radical termination reaction.

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Kinetic Study of γ-Radiation-Induced Polymerization of Ethylene in the Presence of Acetylene

HIROSHI MITSUI, FUMIO HOSOI, and TSUTOMU KAGIYA, *Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment, Takasaki, Gunma, Japan*

Synopsis

The effects of acetylene on the γ-radiation-induced polymerization of ethylene were studied from the viewpoint of kinetics. The experiments were carried out under a pressure of 150–400 kg/cm^2; the temperature was 30°C; the dose rates were 2.7×10^4 and 1.1×10^5 rad/hr; the acetylene content was 0–2.21%. Both the polymer yield and the molecular weight increased acceleratively with the reaction pressure in the polymerization containing 0.18% acetylene. The yield increased almost proportionally with the dose rate, and the molecular weight was found to be almost independent of the dose rate in the polymerization containing 2.21% acetylene. The polymerization rate and the molecular weight increased with reaction time, but the increment decreased with increasing acetylene content. The degree of increase in the molecular weight also decreased with increasing time. These results were analyzed by using a graphical evaluation method for kinetics, and the effects of acetylene on each elementary step in the polymerization discussed.

INTRODUCTION

In the previous paper,[1] the effect of acetylene on the γ-radiation-induced polymerization of ethylene under a high pressure of 400 kg/cm^2 at 30°C was discussed from the viewpoint of the gaseous products and the structure of the polymer formed in the polymerization of ethylene containing acetylene. We concluded that the polymerization of ethylene is markedly retarded by the addition of acetylene and that the retardation can be considered to be caused by the decrease in the rate of propagation. Chain free radicals having an acetylene end scarcely reacted with ethylene or acetylene. The rate of hydrogen formation was not affected by acetylene, and no triple bond was observed in the polymer formed in the polymerization of ethylene containing acetylene. In addition, it was proposed that a reaction which reduces the number of polymer chains formed may be caused by acetylene.

Machi et al.[2] studied the polymerization of pure ethylene at 30°C and observed that the polymer yield increases rapidly with the reaction time and with the pressure, and the molecular weight of the polymer formed increases proportionally with the time and with the pressure. They also found that the dose rate exponents of the polymerization rate and the molecular weight are 0.9 and 0, respectively. On the basis of these results for the polymerization of pure ethylene it was concluded that the stationary-state hypothesis, i.e., that the rate of initiation is equal to that of termination, is not realized. Further, from the kinetics of nonstationary-state polymerization at a dose rate of 2.5 × 10^4 rad/hr, it was concluded that the rates of initiation and propagation are proportional to the density of ethylene and to the square of the fugacity of ethylene, respectively, and that the rates of termination and transfer are very small.

The purpose of this paper is to determine the effects of reaction conditions such as reaction pressure, dose rate, and time on the polymerization of ethylene containing acetylene and to elucidate the roles of acetylene in each step of the polymerization from a kinetic point of view in the connection with the results of the previous paper.[1]

EXPERIMENTAL

The reaction vessel, materials (ethylene and acetylene), irradiation facilities, and experimental procedure were the same as described in the previous paper.[1] The polymerizations were carried out under a pressure of 150–400 kg/cm^2; the dose rates were 2.7 × 10^4 and 1.1 × 10^5 rad/hr; the acetylene content was varied in the range 0–2.21%, and the temperature was 30°C.

RESULTS AND DISCUSSION

Effects of Reaction Conditions

In order to elucidate the effects of the reaction pressure on the polymer yield and the molecular weight, the polymerization was carried out at various pressures at an acetylene content of 0.18%; the results are given in Table I. Figure 1 shows that both the yield and the molecular weight increase rapidly with the pressure. From the logarithmic plot, the exponents of the pressure are found to be 1.6 for the yield and 1.9 for the molecular weight, respectively.

Table II shows the results of the experiments at 2.7 × 10^4 and 1.1 × 10^5 rad/hr. The polymer yield increases almost proportionally with dose rate,

TABLE I
Effect of Reaction Pressure on Polymer Yield and Molecular Weight[a]

Mean pressure, kg/cm^2	Polymer yield, g/l.	Molecular weight × 10^{-4}
149	8.311	2.6
193	12.793	8.4
280	22.874	17.0
359	35.694	26.0
363	34.420	29.0

[a] Reaction conditions: temperature, 30°C; dose rate, 1.1 × 10^5 rad/hr; acetylene content, 0.18%; time, 3 hr; reactor volume, 100 ml.

while the molecular weight is almost independent of dose rate. This fact indicates that the polymerization of ethylene containing acetylene does not follow the square-root law for stationary-state polymerization with bimolecular termination.

TABLE II
Effect of Dose Rate on Polymer Yield and Molecular Weight[a]

Dose rate $\times 10^{-4}$ rad/hr	Reaction time, hr	Polymer yield, g/l.	Molecular weight $\times 10^{-4}$
2.7	2.0	0.933	1.72
	3.0	1.573	2.32
11.0	2.0	4.129	1.90
	3.0	6.193	2.08

[a] Reaction conditions: pressure, 400 kg/cm^2; temperature, 30°C; acetylene content, 2.21%; reactor volume, 100 ml.

TABLE III
Effect of Reaction Time on Polymer Yield and Molecular Weight[a]

C_2H_2 content, %	Reaction time, hr	Yield, g/l.	Molecular weight $\times 10^{-4}$
0.00	1/3	3.076	10.3
	1/2	6.552	12.8
	1.0	21.166	17.7
0.18	1/2	3.216	7.6
	1.0	7.598	12.0
	2.0	20.215	19.5
0.64	1.0	5.570	6.7
	2.0	13.570	13.8
	3.5	24.194	16.3
1.26	1.0	3.183	2.85
	2.0	6.690	4.4
	3.0	12.261	7.4
2.21	1.0	1.820	1.2
	2.0	4.129	1.9
	3.0	6.193	2.08

[a] Reaction conditions: pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 1.1×10^5 rad/hr; reactor volume, 100 ml.

The polymer yield and the molecular weight at various concentrations of acetylene are summarized in Table III. As can be seen in Figure 2, the polymer yield increases acceleratively with reaction time in all series of experiments, and decreases with increasing acetylene content in whole period of the reaction. Figure 3 shows that the molecular weight increases with the time, and the extent of the increment decreases with the time and acetylene content.

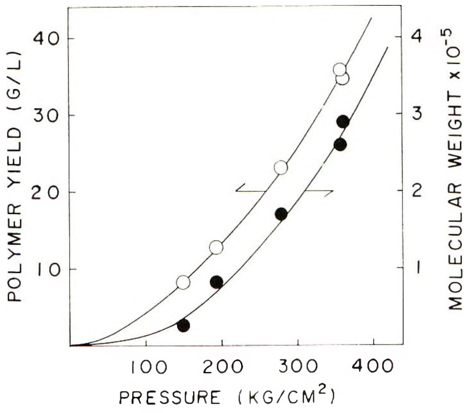

Fig. 1. Effects of reaction pressure on (○) polymer yield and (●) molecular weight in the polymerization of ethylene containing 0.18% acetylene. Reaction temperature, 30°C; dose rate, 1.1 × 10^5 rad/hr; time, 3 hr; reactor volume, 100 ml.

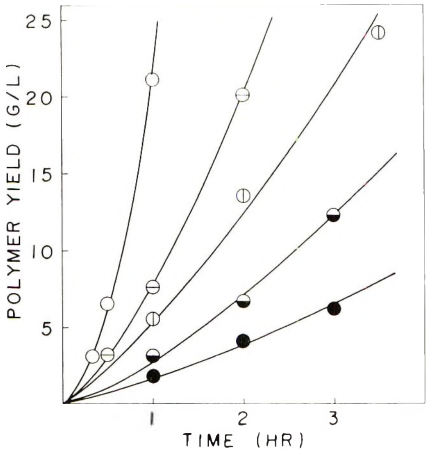

Fig. 2. Relation between polymer yield and reaction time in the polymerization of ethylene containing (○) 0.00%, (⊖) 0.18%, (⦶) 0.64%, (◒) 1.26%, and (●) 2.21% acetylene. Reaction pressure, 400 kg/cm²; temperature, 30°C; dose rate, 1.1 × 10^5 rad/hr; reactor volume, 100 ml.

The effect of the reaction conditions, such as reaction pressure, dose rate, and time, on the polymer yield and on the molecular weight are very similar to those in the polymerization of pure ethylene at room temperature.[2]

Kinetics

Since the polymerizations in all series were carried out under continuous irradiation by γ-radiation, the initiation reaction takes place continuously. Further, as described above, both the rate of polymerization and the molecular weight increase with the reaction time. According to the classification

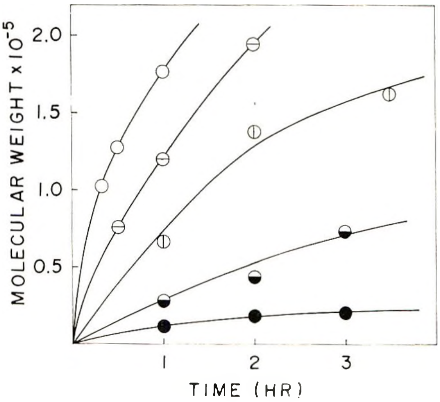

Fig. 3. Relation between molecular weight and reaction time. Reaction conditions same as given for Fig. 2.

from a kinetic point of view proposed by Kagiya et al.,[3] the polymerization of ethylene in the presence of acetylene is classified as a nonstationary successive polymerization with a slow initiation. Accordingly, the kinetic constants of this system can be obtained by using the graphical evaluation method of Kagiya et al.[4]

Rate of Polymerization. Since similar kinetical features to the polymerization of pure ethylene were observed in the polymerization of ethylene containing acetylene, a reaction mechanism, given in eqs. (1)–(9), similar to the one which has already been proposed for the polymerization of pure ethylene,[2] is assumed for this polymerization. In eqs. (1)–(9), E represents the ethylene; A, the acetylene; $R_1\cdot$, the initiating species; E*, the excited ethylene; E_2*, the excited ethylene dimer; $R_n\cdot$, the active polymer chain composed of n monomers; $R_n \ldots A$, the coordination product of acetylene to $R_n\cdot$; Z, the substance by which $R_n\cdot$ is deactivated in the polymerization; P_n, the dead polymer composed of n monomers; Y, the substance to which the activity of $R_n\cdot$ is transferred; $R_nA\cdot$, the chain free radicals having acetylene end; P, polymers such as $R_n\cdot$, $R_n \ldots A$, P_n, and $R_nA\cdot$; R_{iE}, R_{iA}, R_p, R_t, R_{tr}, R_c, and R_c' are the rates of initiation from ethylene, initiation from acetylene, propagation, termination, transfer, polymer linking reactions (8) and (9), respectively; k_{iE}, k_{iA}, k_p, k_t, k_{tr}, k_c, and k_c', the rate constants of these reactions; I is dose rate; ρ_E and ρ_A are the densities of ethylene and acetylene, respectively; f_{E_2}*, f_E, and f_A, the fugacities of excited ethylene dimer, ethylene, and acetylene, respectively; K_e represents the equilibrium constant of the reaction between ethylene and excited one to form the excited ethylene dimer; $[R\cdot]$, the total concentration of all the active polymer chains, irrespective of size (i.e., $\sum_{n=1}^{\infty} [R_n\cdot]$); K_A, the equilibrium constant of the reaction between $R_n\cdot$ and acetylene to form the coordination product; $[R_n \ldots A]$, $[Z]$, $[Y]$, $[R_nA\cdot]$, and $[P]$ represent the concentrations of $R_n \ldots A$, Z, Y, $R_nA\cdot$, and P, respectively.

Initiation:

$$E \overset{k_{iE}}{\rightsquigarrow} R_1\cdot$$

with
$$R_{iE} = k_{iE} I \rho_E \tag{1}$$

$$A \underset{E}{\overset{k_{iA}}{\rightsquigarrow}} R_1\cdot$$

with
$$R_{iA} = k_{iA} I \rho_A \tag{2}$$

Ethylene excitation:

$$E \rightleftharpoons E^*$$

$$E + E^* \overset{K_e}{\rightleftharpoons} E_2^*$$

with
$$f_{E_2}{}^* = K_e f_E{}^2 \tag{3}$$

Propagation:

$$R_n\cdot + E_2^* \xrightarrow{k_p} R_{n+1}\cdot + E^*$$

with
$$R_p = k_p f_{E_2}{}^*[R\cdot] = k_p K_e f_E{}^2[R\cdot] \tag{4}$$

Coordination:

$$R_n\cdot + A \overset{K_A}{\rightleftharpoons} R_n \ldots A$$

with
$$[R_n \ldots A] = K_A f_A [R\cdot] \tag{5}$$

Termination:

$$R_n\cdot + Z \xrightarrow{k_t} P_n$$

with
$$R_t = k_t[Z][R\cdot] \tag{6}$$

Transfer:

$$R_n\cdot + Y \xrightarrow{k_{tr}} P_n + Y\cdot$$

with
$$R_{tr} = k_{tr}[Y][R\cdot] \tag{7}$$

Polymer linking:

$$R_n \ldots A \xrightarrow{k_c} R_nA\cdot$$

with
$$R_c = k_c[R_n \ldots A] = k_c K_A f_A [R\cdot] \tag{8}$$

$$R_nA\cdot + P \xrightarrow{k_c'} P$$

with
$$R_c' = k_c'[R_nA\cdot][P] \tag{9}$$

The rate of initiation may be considered to be proportional to the densities of ethylene and acetylene presented in the reactor and to the intensity of radiation, because the initiation step is brought about by the absorption of the radiation energy by ethylene and acetylene. If it is assumed that the initiation reactions from ethylene and from acetylene take place independently, the overall rate of initiation R_i is represented by eq. (10).

$$\begin{aligned} R_i = R_{iE} + R_{iA} &= k_{iE} I \rho_E + k_{iA} I \rho_A \\ &= k_{iE} I \rho_E (1 + k_{iA} \rho_A / k_{iE} \rho_E) \end{aligned} \qquad (10)$$

Since it has been concluded[1] that the chain free radicals having acetylene ends react to a very small extent with both ethylene or acetylene, $R_n\cdot$ in this mechanism is considered to represent only the chain free radicals having ethylene ends. Accordingly, the propagation is assumed to be brought about by the same mechanism as that in the polymerization of pure ethylene.[5] From the fact that both polymer yield and molecular weight decrease markedly with increasing acetylene content (Figs. 2 and 3), the rate of propagation can be at least considered to be retarded by adding acetylene. The retardation is assumed to be caused by the reduction of the concentration of $R_n\cdot$ through the coordination of acetylene to $R_n\cdot$ to form coordination product $R_n \ldots A$ [reaction (5)].

Since it is considered that the bimolecular termination does not occur in the polymerization of ethylene containing acetylene from the dependence of dose rate for polymer yield described above, the termination is assumed to be brought about only by terminator Z. The same transfer mechanism as that in the polymerization of pure ethylene is assumed.[2] In the previous paper,[1] the occurrence of a reaction which reduces the number of polymer chains has been suggested from the marked decrease in the number of moles of polymer chain with a small amount of acetylene. A polymer linking reaction as is shown by reactions (8) and (9) is, therefore, proposed as a reaction which reduces the number of polymer chains. In reaction (9), the reactions of $R_nA\cdot$ with the active ends of $R_n\cdot$ and $R_nA\cdot$ are, however, assumed not to occur. Assuming a steady state with respect to the concentration of $R_nA\cdot$, the rate of polymer linking is given by eq. (8).

The reaction pressure in the experiments listed in Table III remained essentially constant during polymerization because of the low conversion (below 6% of monomers), and no marked difference in acetylene contents before and after the irradiation has been observed.[1] From these results, it seems reasonable to assume that the density and fugacity of ethylene and of acetylene are constant in the course of the polymerization.

From the long-chain approximation, the overall rate of polymerization R is approximately equal to the rate of propagation; accordingly, it becomes:

$$R = dM_p/dt \simeq R_p = k_p K_c f_E^2 [R\cdot] \qquad (11)$$

where M_p represents the amount of monomer polymerized and t is time. The concentration of active polymer chain $[R\cdot]$ is given by eq. (12) without the assumption of a stationary-state.

$$[R\cdot] = \int_0^t R_i dt - \int_0^t R_t dt - \int_0^t R_c dt - [R_n \ldots A] \qquad (12)$$

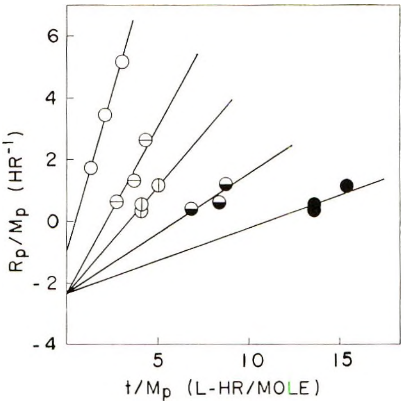

Fig. 4. R_p/M_p vs. t/M_p. Reaction conditions same as given for Fig. 2.

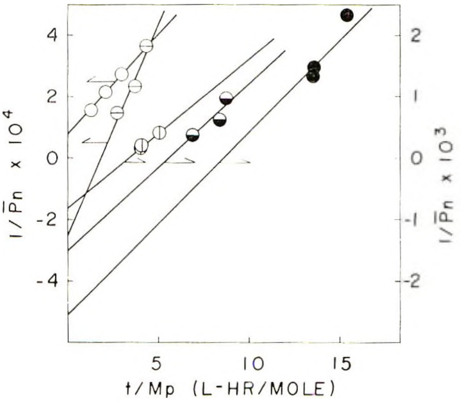

Fig. 5. $1/\bar{P}_n$ vs. t/M_p. Reaction conditions same as given for Fig. 2.

From the combination of eqs. (5), (6), (8), (10), and (12), and the relation of $M_p \simeq \int_0^t R_p dt$ [eq. (11)], $[\mathrm{R}\cdot]$ is given as:

$$[\mathrm{R}\cdot] = \frac{R_i t}{(1 + K_A f_A)} - \frac{(k_t[\mathrm{Z}] + k_c K_A f_A) M_p}{k_p K_e f_E^2 (1 + K_A f_A)} \tag{13}$$

where $[\mathrm{Z}]$ is assumed to be constant throughout the polymerization. By introducing eq. (13) into eq. (11) and rearranging, eq. (14) is obtained.

$$R/M_p \simeq R_p/M_p = \{R_i k_p K_e f_E^2/(1 + K_A f_A)\}(t/M_p) - (k_t[\mathrm{Z}] + k_c K_A f_A)/(1 + K_A f_A) \tag{14}$$

A distinct linear relation exists between R_p/M_p and t/M_p at each respective acetylene content as is indicated in Figure 4. The slope of the line s and the intercept on the ordinate y are represented as follows:

$$s = R_i k_p K_e f_E^2/(1 + K_A f_A) \tag{15}$$

$$y = -(k_t[\mathrm{Z}] + k_c K_A f_A)/(1 + K_A f_A) \tag{16}$$

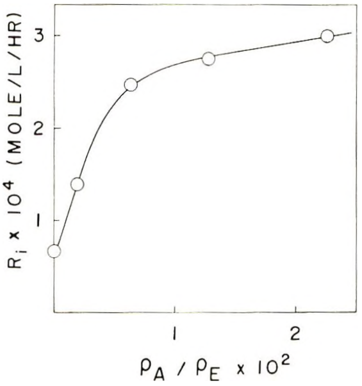

Fig. 6. Relation between the rate of initiation R_i and the ratio of density of acetylene to that of ethylene ρ_A/ρ_E under a pressure of 400 kg/cm² at 30°C with a dose rate of 1.1×10^6 rad/hr.

Degree of Polymerization. The number-average degree of polymerization at a given reaction time is written for the polymerization with the reaction mechanism described above as follows:

$$\bar{P}_n = \int_0^t R_p dt \Big/ \left(\int_0^t R_i dt - \int_0^t R_c dt + \int_0^t R_{tr} dt \right) \tag{17}$$

where $\bar{P}_n$ represents the number-average degree of polymerization. From eqs. (7), (8), (10), and (11), the reciprocal of $\bar{P}_n$ is expressed by:

$$1/\bar{P}_n = R_i(t/M_p) - (k_c K_A f_A - k_{tr}[Y])/k_p K_e f_E^2 \tag{18}$$

where [Y] is assumed to be constant in the course of the polymerization.

The plot of the reciprocal of $\bar{P}_n$ against t/M_p gives a straight line, as is shown in Figure 5. The slope of the line s' represents the value of the rate of initiation R_i, and the intercept on the ordinate y' is represented by eq. (19).

$$y' = -(k_c K_A f_A - k_{tr}[Y])/k_p K_e f_E^2 \tag{19}$$

Effects of Acetylene on the Initiation. As is shown in Figure 6, the extent of increment of the rate of initiation decreases with increasing the ratio of density of acetylene to that of ethylene, that is, ρ_A/ρ_E. This result is inconsistent with the relation of eq. (10). Since it has been reported[1] that the hydrocarbons with low molecular weight are formed during the polymerization of ethylene in the presence of acetylene, the discrepancy between the result of graphical analysis and eq. (10) may be ascribed to the formation of these hydrocarbons because only the rate of formation of initiating species grown into high polymer is given by this analysis.

The value of k_{iA}/k_{iE} calculated from the slope of tangent at ρ_A/ρ_E near zero of the curve in Figure 6 by using the relation of eq. (10) is about 600, which means the rate of initiation from acetylene is about 600 times that from ethylene. The elementary reactions of initiation of the polymerization of pure ethylene are represented by eqs. (20)–(24):[6]

$$C_2H_4 \rightsquigarrow C_2H_4^* \tag{20}$$

$$C_2H_4^* \rightarrow C_2H_3\cdot^* + H\cdot \tag{21}$$

$$C_2H_3\cdot^* \rightarrow C_2H_2 + H\cdot \tag{22}$$

$$2H\cdot + X \rightarrow H_2 + X \tag{23}$$

$$H\cdot + C_2H_4 \rightarrow C_2H_5\cdot \tag{24}$$

Here X represents the wall of the reactor or a substance which acts as a catalyst.

As described in a previous paper,[1] since no triple bond is found in the polymer formed, the initiation from acetylene, which is considerably larger than that from ethylene, is not considered to occur by the addition of ethylene to the initiating species having a triple bond formed by radiolysis of acetylene. The initiation from acetylene is, therefore, considered to be brought about by a mechanism in which various intermediates formed by radiolysis of acetylene abstract hydrogen from ethylene to form $C_2H_3\cdot^*$, and the intermediates from which hydrogen radical is liberated are considered to be still unstable and consecutively abstract hydrogen from ethylene. The vinyl radicals formed by this mechanism will easily decompose to produce C_2H_2 and $H\cdot$ [reaction (22)]. From the fact that the rate of formation of hydrogen is independent of acetylene content,[1] the hydrogen radical formed by this mechanism is considered to form mainly initiating species by reaction (24).

Effects of Acetylene on the Propagation. When the ratio of the value of the slope of the line in Figure 4 to that in Figure 5 is represented as s'', s'' is given as:

$$s'' = s/s' = k_p K_e f_E^2/(1 + K_A f_A) \tag{25}$$

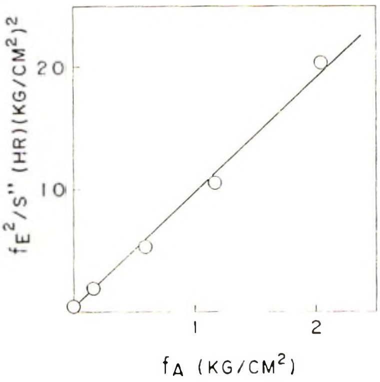

Fig. 7. Relation between the value of f_E^2/s'' and acetylene fugacity f_A. Reaction conditions same as given for Fig. 6.

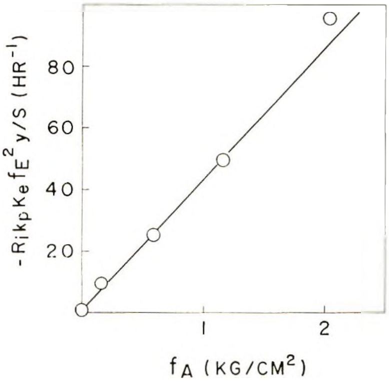

Fig. 8 Relation between the value of $-R_ik_pK_ef_E^2y/s$ and acetylene fugacity f_A. Reaction conditions same as given for Fig. 6.

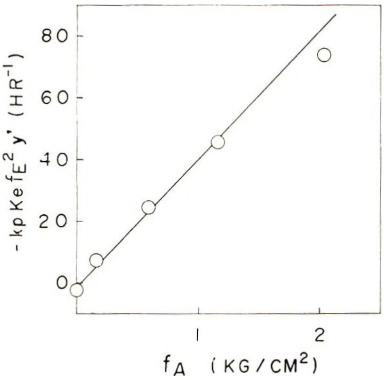

Fig. 9. Relation between the value of $-k_pK_ef_E^2y'$ and acetylene fugacity f_A. Reaction conditions same as given for Fig. 6.

Hence:

$$f_E^2/s'' = 1/k_pK_e + K_Af_A/k_pK_e \tag{26}$$

As is shown in Figure 7, a linear relation is obtained by plotting the values of f_E^2/s'' against acetylene fugacity.

From this result, it seems reasonable to conclude that the propagation is retarded by the coordination of acetylene to the active polymer chain, which is a reaction competing with the addition reaction of ethylene. Further, it is concluded that the rate of addition reaction of ethylene to the active polymer chain [reaction (4)] is not affected by adding acetylene because the value of k_pK_e is considered to remain unchanged.

Effects of Acetylene on the Termination, Transfer, and Polymer Linking. From eqs. (15) and (16), eq. (27) is obtained.

$$-R_ik_pK_ef_E^2y/s = k_t[Z] + k_cK_Af_A \tag{27}$$

where the value of k_pK_e can be obtained from the intercept on the ordinate of the line in Figure 7. As is shown in Figure 8, a linear relation is given between the value of $-R_ik_pK_ef_E{}^2y/s$ and acetylene fugacity. Similarly, by using the relation of eq. (28) which is obtained from eq. (19), a linear relation is given between the value of $-k_pK_ef_E{}^2y'$ and acetylene fugacity (Fig. 9).

$$-k_pK_ef_E{}^2y' = k_cK_Af_A - k_{tr}[\mathrm{Y}] \qquad (28)$$

From these results, it can be considered that both the termination by a terminator Z and the transfer by a transfer agent Y are not affected by adding acetylene. In addition, although the mechanism is not clear, the fact that the slope of the line in Figure 8 is almost equal to that in Figure 9 suggests the occurrence of polymer linking by acetylene such as presumed above [reactions (8) and (9)].

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Investigations on Aromatic Polyesters with Polynaphthalene Systems in the Main Chain. I. Low-Temperature Solution Polycondensation

ZBIGNIEW JEDLIŃSKI and DANUTA SEK, *Department of Polymer Technology, Polish Academy of Sciences, Silesian Polytechnical Institute, Gliwice, Poland*

Synopsis

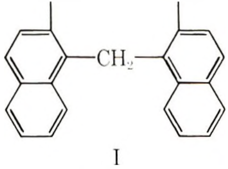
A series of aromatic polyesters has been prepared by low-temperature solution polycondensation of derivatives of dihydroxydinaphthyl or dihydroxydinaphthylmethane with terephthaloyl chloride. The chemical, physical, and thermal properties of some polyesters have been investigated. Some of the polyesters obtained have high melting temperatures (340–420°C) and very good thermal resistance. In spite of their high melting temperatures some polymers give solutions in organic solvents which make it possible to produce films and coatings with good dielectric and mechanical properties and with a relatively high thermal resistance.

INTRODUCTION

Generally, to obtain polymers with a higher thermal resistance, investigators try to replace aliphatic constituents by aromatic ones. Morgan,[1] as well as Korshak,[2] obtained polyesters based on phenolphthalein and 1,2-dihydroxynaphthalene[3] with high melting temperatures.

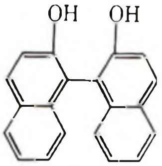
When dihydroxyanthraquinones[4] have been used for the synthesis of polyesters, the resulting products had a melting temperature about 500°C.

In the present study, in order to gather a large quantity of aromatic rings in the polyester chain, bisphenols with condensed aromatic rings (I–V) have been used as the alcohol component in the polyester synthesis. These phenols were esterified with terephthaloyl chloride, and a series of new polyesters with aromatic polynaphthalene systems in the chain has been obtained.



I

2,2′-Dihydroxy-1,1′-dinaphthylmethane

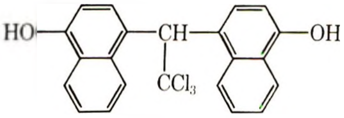


II

2,2′-Dihydroxydinaphthyl-1,1′

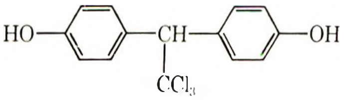
III

4,4′-Dihydroxydinaphthyl-1,1′



IV

1,1-Bis(4-hydroxynaphthyl)2,2,2-trichloroethane



V

1,1-Bis(4-hydroxynaphthyl)2,2,2-trichloroethane

The structure and physical, chemical, and thermal properties of the polymers have been investigated. Some of them show a certain solubility in organic solvents, such as methylene chloride, tetrachloroethane, and they have film-forming properties. Studies of the mechanical, thermal, and dielectric properties of the films show that these polymers may be used as dielectrics with good thermal stability.

EXPERIMENTAL

Reagents

Triethylamine (anhydrous) was a commercial product (L. Light, Colnbrook, England), bp 89.5°C.

Ethylene chloride was dried with anhydrous $CaCl_2$ and distilled at 83°C.

Terephthaloyl chloride, mp 83°C, was obtained from Koch-Light Laboratories Ltd., England.

2,2-Bis(4-hydroxyphenyl)propane, was crystallized in toluene, mp 158°C.

Phenols

2,2′-Dihydroxy-1,1′-dinaphthylmethane (I) was prepared by condensing formalin with 2-naphthol. The reaction was carried out in methyl alcohol and in the presence of crystalline sodium acetate.[5] The product was purified by recrystallization in methyl alcohol, mp 192°C.

2,2′-dihydroxydinaphthyl-1,1′ (II) and 4,4′-dihydroxydinaphthyl-1,1′ (III) were prepared by oxidizing the appropriate naphthols with ferric chloride in aqueous solution.[6] The bisnaphthols were purified by crystallization—2,2′-dihydroxydinaphthyl-1,1′ in toluene, 4,4′-dihydroxydinaphthyl-1,1′ in methyl alcohol—and the products had melting points of 216 and 300°C, respectively.

1,1-Bis(4-hydroxynaphthyl)2,2,2-trichloroethane (IV) was prepared by condensing 1-naphthol with chloral in acetic acid.[7] The product was washed with acetic acid and dried under vacuum, mp 200°C.

1,1-Bis(4-hydroxyphenyl)2,2,2-trichloroethane (V) was prepared by condensing phenol with chloral in the presence of sulfuric acid and acetic acid.[8] The product was purified by crystallization in a mixture of equal volume of ethyl alcohol and water, mp 195°C.

Polycondensation

The polycondensation of dihydroxydinaphthyls or dihydroxydinaphthylmethane with terephthaloyl chloride was carried out by means of the low-temperature solution method, suggested by Morgan for the synthesis of polyesters from phenolphthalein.[1,9]

Ethylene chloride was used as a solvent. Triethylamine was used as acceptor of hydrogen chloride evolved during the esterification and the accelerator of the process was triethylamine; the triethylamine level used was 2 moles per mole bisphenol.

The reaction was carried out at 20°C by adding slowly a solution of acid chloride in ethylene chloride to the appropriate bisphenol solution. The reagent concentration (acid chloride and bisphenol) was 0.2 mole/l. The mixture was vigorously stirred all the time. After 30 min, acetone was added to the reaction mixture and the polymer precipitated. Polymer was separated and washed with acetone, water, and again with acetone. The structure and properties of some polyesters are summarized in Table I.

Measurements of Properties

Melting Point. The melting point determination was carried out in a capillary tube at a heating rate of 5°C/min.

Acid Number. The determination of the carboxyl group content was conducted by titrating the polyester solution in pyridine with 0.1*N* alcoholic KOH.

Hydroxyl Number. The hydroxyl groups were determined by an acetylation method with acetic anhydride in pyridine.

Viscosity. The viscosity was measured in an Ubbelohde viscometer at 18 ± 0.1°C on a solution of 1 g polyester in 100 ml of tetrachloroethane.

Thermogravimetric Analysis. Measurements of weight loss were conducted in a derivatograph (MOM-Budapest, of Paulik, Paulik, and Erdey) at a heating rate of 10°C/min.

TABLE I
Comparison of Properties of the Polyesters

No.	Components		Yield, %	Properties of polymers			η_{red}	$\bar{M}_n$
	Bisphenol	Diacid chloride		Melting point, °C	Acid number, mg KOH/g	Hydroxyl number, mg KOH/g		
1	4,4′-Dihydroxy-dinaphthyl 1,1′ (III)	Terephthaloyl	74.0	420 (dec)	Partially soluble		—	—
2	1,1 Bis(4-hydroxy-naphthyl)2,2,2 trichloroethane (IV)	Terephthaloyl	80.6	340	17.0	35.0	0.313	2160
3	1,1 Bis(4-hydroxy-phenyl)2,2,2-trichloroethane (V)	Terephthaloyl	81.3	270	7.7	5.1	0.425	8760
4[a]	4,4′-Dihydroxydi-naphthyl-1,1′ (III) + 2,2-bis(4-hy-droxyphenyl)-pro-pane	Terephthaloyl	78.2	420	4.3	5.8	2.224	11200
5[a]	4,4′-Dihydroxy-dinaphthyl-1,1′ (III) + 1,1 bis-(4-hydroxyphenyl)-2,2,2-trichloro-ethane	Terephthaloyl	75.5	300	4.3	6.0	1.212	10900

6[a]	2,2′-Dihydroxy-1,1′-dinaphthylmethane (I) + 4,4′-dihydroxydinaphthyl-1,1′ (III)	Terephthaloyl	68.0	240	10.1	19.8	0.480	3750
7[a]	1,1-Bis(4-hydroxynaphthyl)-2,2,2-trichloroethane (IV) + 1,1-bis-(4-hydroxyphenyl)-2,2,2-trichloroethane	Terephthaloyl	77.4	340	14.9	11.4	0.439	4300
8[a]	1,1-Bis(4-hydroxynaphthyl)-2,2,2-trichloroethane (IV) + 2,2-bis(4-hydroxyphenyl)propane	Terephthaloyl	73.6	340	11.1	30.0	0.400	2730
9[a]	2,2′-Dihydroxy-1,1′-dinaphthylmethane (I) + 2,2-bis-(4-hydroxyphenyl)-propane	Terephthaloyl	61.9	190	10.0	46.3	0.176	2000
10[a]	2,2′-Dihydroxy-dinaphthyl-1,1′ (II) + 2,2-bis-(4-hydroxyphenyl)-propane	Terephthaloyl	59.0	260	14.9	54.1	0.164	1625

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[a] In the case of copolyesters, the molecular ratio of bisphenolic components is 1:1.

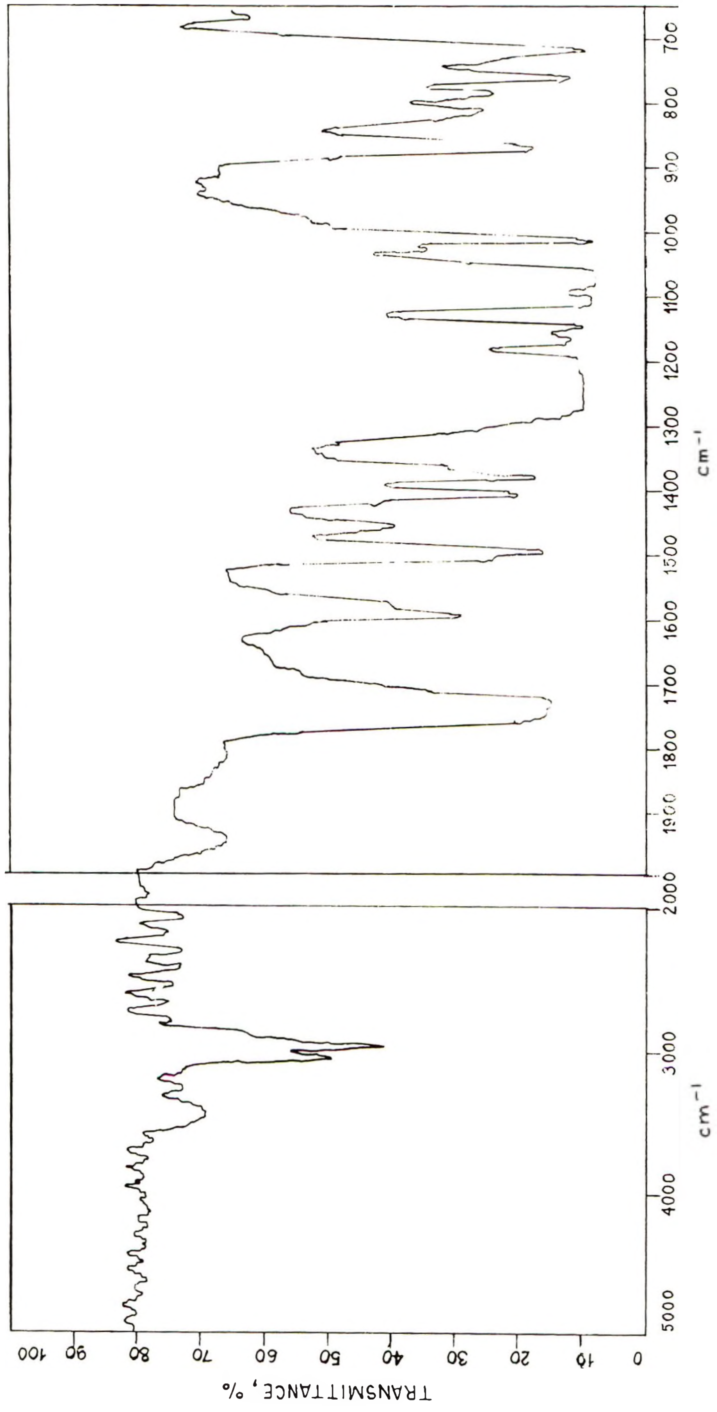


Fig. 1. Infrared spectrum of polyester 4.

Electrical Properties. Measurements of electrical properties followed ASTM methods.

DISCUSSION OF RESULTS

Polymer Structure

The structure of polymers was studied by means of the spectrophotometric and chemical analysis. As an example the infrared spectrum for the copolyester from 4,4′-dihydroxydinaphthyl-1,1′, Bisphenol A, and terephthalic acid (4 in Table I) is shown in Figure 1. The three absorption bands in the region 730–880 cm^{-1} are assigned to the out-of-plane deformation vibration of the hydrogen atoms, remaining on the ring of naphthol. The absorption bands at 1030 and 1090 cm^{-1} are assigned to in-plane C — H deformation vibration and those in the range of 1580–1600 cm^{-1} to the C=C stretching vibration in the ring. The strong absorption bands at 1220 and 1280 cm^{-1} are derived from the —C—O— stretching vibration in aromatic esters. The strong absorption bands at 1380 cm^{-1} are derived from symmetrical scissoring vibrations in $-\mathrm{CH}_3$ groups and those at 1490 cm^{-1} from asymmetric scissoring vibration in $-\mathrm{CH}_3$ groups. A strong absorption band at 1750 cm^{-1} is characteristic for C=O stretching vibration and that at 2960 cm^{-1} is caused by the asymmetric stretching vibration in the $-\mathrm{CH}_3$ group. A weak absorption band at 3500 cm^{-1} is assigned to free —OH group stretching vibration.

The results of the infrared spectral analysis as well as the chemical analysis show that the copolyester has a linear structure.

Molecular Weight and Physical and Chemical Properties

Polyesters obtained from 2,2′-dihydroxy-1,1′-dinaphthylmethane (I) and 2,2′-dihydroxydinaphthyl-1-1′ (II) have low molecular weights.

Higher molecular weights are obtained for polymers from 4,4′-dihydroxydinaphthyl-1,1′ (III). This may be the result of symmetric dislocation of the functional groups in the molecule. Because the condensation product of 4,4′-dihydroxydinaphthyl-1,1′ (III) and terephthalic acid is only slightly soluble in most solvents, some syntheses have been carried out with the addition of 2,2 bis(4-hydroxyphenyl) propane.

Copolyester 4 (Table I), containing 50 mole-% 4,4′-dihydroxydinaphthyl-1,1′, 50 mole-% 2,2 bis(4-hydroxyphenyl)propane (Bisphenol A) and terephthalic acid has a good solubility as well as a high molecular weight. From this polyester films and coatings can be produced.

It has been noticed that the increase of 4,4′-dihydroxydinaphthyl-1,1′ contents in such copolyesters causes an increase of the viscosity of polymers (Fig. 2). The increase of 4,4′-dihydroxydinaphthyl-1,1′ content in copolyesters decreases the solubility and with total phenol contents of more than 75 mole-% such polymers are partially soluble.

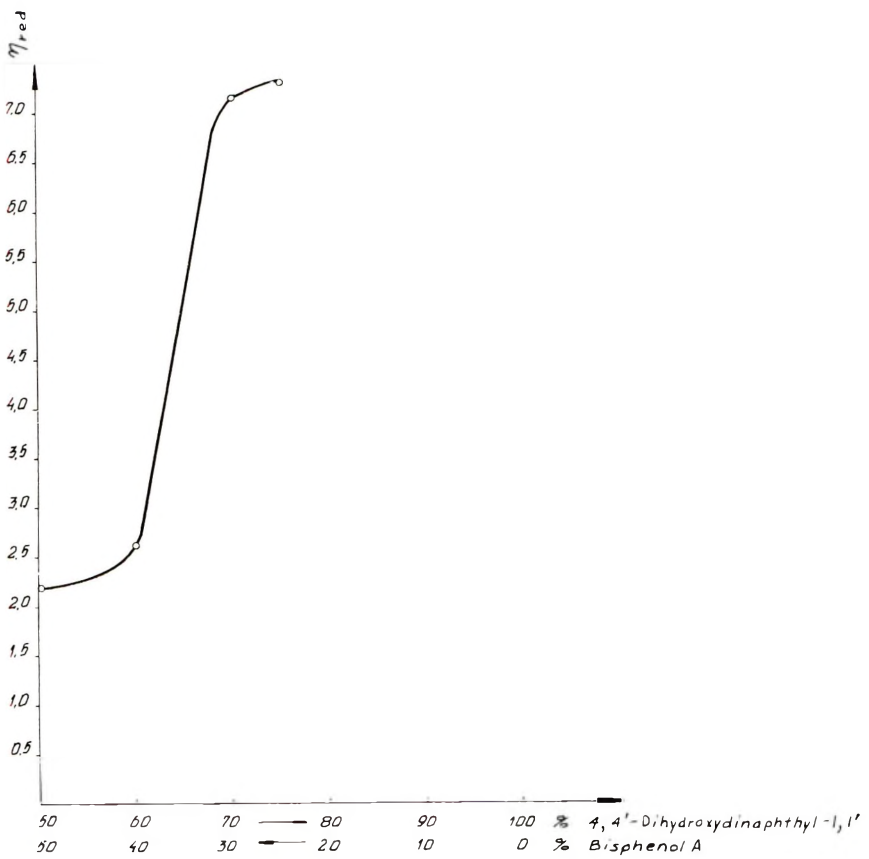


Fig. 2. Dependence of the reduced viscosity η_{red} on the mole ratio of 4,4'-dihydroxydinapththyl-1,1'- and Bisphenol A.

Thermal Properties

The thermal properties of aromatic polyesters were determined from measurements of weight loss during heating in air at 250°C for 180 hr. Polyester 1, 2, 3, 4, 5, 7, 8, and 10 (Table I) were examined. The results are presented in Figure 3. All polyesters were examined under the same conditions.

The least weight loss (5.70%) after 180 hr of heating is shown by the copolyester 4,4'-dihydroxydinaphthyl-1,1' and Bisphenol A with terephthalic acid.

Polyesters and copolymers containing chlorine atoms in the molecules (polyesters 2, 3, 5, 7, 8) show greater weight losses, probably on account of the evolution of hydrogen chloride during heating.

A more exact opinion on the thermal properties of polymers has been obtained from the results of the differential thermal analysis and thermogravimetric analysis.

The results of the differential thermal analysis and of thermogravimetric analysis in air are presented in Figure 4. The decomposition of polyester 1 in air begins at about 420°C. The decomposition ceases at 980°C. The thermal decomposition of polyester 4 begins at about 400°C and ends at about 840°C. Polyesters containing chlorine in their molecule (polyesters 5, 7, 8) show a low thermal resistance and begin to decompose at about 280°C.

The thermal decomposition in nitrogen of all examined polyesters is much slower than in air, but the beginning of the decomposition in air and nitrogen do not differ appreciably.

Mechanical and Electrical Properties of Films

Polyesters with the highest reduced viscosities, e.g., 3, 4, 5, and 7 (Table I) have film forming properties. The remaining polymers either do not form films or, if so, form very brittle films. Films were formed from a 8% polymer solution in tetrachloroethane. The foils were not set. The mechanical and electrical properties of the films are presented in Table II.

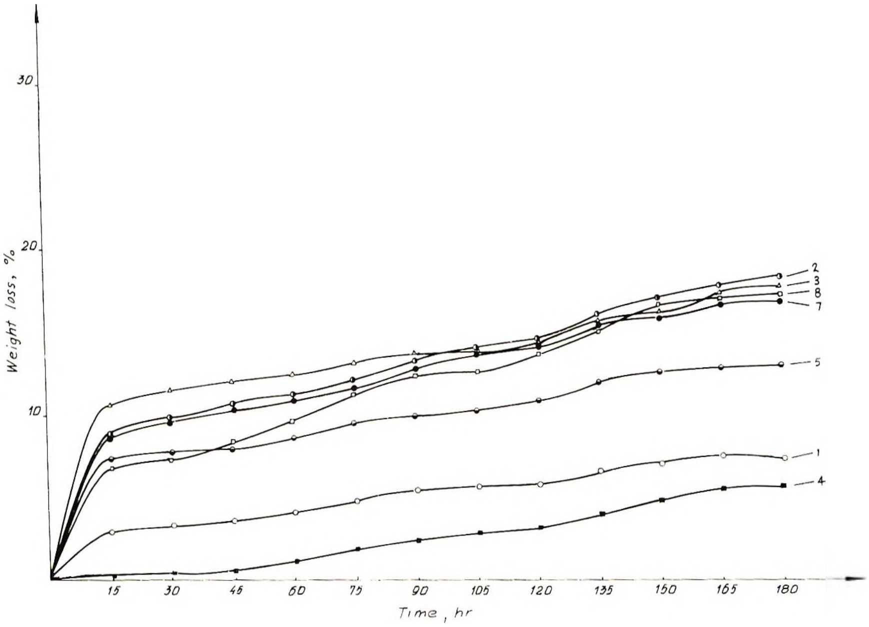


Fig. 3. Weight loss of polyesters 1, 2, 3, 4, 5, 7, and 8 at 250°C.

For the sake of comparison, Table II shows also some properties of commercial films, investigated under the same conditions. Before measurements, the films were stored in air under the following conditions: time, 24 hr; temperature, 20 ± 5°C; humidity, 65 ± 3%.

To investigate the influence of temperature and time of aging upon the dielectric properties, the films were heated at 175°C for 48, 96, and 192 hr.

TABLE II
Mechanical and Electrical Properties of Films

Polymer	Tensile strength, kg/cm²	Volume resistivity (20°C), ohm-cm	Surface resistivity (20°C), ohm	tan δ			
				50 Hz, 20°C	800 Hz, 20°C	300 kHz, 20°C	300 kHz, 180°C
4	475	1.8×10^{14}	2.1×10^{15}	0.0030	0.0016	0.0048	0.0052
5	865	3.4×10^{15}	6×10^{16}	0.0050	0.0016	0.0042	0.0051
3	372	3.3×10^{16}	5.9×10^{16}	0.0043	0.0018	0.0064	0.0059
7	270	4.8×10^{15}	8.4×10^{15}	0.0030	0.0019	0.0048	0.0050
Polycarbonate	610	2.7×10^{17}	1.5×10^{16}	0.0030	0.0019	0.0069	0.0051
Cellulose acetobutyrate	846	1.4×10^{17}	8.4×10^{15}	0.0031	0.0026	0.0069	0.0058

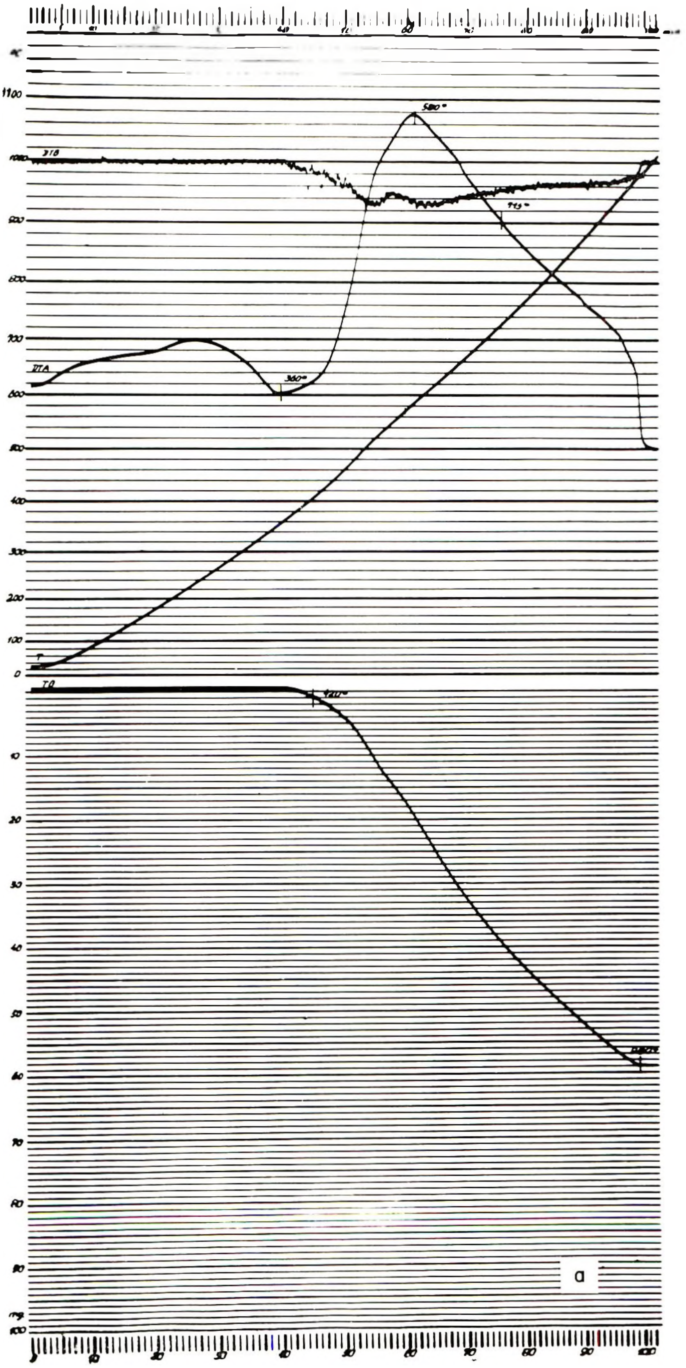
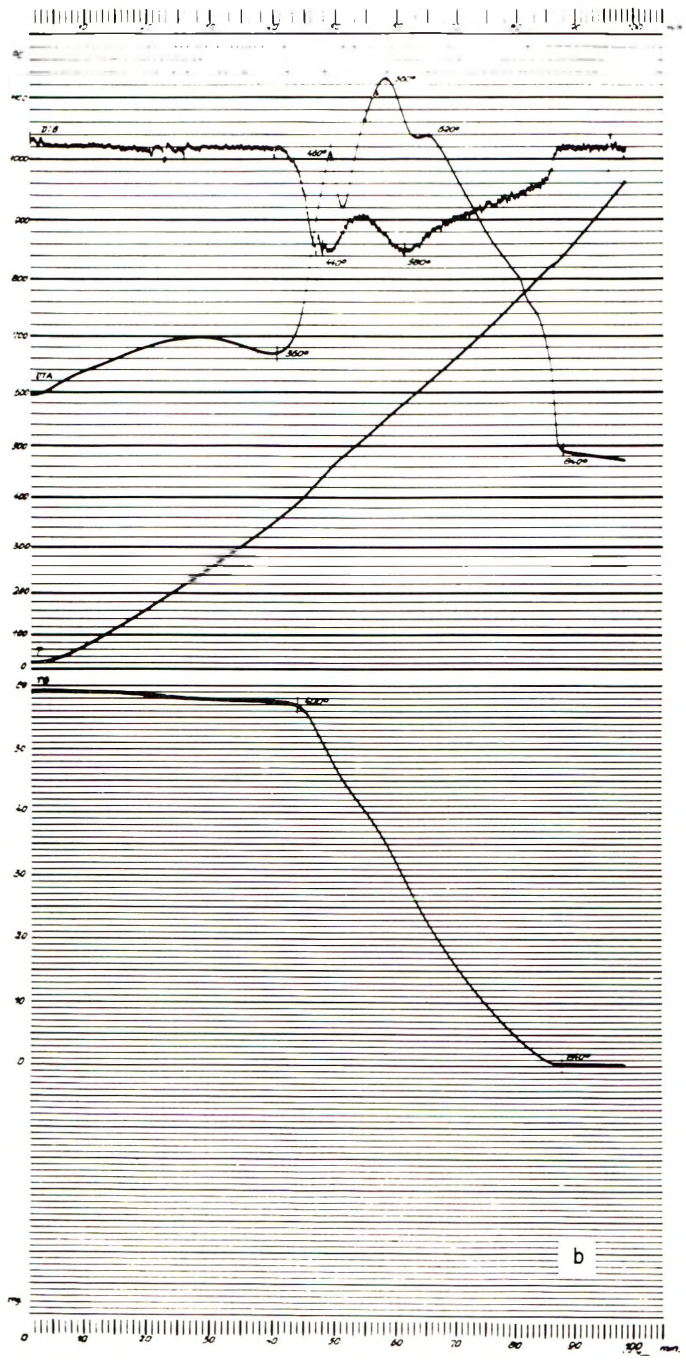


Fig. 4 (*continued*)



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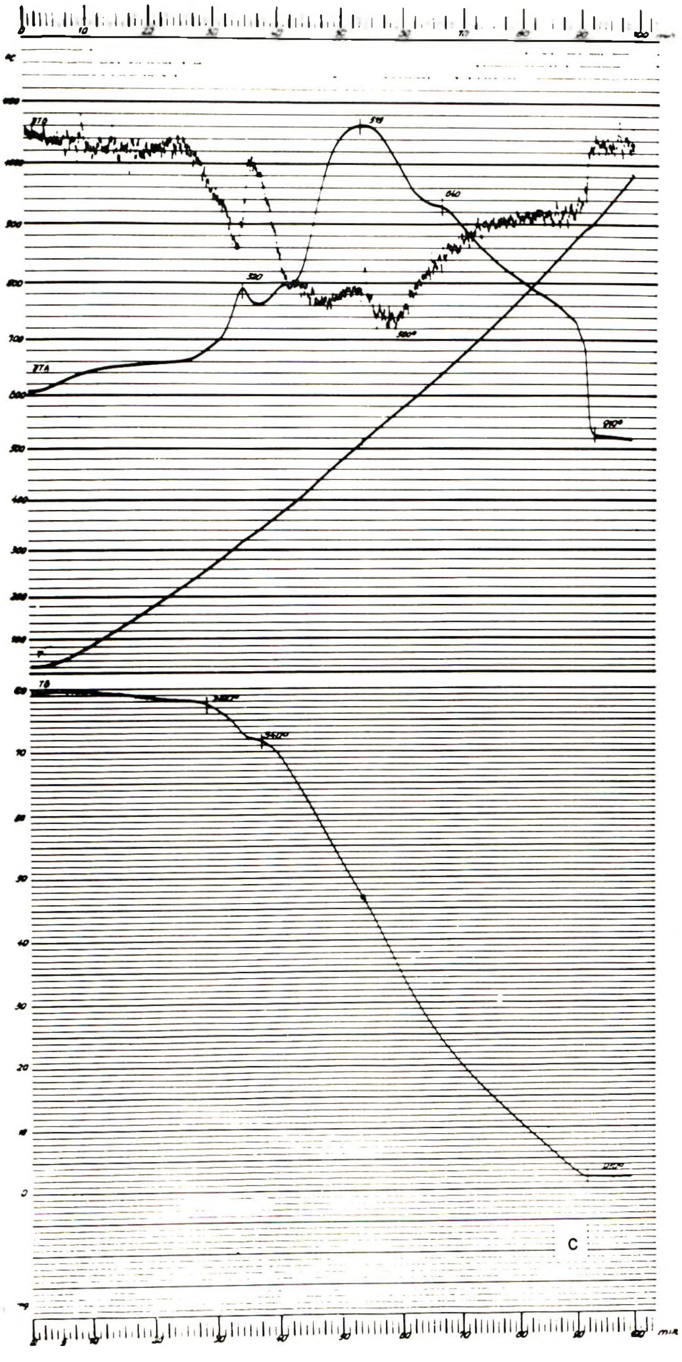

Fig. 4. (*continued*)

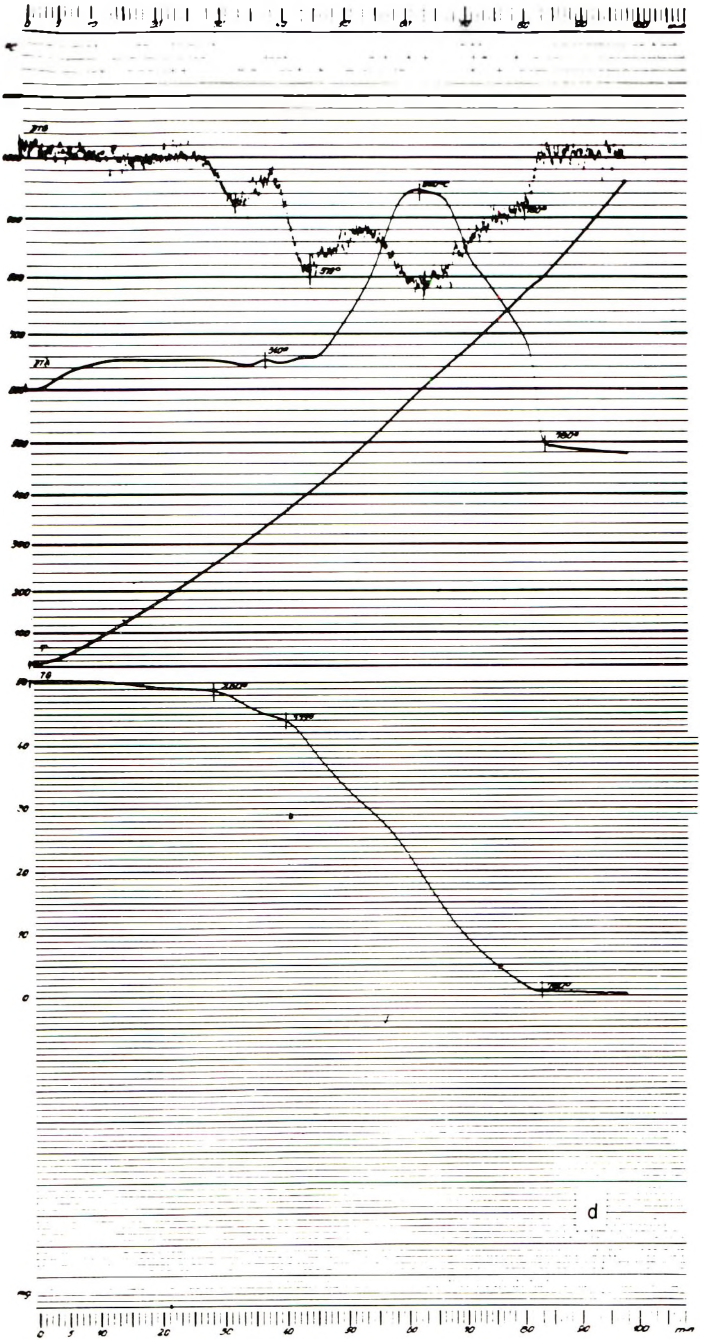

Fig. 4 (*continued*)

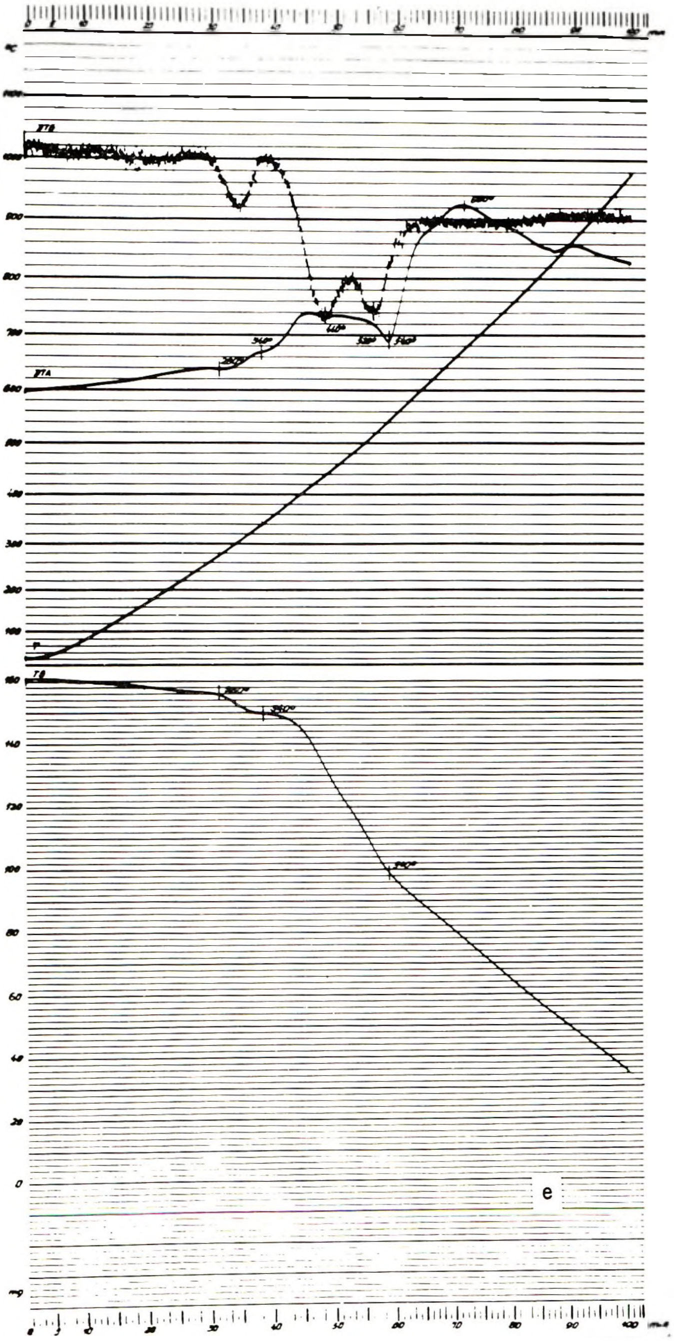

Fig. 4. Differential thermal analysis curves of polyesters, 1, 4, 5, 7, and 8 heated in air: (*a*) polymer 1; (*b*) polymer 4; (*c*) polymer 5; (*d*) polymer 7; (*e*) polymer 8.

Figures 5 and 6 represent the dissipation factor, depending on the aging time at 175°C and on the frequency of the current. In comparison with other films a film made of polyester 4 shows an unchanged and lowest dissipation factor for a frequency of 800 Hz after aging at an elevated temperature (Fig. 5). With 300 kHz frequency the dissipation factor for the film made of polyester 4 also shows lower values than commercial foils, especially after a longer period of aging (Fig. 6).

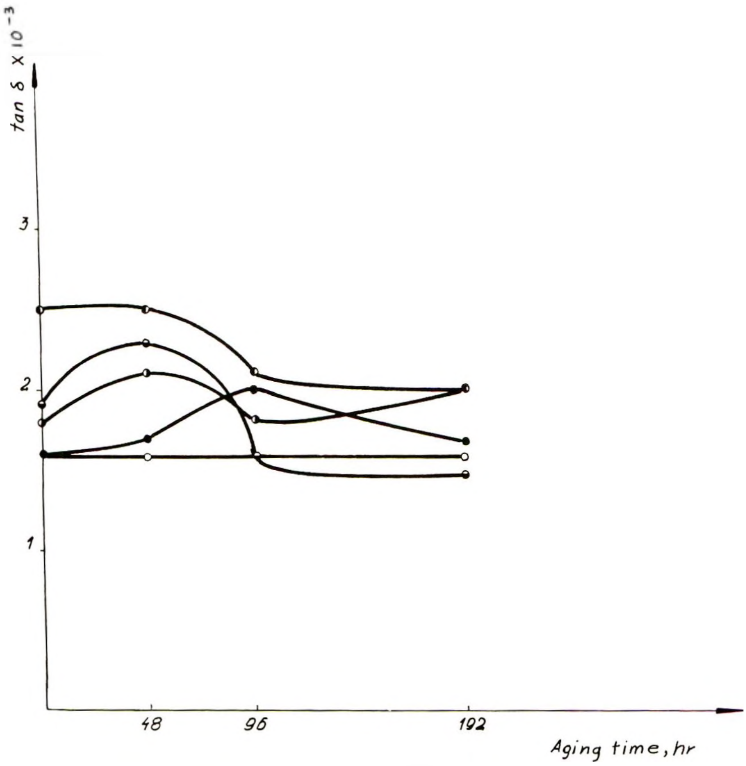

Fig. 5. Dependence of dissipation factor (800 Hz, 20°C) on aging time: (○) polymer 4; (●) polymer 5; (◑) polyethylene terephthalate; (◒) polycarbonate; (◐) cellulose acetobutyrate.

Solutions of polymers 3, 4, 5, and 7 form adhesive, flexible coatings on steel or nonferrous metals (copper or aluminum).

Films and coatings made of polymers with chlorine atoms in the molecule (3, 5, 7) have self-extinguishing properties.

CONCLUSIONS

The results of investigations of the synthesis and properties of aromatic polyesters with polynaphthalene units in the main chain show that there exists a close connection between the structure of the monomers and the properties of product.

Polyesters which were obtained from monomers with a symmetrical structure, like 4,4′-dihydroxydinaphthyl-1,1′ (III), have the highest melting point and a very good thermal resistance. Several polymers are soluble in some organic solvents, which makes it possible to produce coatings and films with good thermal, dielectric, and mechanical properties.

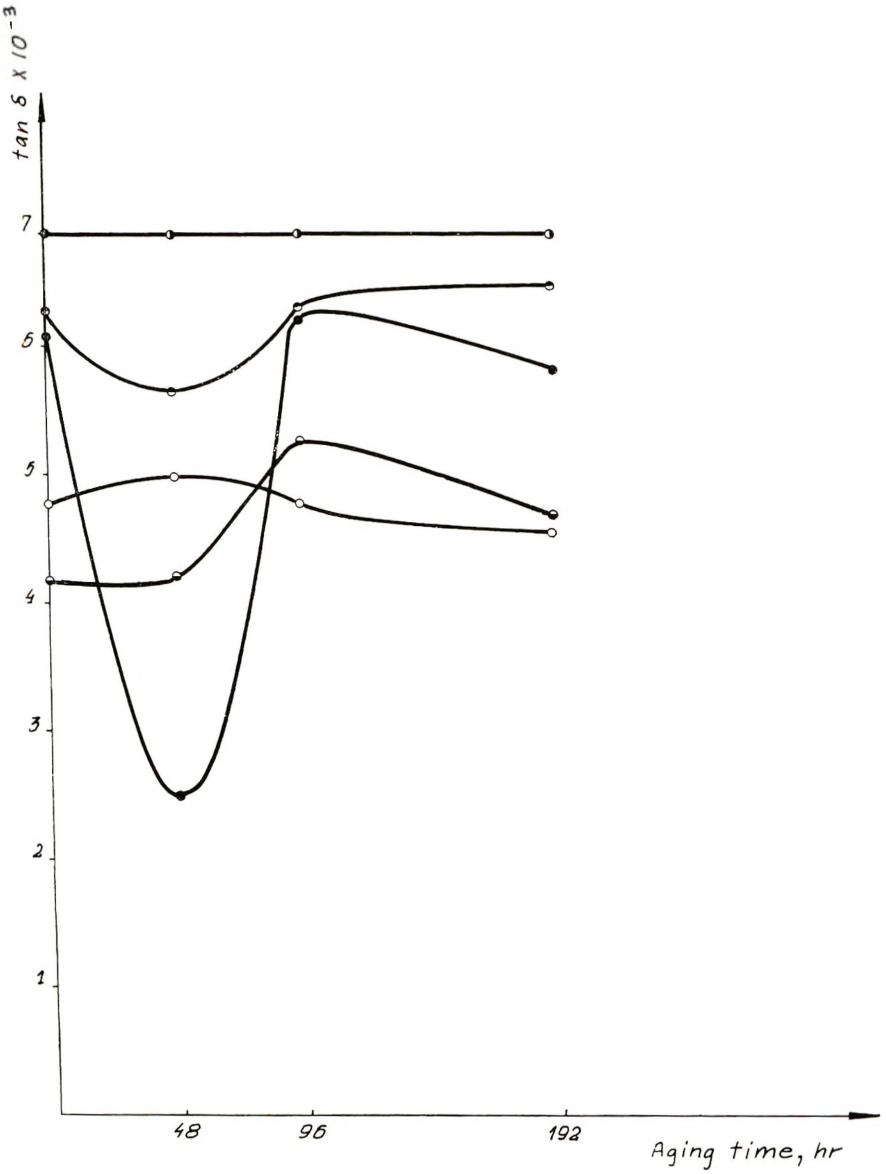

Fig. 6. Dependence of dissipation factor (300 kHz, 20°C) on aging time: (○) polymer 4; (◒) polymer 5; (●) poly(ethylene terephthalate); (◓) polycarbonate; (◑) cellulose acetobutyrate.

Tests of accelerated aging of films of some of the polymers at 175°C for 48, 96, and 192 hr and the investigation of their properties show that the dielectric properties deteriorated only slightly on aging, whereas in some cases they were not changed. Thus these materials may be suitable for use as dielectrics.

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Chain Transfer Constants for Vinyl Monomers Polymerized in Methyl Oleate and Methyl Stearate

EDMUND F. JORDAN, JR., BOHDAN ARTYMYSHYN, and
A. N. WRIGLEY, *Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Philadelphia, Pennsylvania 19118*

Synopsis

Chain transfer constants were obtained for styrene, methyl methacrylate, methyl acrylate and vinyl acetate, polymerized in methyl oleate and methyl stearate at 60°C. Transfer constants increased in the order: methyl methacrylate $<$ styrene $<$ methyl acrylate $\ll$ vinyl acetate in both solvents. Average values of the transfer parameters were: for methyl oleate, $Q_{tr} = 2.04 \times 10^{-4}$, $e_{tr} = 1.08$; for methyl stearate, $Q_{tr} = 0.373 \times 10^{-4}$, $e_{tr} = 1.01$. Indication that polar species predominate in the transition state is supported by the observed order of reactivity The usual rate dependence appeared to be followed by all of the monomers except vinyl acetate, which was retarded, severely in methyl oleate. Transfer in methyl oleate was about 5.8 times greater than that found in methyl stearate for these four monomers. The internal allylic double bond of methyl oleate had about the same reactivity in transfer as had the terminal unsaturation in *N*-allylstearamide at 90°C. Rough estimates were obtained of the monomer transfer constants for the long side-chain homologs of these four monomers from the respective monomer transfer constants and the experimental transfer constants, corrected for transfer to the labile groups of the solvent. It was concluded that the rate of polymerization would determine in large measure the degree of polymerization for the reactive 18-carbon homologs but that the molecular weight of poly(vinyl stearate) and (oleate) will be regulated primarily by transfer to monomer.

INTRODUCTION

Few determinations are available of chain transfer constants for vinyl monomers polymerized in saturated and unsaturated esters.[1a] Studies with saturated esters include those of styrene polymerized in ethyl acetate,[2] methyl methacrylate in ethyl acetate,[3,4] and vinyl acetate in ethyl acetate,[5-8] a variety of esters including methyl *n*-butyrate,[8] *n*-amyl acetate,[9] and selected *n*-alkyl acetate homologs.[10] Values of the transfer constant were generally small (ca. 0.4 to 3×10^{-4}), increasing with decreasing monomer reactivity[2-7] and increasing length of the acyl group.[8,9] However, in one work,[10] where the length of the *n*-alkyl group in a series of *n*-alkyl acetates was varied, the labile α-methylene group alone appeared to determine the magnitude of the transfer constant. Only two papers[11,12] compared transfer constants for two structurally different radicals toward a common solvent (ethyl acetate). Of special significance to this work was the observation[13] that transfer constants for vinyl acetate increased proportionately as the side-chain length increased, when ethyl esters of the homologous series of fatty acids were used as solvents.

Even fewer studies were made of chain transfer in unsaturated systems. The available data included vinyl acetate polymerized in allyl acetate, in methyl oleate, and in selected alkenes;[8] styrene[14] and methyl methacrylate[15] in several alkenes, and four vinyl monomers in *N*-allylstearamide.[16]

In this work are reported chain transfer constants and transfer parameters for styrene, methyl methacrylate, methyl acrylate, and vinyl acetate polymerized at 60°C in methyl oleate and in methyl stearate. This choice of monomers should define the relative magnitude of transfer of radicals having a wide range of reactivity toward a saturated and unsaturated ester of otherwise identical structure. The corresponding degree of rate retardation should reflect on the ease of addition of the two solvent radicals to these monomers. Comparison can also be made of transfer by the methylene-flanked, internal double bond of methyl oleate, and the external allylic double bond of *N*-allylstearamide.[16] The recent observation[17] that homopolymers and copolymers having 18-carbon oleyl side chains do not exhibit side-chain crystallinity gave added impetus to this investigation. Side-chain crystallinity characterizes the linear alkyl side-chains of equal carbon length. This often leads to undesirable embrittlement in copolymers made by use of fat-derived vinyl monomers.[18] Therefore, it seemed important to know the extent of transfer and rate retardation to be expected for various radicals in the presence of unsaturation in the side chain. Finally, if transfer by the long side chains can be isolated, rough approximations of the monomer transfer constants can be calculated for 18-carbon homologs of these four monomers.

EXPERIMENTAL

Materials

Methyl oleate was purchased from Applied Science Laboratories and was 99.7% pure by gas–liquid chromatography, mp −19.9°C, and contained no *trans*- isomer by infrared analysis.

Methyl stearate was obtained by esterification of stearic acid (Hystyrene, Humpko Products), twice crystallized from acetone (10 ml/g) at 0°C. The stearic acid was esterified with a 7 mole ratio of methyl alcohol, with the use of 2% sulfuric acid as catalyst and 4 hr reflux time, isolated in excess hot water; the crude product was twice crystallized (10 ml/g) from acetone at 0°C to yield the ester in 74% yield, 99% pure by gas–liquid chromatography. The saponification number was 186.8 and the melting point was 39–40°C.

Polymerization Procedure

The procedure previously described[16] was used, and similar sample weights of monomer and solvent were employed, although in some cases the quantities were doubled. Most of the polymerizations were conducted at 60°C. No thermal polymerization was noted at this temperature. Some poly(methyl methacrylate) precipitated in both solvents; a little gel was found for methyl acrylate polymerized in methyl stearate. All of the other polymers were soluble. The polymers were isolated and freed of the fatty ester by extraction with hot methanol (5 ml/g), except for methyl acrylate, which was treated with hot Skellysolve B. Usually five or six extractions with hot petroleum ether were carried out to remove solvent from the vinyl acetate polymers; products obtained in methyl oleate were extracted five or six times with *n*-hexane at room temperature. These experiments were repeated with the use of a single room-temperature extraction as in the technique employed by Clarke.[8] Because similar molecular weights were obtained in both sets, it was concluded that low molecular weight polymer was not being extracted and lost through the repeated extractions. Elemental analyses were obtained on selected polymers and yielded the expected values.

Solution Properties

The procedure of Jordan et al.[16] was followed by use of a Mechrolab osmometer. Intrinsic viscosities in benzene at 25°C were obtained from ArRo Laboratories on the methyl methacrylate polymers polymerized in methyl stearate at 60°C.

Computations

The regression parameters and their intercepts for eqs. (1), (3), and (4) were evaluated by an IBM 1130 computer using program designation VGM-58 and were carried through third-degree polynomials. Programs for the remaining calculations were written for insertion in a general calculation subroutine designated QREAD.

RESULTS AND DISCUSSION

Experimental Results and Rate Data

All transfer and rate data are given in Table I for the monomers polymerized in methyl oleate and in Table II for the polymerizations carried out in methyl stearate. Values of the chain transfer constants for these monomers in both solvents are listed in Table III. Transfer constants were obtained by using the equation of Mayo,[19]

$$1/\bar{X}_n = 1/\bar{X}_{n0} + C_S[\mathrm{S}]/[\mathrm{M}] \tag{1}$$

where $1/\bar{X}_n$ is the reciprocal number-average molecular weight, $[\mathrm{S}]/[\mathrm{M}]$ is the solvent–monomer ratio, and C_S is the chain transfer constant. $1/\bar{X}_{n0}$ is defined as

$$1/\bar{X}_{n0} = C_M + k_t/k_p{}^2R_p/[\mathrm{M}]^2 \tag{2}$$

TABLE I
Transfer and Rate Data for Selected Vinyl Monomers Polymerized in Methyl Oleate at 60°C

	Transfer data				Rate data			
Experiment	$\bar{M}_n$	$1/\bar{X}_n \times 10^3$	[S]/[M]	Conversion, %	[M], mole/kg	$[I] \times 10^3$, mole/kg	$R_p \times 10^4$, mole/kg-sec	$R_p/[M]^2 \times 10^6$, kg/mole-sec
Styrene, no added initiator, 90°C								
1	484 900	0.215	0	9.09	9.60	0	0.303	0.329
2	248 400	0.419	0.240	10.9	5.71		0.429	1.32
3	175 700	0.593	0.495	10.4	3.99		0.287	1.80
4	113 300	0.919	0.975	9.88	2.54		0.145	2.23
5	71 200	1.46	1.86	8.78	1.53		0.068	2.90
6	43 300	2.41	3.92	7.37	0.79		0.021	3.35
Styrene, [benzoyl peroxide]/[monomer] = 3.54×10^{-4}								
7	331 200	0.314	0	6.55	9.60	3.62	0.250	0.271
8	228 900	0.455	0.254	7.42	5.57	2.03	0.128	0.411
9	223 700	0.466	0.507	8.77	3.93	1.48	0.080	0.516
10	152 300	0.684	1.00	9.88	2.50	0.911	0.038	0.611
11	107 500	0.969	1.93	9.03	1.48	0.522	0.016	0.707
12	65 150	1.60	4.03	8.54	0.77	0.283	0.004	0.642
Styrene, [AIBN]/[monomer] = 3.63×10^{-4}								
13	234 900	0.443	0	9.74	9.60	3.58	0.433	0.470
14	208 300	0.500	0.247	9.63	5.64	2.05	0.201	0.632
15	185 400	0.562	0.491	8.95	4.01	1.45	0.111	0.690
16	134 400	0.775	1.01	10.4	2.48	0.905	0.051	0.833
17	89 500	1.16	1.95	10.9	1.47	0.529	0.019	0.902
18	59 100	1.76	3.86	11.8	0.80	0.283	0.005	0.848

Methyl methacrylate, [AIBN]/[monomer] = 3.38×10^{-4}

19	813 900	0.123	0	10.9	9.99	3.55	1.65	1.66
20	462 700	0.216	0.247	11.8	5.77	2.05	0.874	2.63
21	556 000	0.180	0.489	12.1	4.08	1.45	0.782	4.69
22	513 700	0.195	0.954	10.9	2.61	0.897	0.394	5.78
23	261 300	0.383	1.84	8.36	1.55	0.535	0.120	4.99
24	126 500	0.791	3.89	8.54	0.80	0.280	0.027	4.24

Methyl acrylate, [AIBN]/[monomer] = 3.66×10^{-4}

25	264 700	0.325	0	5.15	11.62	4.26	0.511	0.379
26	122 300	0.704	0.252	5.30	6.22	2.28	0.183	0.473
27	135 600	0.635	0.502	5.58	4.26	1.56	0.097	0.533
28	94 550	0.911	1.01	7.11	2.60	0.954	0.057	0.844
29	92 350	0.932	1.99	5.26	1.48	0.541	0.012	0.548
30	44 000	1.96	3.90	5.04	0.80	0.296	0.003	0.405

Vinyl acetate, [AIBN]/[monomer] = 3.61×10^{-4}

31	340 400	0.253	0	9.27	11.62	4.21	9.06	6.72
32	376 500	0.229	0	8.38	11.62	4.21	9.01	6.68
33	99 000	0.870	0.0209	10.2	10.84	3.89	0.577	0.492
34	98 850	0.871	0.0211	7.80	10.83	3.92	0.521	0.445
35	66 300	1.30	0.0426	10.3	10.13	3.68	0.276	0.269
36	71 100	1.21	0.0424	8.40	10.14	3.67	0.249	0.242
37	46 950	1.83	0.0657	9.22	9.47	3.42	0.157	0.174
38	45 400	1.90	0.0638	8.63	9.52	3.42	0.146	0.161
39	43 000	2.00	0.0866	11.2	8.95	3.24	0.107	0.134
40	37 600	2.29	0.0871	9.49	8.94	3.21	0.096	0.120
41	33 275	2.59	0.116	9.53	8.30	2.99	0.065	0.094
42	28 850	2.98	0.111	9.34	8.40	3.04	0.066	0.094

(continued)

TABLE I (*continued*)

Experiment	Transfer data				Rate data			
	$\bar{M}_n$	$1/\bar{X}_n \times 10^3$	[S]/[M]	Conversion, %	[M], mole/kg	[I] × 10^3, mole/kg	$R_p \times 10^4$, mole/kg-sec	$R_p/[M]^2 \times 10^6$, kg/mole-sec
Vinyl acetate, [AIBN]/[monomer] = 3.61 × 10^{-4}, 90°C								
43	181 730	0.478	0	9.40	11.62	4.16	178.4	132.2
44	70 550	1.22	0.0208	7.94	10.84	3.93	31.9	27.1
45	46 750	1.84	0.0425	7.55	10.13	3.63	11.8	11.5
46	37 000	2.33	0.0642	9.77	9.51	3.45	6.15	6.79
47	31 750	2.71	0.0876	7.91	8.92	3.24	2.93	3.68
48	27 550	3.13	0.1125	8.21	8.37	3.02	1.14	1.63

TABLE II

Transfer and Rate Data for Selected Vinyl Monomers Polymerized in Methyl Stearate at 60°C

	Transfer data				Rate data			
Experiment	$\bar{M}_n$	$1/\bar{X}_n \times 10^3$	[S]/[M]	Conversion, %	[M], mole/kg	[I] × 10³, mole/kg	$R_p \times 10^4$, mole/kg-sec	$R_p/[M]^2 \times 10^6$, kg/mole-sec
Styrene, no added initiator, 90°C								
1	459 200	0.227	0	9.31	9.60	0	0.292	0.317
2	932 550	0.112	0.252	7.95	5.58		0.107	0.344
3	777 450	0.134	0.508	7.95	3.91		0.054	0.353
4	477 200	0.218	0.984	8.09	2.51		0.022	0.344
5	462 800	0.225	1.90	8.28	1.49		0.009	0.387
6	282 050	0.369	3.84	28.4	0.80		0.002	0.290
Styrene, [AIBN]/[monomer] = 3.62 × 10⁻⁴								
7	194 200	0.536	0	9.89	9.60	3.48	0.480	0.520
8	253 700	0.410	0.248	8.24	5.61	2.02	0.183	0.583
9	245 400	0.424	0.503	10.3	3.93	1.43	0.118	0.764
10	195 500	0.533	1.000	9.46	2.49	0.908	0.047	0.754
11	153 400	0.679	1.96	10.02	1.45	0.523	0.017	0.815
12	131 400	0.790	3.97	11.24	0.78	0.280	0.005	0.856
Methyl methacrylate, [AIBN]/[monomer] = 3.52 × 10⁻⁴								
13	1 290 000	0.0776	0	11.3	9.99	3.63	1.79	1.79
14	4 689 000	0.0213	0.245	12.5	5.77	2.03	1.71	5.14
15	3 030 000	0.0330	0.495	12.2	4.03	1.44	1.64	10.1
16	1 683 000	0.0595	0.970	12.9	2.57	0.91	0.69	10.5
17	1 237 000	0.0809	1.88	10.2	1.51	0.52	0.26	11.3
18	818 900	0.1222	3.71	12.7	0.83	0.28	0.10	15.0

(continued)

TABLE II (*continued*)

Experiment	Transfer data				Rate data			
	$\bar{M}_n$	$1/\bar{X}_n \times 10^3$	[S]/[M]	Conversion, %	[M], mole/kg	[I] × 10^3, mole/kg	$R_p \times 10^4$, mole/kg-sec	$R_p/[M]^2 \times 10^6$, kg/mole-sec
	Methyl acrylate, [AIBN]/[monomer] = 3.57 × 10^{-4}							
19	336 700	0.256	0	7.81	11.62	4.18	0.746	0.553
20	287 700	0.299	0.248	10.6	6.25	2.26	0.293	0.750
21	396 100	0.217	0.493	11.6	4.29	1.55	0.197	1.08
22	356 500	0.241	0.981	9.50	2.64	0.955	0.119	1.71
23	271 800	0.317	1.92	12.4	1.52	0.538	0.070	3.01
24	160 300	0.537	3.72	12.4	0.83	0.288	0.015	2.15
	Vinyl acetate, [AIBN]/[monomer] = 3.59 × 10^{-4}							
25	303 000	0.284	0	8.13	11.62	4.21	8.20	6.08
26	227 000	0.379	0.0224	8.61	10.79	3.89	6.00	5.16
27	179 900	0.479	0.0429	10.5	10.11	3.68	5.08	4.97
28	159 900	0.539	0.0656	10.0	9.47	3.38	3.93	4.39
29	134 100	0.642	0.0888	11.3	8.88	3.18	3.03	3.84
30	120 300	0.716	0.113	10.9	8.35	3.00	2.52	3.62
31	84 500	1.02	0.251	9.45	6.21	2.24	0.98	2.53
32	64 050	1.34	0.492	13.9	4.29	1.53	0.47	2.56
33	41 250	2.09	0.967	11.2	2.67	0.946	0.13	1.79
34	25 980	3.32	1.97	12.4	1.49	0.538	0.03	1.22

TABLE III

Transfer and Kinetic Constants for Selected Vinyl Monomers Polymerized in Methyl Oleate and Methyl Stearate at 60°C

		Transfer constants[a]		Kinetic constants[b]	
Monomer	Solvent	$C_S \times 10^4$	$1/\bar{X}_{n0} \times 10^4$	a	$\ln K$
Styrene, thermal, 90°C	Me Oleate	6.64 ± 0.19	2.48 ± 0.19		
Styrene, benzoyl peroxide	"	3.15 ± 0.09	3.42 ± 0.19	1.10 ± 0.06	−9.79 ± 0.17
Styrene, AIBN	"	3.52 ± 0.11	4.25 ± 0.20	1.17 ± 0.04	−9.27 ± 0.10
Methyl methacrylate	"	1.68 ± 0.17	1.07 ± 0.31	1.08 ± 0.12	−7.79 ± 0.32
Methyl acrylate	"	3.66 ± 0.52	4.44 ± 0.96	1.30 ± 0.10	−9.29 ± 0.25
Vinyl acetate	"	217.0 ± 11.8	3.38 ± 0.79	5.37 ± 0.27	−7.84 ± 0.16
Vinyl acetate, 90°C	"	358.0 ± 16.9	4.99 ± 0.40	9.76 ± 0.80	−1.64 ± 0.44
Styrene, thermal, 90°C	Me Stearate	0.676 ± 0.09	1.10 ± 0.19		
Styrene, AIBN	"	1.06 ± 0.17	4.03 ± 0.34	1.20 ± 0.03	−9.20 ± 0.08
Methyl methacrylate	"	0.282 ± 0.03	0.222 ± 0.06	0.82 ± 0.14	−7.70 ± 0.36
Methyl acrylate	"	0.751 ± 0.18	2.19 ± 0.32	0.91 ± 0.08	−9.20 ± 0.22
Vinyl acetate	"	38.2 ± 1.44	2.95 ± 0.10	1.82 ± 0.07	−6.75 ± 0.08

[a] In the calculation of C_S and $1/\bar{X}_{n0}$, experiment 6 of Table I and experiments 1, 7, 13, and 31–34 of Table II were not used.

[b] In the calculation of a and $\ln K$, experiments 31 and 32 of Table I and experiments 31 and 34 of Table II were not used.

where C_M is the constant for transfer to monomer and the second term expresses the variation of $\bar{X}_n$ by the rate.

Equation (1) applies only at low conversion when a constant ratio of initiator to monomer is employed, so that $R_p/[M]^2$ [eq. (2)] stays constant. Other requirements are that low concentrations of initiator, preferably azobisisobutyronitrile, be used, and that rate retardation be minimal.[20]

Because rates of polymerization were obtained at constant ratios of initiator and monomer, exponents of the monomer and initiator concentrations in the rate expression for steady-state polymerization could not be ascertained in the usual way from the data. However, the rate law can be expressed as

$$R_p = K([M][I]^{1/2})^a \qquad (3)$$

where R_p is the rate of polymerization (in mole/kg sec), $K = k_p f k_d^{1/2}/k_t^{1/2}$, and [I] is the initiator concentration. No rate retardation is present when a is unity; an increase in a reflects the degree of retardation. Values of a and K, obtained as the regression coefficient and intercept, respectively, from plots of $\ln R_p$ versus $\ln [M] + 0.5 \ln [I]$, are given in Table III. Essentially no deviation from unity was found for a in all of the systems studied except those employing vinyl acetate. Here, retardation was contributed by both solvents, but methyl oleate was more rate-reducing, especially at 90°C. R_p was also found[20] to be directly proportional to $[M]^{3/2}$ for all of the monomers in both solvents, except vinyl acetate. Retardation for this unreactive monomer is not unusual.[8] Solvent radicals are often more stable than the monomer radical and addition to monomer is thereby thwarted. The kinetic treatment for this situation has been given for retardation in vinyl acetate by Allen et al.,[21] and a complete general treatment was presented by Kice.[22] Values of the retardation ratio q,[8] which is the ratio of the retardation rate to the rate in the absence of solvent at the concentration of pure monomer,

$$q = R_p/R_{p0}$$

were obtained for the vinyl acetate experiments. Values of q were 0.8–0.07 for methyl stearate and 0.07–0.01 for methyl oleate, and decreased with dilution in both solvents. Because insufficient rate data were available, the treatment of Kice[22] could not be applied. Consequently, transfer constants for vinyl acetate (Table III) may be considered only apparent[8] values.

The molecular weights for styrene and methyl methacrylate (Table II) were considerably higher at low ester concentrations than were the values for the pure monomer. Molecular weights, calculated from intrinsic viscosities run in benzene at 25°C by using a molecular weight relation,[23] confirmed these results. This appeared to be an example of diffusion-controlled termination,[24–26] introduced by the solvent viscosity, and known to be characteristic of methyl methacrylate[24] and styrene.[27] However, especially because methyl methacrylate was somewhat insoluble in both solvents, delayed termination in precipitation polymerization[28] may be operating in this case. Even theta-solvent retardation[29] could not be dismissed as possibly contributing to the effect in styrene. While the regression coefficients for transfer for the two monomers in methyl stearate were obtained in Table III, by omitting the value for pure homopolymer (at $[S]/[M] = 0$), values of the constant could have been affected somewhat by the imposition of one of the above effects, even though the one that pertains is unknown. Of course, this reduction could be present in most of the data but be masked by the greater magnitude of transfer in the others.

Transfer Constants and Transfer Parameters

Plots of $1/\bar{X}_n$ against $[S]/[M]$, as in eq. (1), are given in Figures 1 and 2 for all of the monomers at 60°C, in both solvents. Values of the regression coefficients C_S and intercepts $1/\bar{X}_{n0}$ are given in Table III. Transfer in methyl stearate was much less than in methyl oleate, as would be expected. Relative rates were: methyl methacrylate < styrene < methyl acrylate ≪ vinyl acetate in both solvents. Except for vinyl acetate, literature values[2-8] for the short-chain homologs are similar to those found here. Consequently, the contribution of the side-chain methylene groups to the numerical value of the transfer constants is small for all of the monomers except vinyl acetate. The magnitude of the constant, found by Buselli[13] for vinyl acetate in ethyl stearate at 50°C, is higher than that found here for methyl stearate by a factor of about 3.7. The reason for this is unknown, but the intercept in the former work also seems to be unusually large. A smaller value was found in this work for vinyl acetate in methyl oleate than was previously found,[8] where C_S was reported to be 0.1.

Transfer constants for styrene, thermally polymerized at 90°C in N-allylstearamide[16] and, in the present work, in methyl oleate at the same

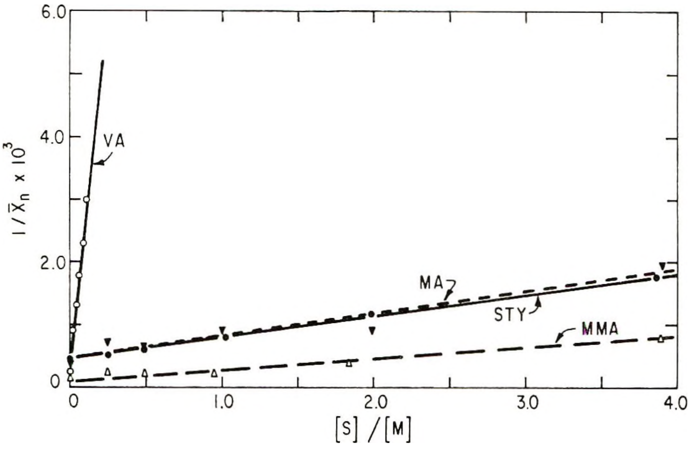

Fig. 1. Reciprocal number-average degree of polymerization vs. the solvent/monomer ratio for the monomers polymerized in methyl oleate at 60°C.

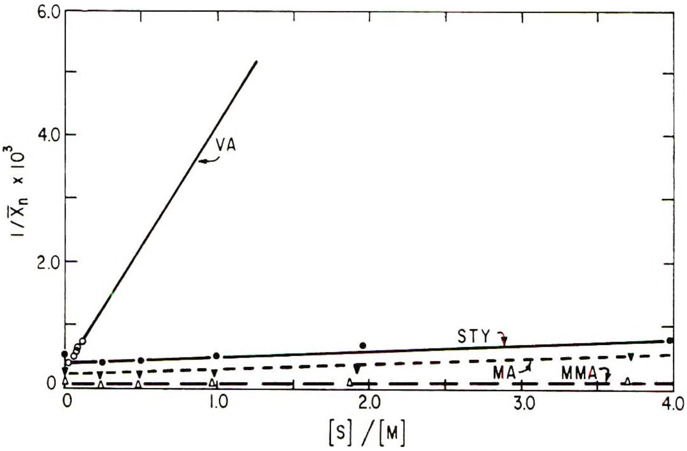

Fig. 2. Reciprocal number-average degree of polymerization vs. the solvent/monomer ratio for the monomers polymerized in methyl stearate at 60°C.

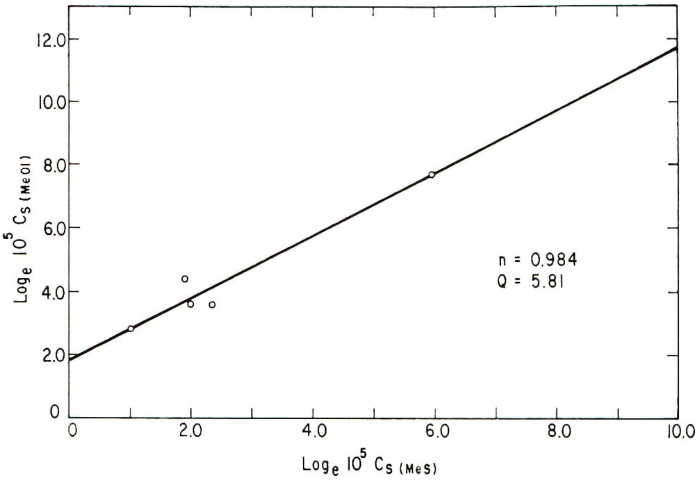

Fig. 3. Relation between the transfer constants in methyl oleate and in methyl stearate.

temperature, had similar values, being, respectively, 5.82×10^{-4} and 6.64×10^{-4}. Corresponding values for inititated vinyl acetate were somewhat different (620×10^{-4} and 358×10^{-4}, respectively). Kinetic complications of the former system[16] and structural differences might explain this lack of correspondence. Because reasonably close values were found[14] for styrene polymerized in 1- and 2-alkenes, it may be tentatively postulated that similar reactivities apply to both internal and external allylic unsaturation.

A plot of ln C_S for methyl oleate (MeOl) versus ln C_S for methyl stearate (MeS) was linear (Fig. 3) and corresponded to the relation

$$C_{S(\text{MeOl})} = Q[C_{S(\text{MeS})}]^n \qquad (4)$$

TABLE IV

Transfer Parameters for Selected Vinyl Monomers Polymerized in Methyl Oleate and Methyl Stearate at 60°C

Monomer pairs[a]	Solvent	Transfer parameters		Specific transfer constant		Transfer constants	
		$Q_{tr} \times 10^4$	e_{tr}	Monomer	k_{tr}, kg/mole-sec	Calcd	Found
Sty–MMA	Me oleate	1.28	0.47	Sty	0.0620	9.16	3.52
Sty–MA		1.36	0.39	MMA	0.0617	2.11	1.68
Sty–VA		8.05	−1.83	MA	0.765	3.65	3.66
MMA–MA		1.03	−0.06	VA	80.3	104.0	217.0
MMA–VA		3.02	2.62				
MA–VA		3.49	1.97				
	Avg[b]	2.04	1.08				
Sty–MMA	Me stearate	0.261	0.95	Sty	0.0187	1.58	1.06
Sty–MA		0.328	0.67	MMA	0.0104	0.40	0.28
Sty–VA		1.16	−0.91	MA	0.157	0.70	0.75
MMA–MA		0.116	−1.07	VA	14.1	18.7	38.2
MMA–VA		0.523	2.70				
MA–VA		0.640	1.78				
	Avg[b]	0.373	1.01				

[a] Sty signifies styrene; MMA, methyl methacrylate; MA, methyl acrylate; VA, vinyl acetate.

[b] Q_{tr} and e_{tr} for the styrene–vinyl acetate pairs were not included in the average.

Because n is almost unity (Fig. 3), rates of transfer in methyl oleate are roughly greater than those in methyl stearate by the factor $Q = 5.8$. The products QC_S for styrene in hexane and heptane at 100°C[1a,14] are, respectively, 5.2 and 5.5×10^{-4}. Found values of C_S for 2-hexene and 2-heptene were[14] 3.6 and 3.2×10^{-4}, respectively, indicating qualitative correspondence.

When transfer data are available for a number of monomers toward a common solvent it is possible to calculate the transfer parameters, Q_{tr} and e_{tr}, corresponding to the copolymerization parameters of Price and Alfrey.[30] This was demonstrated some years ago by Fuhrman and Mesrobian[31] and has been applied to several solvents.[32–34] Values of Q_{tr} and e_{tr} are given in Table IV for all possible monomer pairs by using the relation

$$C_S = k_{tr}/k_{11} = Q_{tr}/Q_1 e^{-e_1(e_{tr}-e_1)} \tag{5}$$

Somewhat similar values of the polarity parameter e_{tr} were found for both solvents, especially if one compares the average values. The generally positive nature of e_{tr} suggests that both solvents act as strong electron acceptors in the transition state. Larger transfer constants should therefore be found for electron-donating styrene compared to electron withdrawing methyl methacrylate in these solvents, in spite of the opposite magnitudes of their propagation rate constants.[31] The ratios of the propagation constants and the absolute transfer constants (the latter given in Table IV) are lower for styrene and vinyl acetate in both solvents and thus are in harmony with this concept.[31] The calculated transfer constants in Table IV, computed using the average values given in the table by substitution in eq. (5), are in fairly good agreement with observed values.

It is possible to estimate k_t/k_p^2 by rearranging eq. (2)

$$k_t/k_p^2 = (1/\bar{X}_{n0} - C_M)/R_p/[M]^2 \tag{6}$$

Literature values for C_M for catalyzed experiments at 60°C were taken,[1b] and R_p was calculated by using a and K of Table III in eq. (3) at $[S]/[M] = 0$. Values of k_t/k_p^2 for comparison were obtained by using absolute values of k_t and k_p at 60°C.[1c] Values of k_t/k_p^2 were, respectively, for methyl oleate, methyl stearate, literature: styrene 678, 619, 1 163; methyl methacrylate 38, 4.0, 36.2; methyl acrylate 861, 323, 2.2; vinyl acetate 144 (2.9 at 100°C), 8.7, 2.8. Agreement was fair for all systems except methyl acrylate, considering the assumptions made and the experimental errors involved. Autoacceleration[35] may have affected the results for methyl acrylate.

Estimates of Monomer Transfer Constants for Monomers with Long Side Chains

Rough estimates may be obtained of the limiting degree of polymerization at zero rate for homologs of the four monomers containing 18 carbon side-chains. To accomplish this the alkane (or alkene) portion of the fatty acyl group of the solvent is considered to replace one hydrogen atom of the acyl methyl in vinyl acetate, the side-chain methyl in the acrylate and methacrylate ester, and the *p*-hydrogen in styrene. The limiting degree of polymerization for the homologs becomes

$$\bar{X}_n \approx 1/C_{M(C_{18})} \approx 1/[C_M + (C_S - C_A)] \qquad (7)$$

where C_M is the monomer transfer constant and C_A is the transfer constant of the radical toward ethyl acetate, in catalyzed experiments.[1a] This ester is taken as the approximate model for the contributions to transfer conferred by the labile groupings in the two solvents,[13] while C_S is the value of the transfer constant listed in Table III at solvent to monomer ratio of unity. Because C_A was not available for methyl acrylate, the value of the polymer transfer constant C_P,[a] equal to 0.5×10^{-4}, was taken as approximating the value, because the labile groups are similar. It is assumed in eq. (7) that all members of a homologous series have equal reactivity, an assumption that seems to be valid.[36,37] Values of $\bar{X}_n$ in eq. (7) were 8 400 and 2 700 for *p*-*n*-octadecyl- and *p*-oleylstyrene, respectively; 44 800 and 6 160 for *n*-octadecyl and oleyl methacrylate, respectively; 17 400 and 2 870 for *n*-octadecyl and oleyl acrylate, respectively; 254 and 46 for vinyl stearate and oleate, respectively. These constants are, of course, very approximate and cannot be confirmed directly. Degrees of polymerization for initiated low conversion poly(*n*-octadecyl acrylate) were about 650,[33] but values for inititated bulk polymers can be 1 000–1 500, and values for poly(vinyl stearate) prepared at this laboratory are usually about 150–200. Poly(vinyl oleate) is known to be oligomeric,[39] and poly-*p*-*n*-octadecyl-styrene apparently has a high molecular weight,[40] in qualitative agreement with predicted values. More significantly, these data suggest that the rate of polymerization primarily determines the molecular weight for monomers having long alkane or alkene side chains except for the vinyl esters. Here chain termination occurs primarily by transfer to monomer.[41]

SUMMARY AND CONCLUSIONS

Styrene, methyl methacrylate, methyl acrylate, and vinyl acetate were polymerized at 60°C in both methyl stearate and methyl oleate. Transfer constants were in the order, methyl methacrylate < styrene < methyl acrylate ≪ vinyl acetate, in both solvents. The presence of polar species in the transition state was supported by the order of reactivity. Transfer toward methyl oleate was about 5.8 times greater than that toward methyl stearate for all of the monomers. The internal allylic double bond of methyl oleate had about the same reactivity as the terminal unsaturation in *N*-allylstearamide. Rough estimates of the monomer transfer constants were derived for homopolymers having long alkane or alkene side chains. It was concluded that the rate of polymerization determined, for the most part, the degree of polymerization for the reactive monomers, but that the molecular weight of the vinyl esters was regulated primarily by transfer to monomer.

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Kinetics of Dispersion Polymerization of Soluble Monomers. I. Methyl Methacrylate

K. E. J. BARRETT and H. R. THOMAS, *Imperial Chemical Industries (Paints Division) Limited, Slough, Bucks, England*

Synopsis

The kinetics of the free-radical-initiated polymerization of methyl methacrylate in *n*-dodecane to produce dispersions of polymer stabilized with a steric barrier of soluble polymer chains have been determined by thermal analysis. The mode of the polymerization can be described in terms of a bulk polymerization within the monomer-swollen polymer particles. A theoretical expression has been derived on the basis of a reaction scheme in which all the radicals produced in the diluent phase are transferred immediately to the polymer particles, monomer swells the polymer particles in partition equilibrium with monomer in the diluent, and polymerization proceeds within the polymer particle according to the kinetics of bulk polymerization, taking into account Trommsdorff acceleration and plasticization effects.

INTRODUCTION

Precipitation polymerization processes, in which the polymer produced separates from an initially homogeneous reaction mixture, are characterized by a marked, autocatalytic rise in polymerization rate and an increase in molecular weight of the polymer produced in comparison with a corresponding but otherwise entirely homogeneous polymerization. The general features of precipitation polymerization have been established largely from a study of the bulk polymerization of monomers, such as acrylonitrile or vinyl chloride, which produce polymers insoluble in their own monomers. Studies have also been made of the polymerization of monomers in diluents in which the polymers are insoluble,[1] such as methyl methacrylate in cyclohexane.[2] The kinetics of such heterogeneous polymerization processes have been interpreted in terms of a diffusion-controlled reaction of polymeric radicals occluded in a highly viscous polymer matrix.[3] These conditions are analogous to those in homogeneous bulk polymerizations, such as of methyl methacrylate, at high conversions.[4] In these systems, the enhancement of polymerization rate and increase in chain length have been ascribed to a reduction in termination rate due to the retardation of diffusion of polymeric radicals within the swollen polymer. However, a satisfactory quantitative demonstration of this effect has been difficult to obtain because the uncontrolled polymer-particle growth and flocculation lead to irreproducible rates of polymerization limited in part by the rate of diffusion of monomer into the polymer aggregates.

Practical methods for the stabilization and control of the growth of such polymer particles have been developed by Osmond and co-workers in this laboratory.[5–7] The polymer particles produced (typically in the range 0.1–1 μ diameter) are stabilized in dispersion by a steric barrier of soluble polymer chains. This is achieved by the use of amphipathic copolymers which contain one component insoluble in the medium and associated with the polymer particles, and one component soluble in the aliphatic diluent.[8] This process, for which we shall use the term dispersion polymerization, is of practical importance as well as of theoretical interest, and a study of its kinetics and mechanism has been undertaken, in the first place by using methyl methacrylate in *n*-dodecane.

THEORETICAL MODEL OF DISPERSION POLYMERIZATION

The following model has been used as the basis for interpreting the experimental results which follow.

At the start of the process of dispersion polymerization, monomer, stabilizer and initiator are in homogeneous solution in the diluent. Initially, polymer molecules formed by solution polymerization aggregate in small groups with stabilizer molecules to form stabilized particle nuclei, probably less than 0.01 μ in diameter. This stage is completed very rapidly (well under 1% conversion) and the detailed mechanism of the production of primary particles need not be examined here, since for the kinetic analysis of the course of polymerization it is sufficient to assume that particles are present from the start. The number of particle nuclei increases (and particle size decreases) with increasing stabilizer content, but very few new particles are formed after the first crop, unless a substantial further amount of stabilizer is added.

Once particles have formed they absorb monomer from the diluent phase. Within the particles, polymerization takes place according to the laws of bulk polymerization kinetics. In the conditions used here, the high viscosity of this monomer-swollen polymer phase greatly hinders radical termination. The resulting increase in radical concentration accelerates the rate of polymerization (Trommsdorff effect[9]), while the slow rate of termination also ensures that many radicals can coexist in each particle, in contrast to the situation envisaged in classical Harkins-Ewart-Smith emulsion polymerization kinetics.[10–12]

Any radicals initiated in the diluent phase are swept up by particles before they have had time to grow more than a very few monomer units. This results in an enormous decrease in the effective radical concentration in the diluent phase, suppressing both solution polymerization and the formation of new particles. Since all radicals formed rapidly find their way to the particles, this implies that we can treat the initiator from the kinetic point of view as if it were all in the particle phase, even though if fact the typical initiators used are partitioned between particles and diluent.

We can now deduce a kinetic equation corresponding to this model. In the particles at a given time occupy a volume fraction v of the whole dispersion, and the rate of initiation in the whole dispersion is R_i, then the effective initiation rate in the particles will be given by

$$R_i' = R_i/v \tag{1}$$

If the monomer concentration in the particles is c_p, the overall polymerization rate in the particles will be given by the usual expression for bulk or solution kinetics

$$R_p' = c_p k_p (R_i'/k_t)^{1/2} = c_p k_p (R_i/v k_t)^{1/2} \tag{2}$$

Here k_p is the propagation rate constant and k_t is the termination rate constant (defined[1] with respect to rate of disappearance of single radicals, not pairs).

Since this takes place in the volume fraction v, the overall rate of polymerization in the whole dispersion is

$$R_p = vR_p' = c_p k_p (vR_i/k_t)^{1/2} \tag{3}$$

This is the basic equation for dispersion polymerization on the model proposed here, and is essentially equivalent to case III of Smith and Ewart's consideration of possible mechanisms for emulsion polymerization.[11] Since the rate is based on bulk polymerization kinetics it is in principle independent of particle size and number, provided that it is not limited by rate of diffusion of monomer into the particles.

In emulsion polymerization, the monomer concentration in the particles is generally taken to be in equilibrium with a saturated aqueous solution throughout much of the course of polymerization and is only limited by the counter effects of interfacial tension in the very small droplets.[13] Thus the concentration of monomer in the particles is usually taken as constant up to the point where free monomer droplets disappear. In dispersion polymerization the situation is very different because monomer is completely miscible with diluent and the monomer concentration in the particles is subject to a conventional partition equilibrium, which greatly outweighs any effects of interfacial tension. Here we shall assume it can be represented by a simple partition coefficient α which may to a first approximation be taken as constant (but may in fact vary slightly with monomer concentration). We can then write for the overall rate of polymerization an approximate expression:

$$R_p = \alpha\, c_m k_p (vR_i/k_t)^{1/2} \tag{4}$$

where c_m is the overall monomer concentration in the dispersion (it should strictly be the monomer concentration in the diluent).

It is shown in the Appendix that this expression can, with two further small approximations, be transformed into

$$dx/dt = \alpha\, x^{1/2}\,(1 - x)\,(c_0 v_p c_i k_i)^{1/2}\,(k_p/k_t^{1/2}) \tag{5}$$

where x is fractional conversion, c_0 is initial monomer concentration, v_p is the molar volume of the polymer (in liters per monomer unit). c_i is initiator concentration, k_i is initiation rate constant $= 2fk_d$, k_d is initiator decomposition rate constant, and f is initiation efficiency.

Rearranging, we obtain

$$\alpha(2f)^{1/2}\,(k_p/k_t^{1/2}) = (dx/dt)/x^{1/2}\,(1 - x)\,(c_0 v_p c_i k_d)^{1/2} \tag{6}$$

More exact expressions corresponding to eqs (5) and (6) are derived in the Appendix with elimination of the approximations used in eqs. (7)–(11) of the Appendix. These fully corrected forms have been used wherever possible but require a value for α, which must first be estimated.

It must be emphasized that k_p and k_t are the values for propagation and termination rate constants which hold within the swollen polymer phase and therefore, correspond to a bulk polymerization at high conversion and not to polymerization in dilute solution. The termination rate constant k_t, in particular, is expected to fall rapidly as monomer content diminishes with resulting increase in rate. The ratio $k_p/k_t^{1/2}$ should however have a characteristic value for each value of monomer concentration in the particles. If the partition coefficient α and the initiator efficiency f can be taken as roughly constant, then the values of $\alpha(2f)^{1/2}(k_p/k_t^{1/2})$ obtained from experimental data by using eq. (6) should show the same pattern of relation to monomer concentration as the values of $k_p/k_t^{1/2}$ obtained from bulk polymerization data, subject to minor displacements due to plasticizing effects of other components present.

Bulk polymerization of methyl methacrylate has been studied in detail by Schulz,[4] Burnett and Loan[14] and others. Schulz, in particular, showed that the ratio of the values of $k_p/k_t^{1/2}$ found in bulk and dilute solution polymerization is almost independent of the initiation rate but shows a characteristic relation to the monomer content of the polymer–monomer mixture, rising exponentially to a peak value and then falling rapidly as the glass transition is approached. Some of Schulz's curves for 50, 70, and 90°C are shown (on a logarithmic scale) in Figure 4, together with an interpolated curve for 80°C.

We should therefore expect curves obtained from dispersion polymerization runs by eq. (6) to correspond to a portion of these curves in the high conversion region.

EXPERIMENTAL

Materials

Methyl methacrylate was distilled under reduced pressure in a nitrogen stream and stored at −10°C before use. Azobisisobutyronitrile was recrystallized from ethyl acetate. *n*-Dodecane of purity better than 99%

(Koch-Light Laboratories Limited) was used without further purification. The amphipathic copolymer used as dispersion stabilizer contained the pentamer of 12-hydroxystearic acid as the soluble component and poly-(methyl methacrylate) as the insoluble component. This was prepared with pure 12-hydroxystearic acid, obtained from commercial material (Price's, Bromborough) purified by recrystallization of the corresponding methyl ester from cyclohexane. The 12-hydroxystearic acid was condensed in the presence of stearyl alcohol (as chain modifier) and *p*-toluenesulfonic acid in toluene at 180–190°C until the acid value was less than 1 mg KOH/g. This material was reacted with methacrylic anhydride and the resulting "macromonomer" copolymerized with an equal weight of methyl methacrylate in butyl acetate, azobisisobutyronitrile being used as initiator. The resulting polymer was used as a solution (50% by weight) in *n*-butyl acetate.

Methods

Measurements of the rate of dispersion polymerization were made by following the evolution of the heat of polymerization with respect to time at a given temperature by means of a commercial differential scanning calorimeter (Perkin-Elmer DSC-1). The use of this instrument to determine kinetic parameters of reactions has been described previously.[15] In the present application the rate of production of the heat of polymerization was measured under isothermal conditions because of the complicating effect of a rising temperature base on the interpretation of the results of the heterogeneous polymerization. A sealed sample holder was developed so that relatively volatile monomers, such as methyl methacrylate, could be examined. The type eventually evolved made use of commercially available aluminum cylinders of suitable dimensions (Mullard Limited, Type T0.1, size 9 mm high, 6 mm diameter) sealed with a PTFE plug stamped out from a sheet of the plastic. For each polymerization run, a portion (weight ca. 50 mg) of a freshly prepared reaction mixture was placed in the sample can which was sealed and weighed. The sample can was placed on the sensor at room temperature, together with an empty container to assist output balance, and rapidly heated to the required temperature. The resulting exotherm was recorded with respect to time.

A mean determined value of 11.8 kcal/mole (12.6, 11.8, 11.0, 11.6, 12.4, 11.7) was obtained for the heat of polymerization of methyl methacrylate; a value of 13.2 kcal/mole has been reported.[16]

Swelling of poly(methyl methacrylate) by methyl methacrylate was determined by using a dried, monomer-free sample of polymer prepared by dispersion polymerization. The dried polymer was redispersed in cyclohexane to give a 30% solids dispersion of particle size in the range 0.1–0.2 μ (as determined by electron microscopy). The dispersion was stirred under reflux at 80°C in the presence of a known amount of monomer and hydroquinone to inhibit thermal polymerization and samples of the total dispersion were removed over a period of 3–4 hours to ensure equilibration. The sample removed was divided into two portions. The first was dissolved in benzene and total monomer determined by direct gas-liquid chromatographic (GLC) analysis as a check on any thermal polymerization. The second portion was centrifuged and residual monomer in the supernatant phase was determined separately by GLC analysis by calibrated standards.

Number-average molecular weights of poly(methyl methacrylate) were determined with a Mechrolab vapor pressure osmometer, Model 301A, in methyl ethyl ketone at 37°C and with a Dohrmann automatic membrane osmometer in toluene at 35°C.

RESULTS AND DISCUSSION

Form of the Time–Conversion Curve

Figure 1 shows a typical differential thermal analysis curve obtained for a polymerization run at 80°C, together with the corresponding time–conversion plot obtained by integrating the cumulative area under the curve.

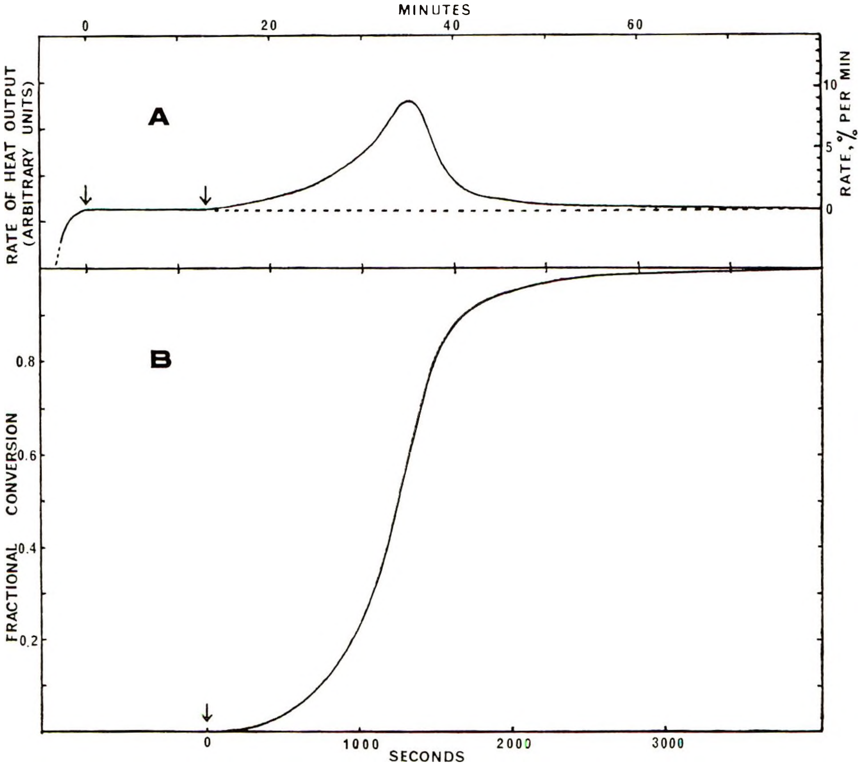

Fig. 1. Typical dispersion polymerization of methyl methacrylate: (*A*) differential thermal analysis curve of rate of heat output against time; (*B*) corresponding time/conversion curve obtained by integration of (*A*). Methyl methacrylate 50%, AIBN 0.2%, stabilizer 2.5%, in *n*-dodecane at 80°C. Arrows mark establishment of reaction temperature and start of polymerization.

The shape of the time-conversion curve is sigmoid, as expected qualitatively on the basis of the proposed model. The initial acceleration corresponds to increasing particle volume [R_p proportional to $v^{1/2}$ in eq (4)] while the tailing-off corresponds to gradual diminution in the residual monomer content. The initial acceleration is quite distinct from a short period of true inhibition, when polymerization cannot be detected at all.

A preliminary comparison of polymerization runs can conveniently be made on the basis of pseudo-first-order kinetics in the region of fast reaction, i.e., ignoring the initial acceleration region. According to eq. (5) the pseudo-first-order rate constant k will correspond to the average value of $\alpha x^{1/2} (c_0 v_p c_i k_i)^{1/2}$ over the fast region, i.e., about 50–85% conversion where $x^{1/2}$ changes only slightly and $k_p/k_t^{1/2}$ is in the "plateau" around the peak value (see below).

Comparison with Solution Polymerization: Rates and Molecular Weights

In Figure 2, three runs are compared, in dodecane with stabilizer, dodecane without stabilizer, and in benzene, all at 80°C with 50% monomer and 0.1% AIBN. It is apparent that the rate of dispersion polymerization is very much faster than that of solution polymerization. Without stabilizer (i.e., in precipitation polymerization with uncontrolled aggregation), the curve is of the same form but the rate is distinctly slower. The same mechanism presumably operates, but diffusion of monomer into the aggregates is probably a controlling factor.

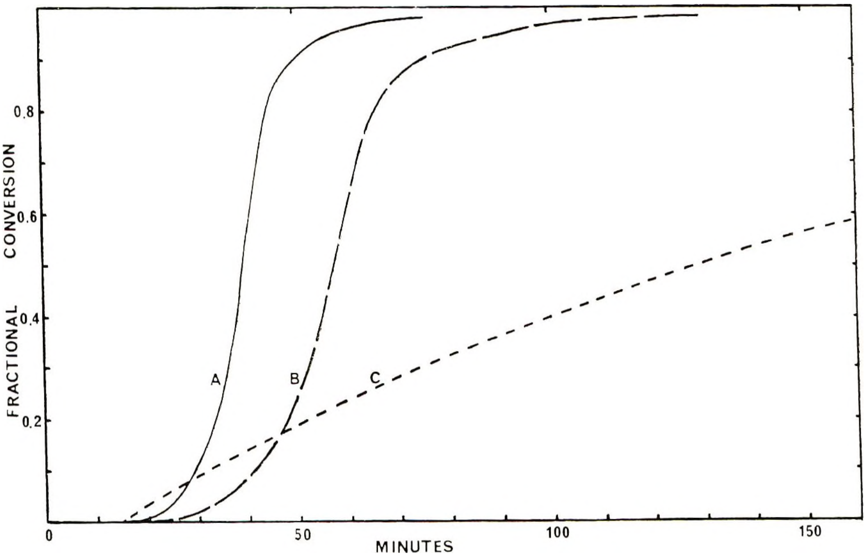

Fig. 2. Comparative rates of dispersion, precipitation, and solution polymerization: (*A*) in *n*-dodecane with stabilizer, (*B*) in *n*-dodecane without stabilizer, (*C*) in benzene. All at 80°C with methyl methacrylate 50%, AIBN 0.1 %.

Maximum rates reached in the three runs were in the approximate ratio 12.5:7.5:1.

The small scale of these polymerization runs (20 mg monomer) precluded accurate determination of molecular weights on the polymer produced. A comparable series of 1-kg scale polymerization runs in cyclohexane was carried out (10% monomer, 0.04% AIBN, under reflux), polymer precipitated and washed with methanol, and number-average molecular weights determined by vapor pressure osmometer (VPO) and membrane osmometer (MO). As expected, the MO results (Table I) are slightly higher, as the membrane allows some very low molecular weight fractions to pass through.

Both the greatly accelerated rate and the much higher molecular weight found in dispersion polymerization are characteristic of restricted radical termination, either by isolation, as in emulsion systems, or by diffusion control, as in high-conversion bulk polymerization.

TABLE I
MOLECULAR WEIGHTS FROM SOLUTION AND DISPERSION

	Temp, °C	$\bar{M}_n$	
		VPO	MO
Solution in benzene	80	26 400 ± 8%	33 500 ± 5%
Solution in ethyl acetate	77	24 300 ± 10%	34 400 ± 6%
Dispersion in cyclohexane	81	71 000 ± 20%	84 000 ± 5%

Effect of Stabilizer Concentration (Particle Size)

A series of runs carried out at 80°C with 50% initial monomer, 1% AIBN and a range of stabilizer content from 0 to 5% on monomer gave practically superposable curves except for stabilizer contents of 0.5% or less when visible flocculation becomes apparent. Pseudo-first-order rate constants k are given in Table II.

A similar series carried out with degraded rubber as stabilizer and benzoyl peroxide initiator at 60°C[17] gave pseudo-first-order rate constants

TABLE II
Rates with Varying Stabilizer Content [a]

Stabilizer, % on monomer	Rate constant $k \times 10^3$, sec^{-1}
0	6.3
0.5	7.6
1.0	11.6
2.5	10.8
5.0	10.2

[a] Runs at 50% initial monomer, 1% AIBN, 80°C.

uniform within ±2% over the whole range from 0.6% to 5% on monomer corresponding to a particle size range of 0.25–0.5 μ.

This constancy of rate over at least eight fold range of particle number per unit volume appears to rule out a mechanism of the classical emulsion polymerization type[10,11] in which the rate is proportional to particle number. It also indicates that the rate is unlikely to be limited by diffusion of monomer into the interior of the particles.

Change of Polymerization Rate Constants with Conversion

Application of eq. (6) to the data of Figure 1 gives the curve shown in Figure 3, in which values of $(dx/dt)/x^{1/2}(1-x)(c_0v_pc_ik_d)^{1/2}$ are plotted on a logarithmic scale against fractional conversion and total monomer content in the dispersion. (A small correction has been made to allow for approximately 1% residual monomer at the end of the run, and for breakdown of initiator.) These values should be equal to $\alpha(2f)^{1/2}(k_p/k_t^{1/2})$.

There is a nearly exponential increase with conversion to a well defined peak at about 70% conversion, followed by a rapid fall. While there may be small changes in the values of partition coefficient α and initiation efficiency f with conversion, these are unlikely to be significant, and the seven fold range of values found must be taken as corresponding to changes in the combined rate constant $k_p/k_t^{1/2}$.

Correlation with Bulk Polymerization at High Conversion

The form of Figure 3 corresponds closely to Schulz's curves for bulk polymerization[4] shown in Figure 4. Comparison with the interpolated

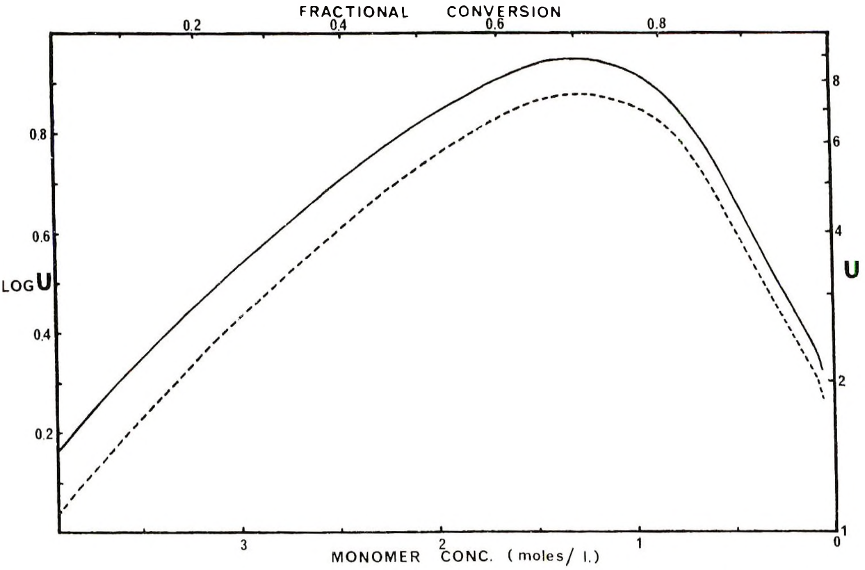

Fig. 3. Variation of relative rate constants with conversion. $U = \alpha(2f)^{1/2}k_p/k_t^{1/2}$ calculated from Fig. 1: (——) by use of eq. (6); (– – –) by use of fully corrected eq. (23).

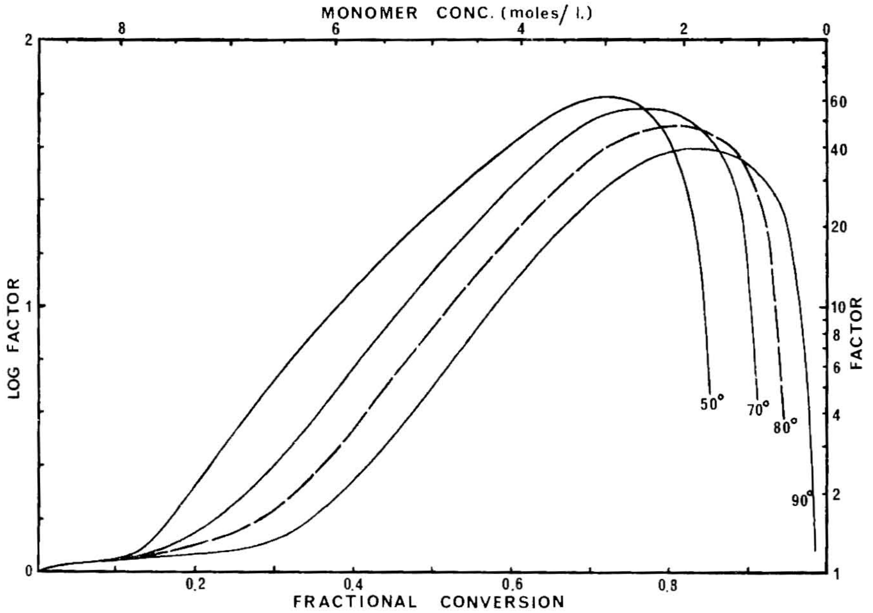

Fig. 4. Variation of Trommsdorff acceleration factor with conversion in bulk polymerization. Adapted from Schulz[4] (80°C curve by interpolation). All at 0.25% benzoyl peroxide; monomer concentrations calculated for density at 80°C. The Trommsdorff acceleration factor is defined as the ratio of apparent first order rate constant to its initial value at low conversion at the same temperature.

curve for 80°C indicates that the complete dispersion polymerization starting with 50% monomer corresponds to the bulk conversion curve in the range 50–95% conversion, so that the polymer particles in the dispersion appear slightly plasticized even at full conversion.

This is not surprising in view of the presence of a small amount of butyl acetate added as solvent for the stabilizer. It has also been shown that a small amount of aliphatic hydrocarbon can be taken up in the presence of monomer,[17] and this may also contribute to plasticization.

In addition, initiator efficiency may be much reduced in bulk polymerization at high conversion, due to the cage effect, but in dispersion polymerization an appreciable proportion of initiator remains in dilute solution in the diluent and can initiate with unimpaired efficiency radical chains which are then taken up by the polymer particles.

Estimation of Partition Coefficient from Kinetic Data

If we assume that the peak values in Figures 3 and 4 correspond, we can express the values at any given conversion as a fraction of the peak value. Monomer contents in the whole dispersion can then be plotted against corresponding monomer contents in bulk polymerization to give the same fraction of the peak value. These are in effect the apparent monomer contents in polymer which would give the same overall plasticizing action.

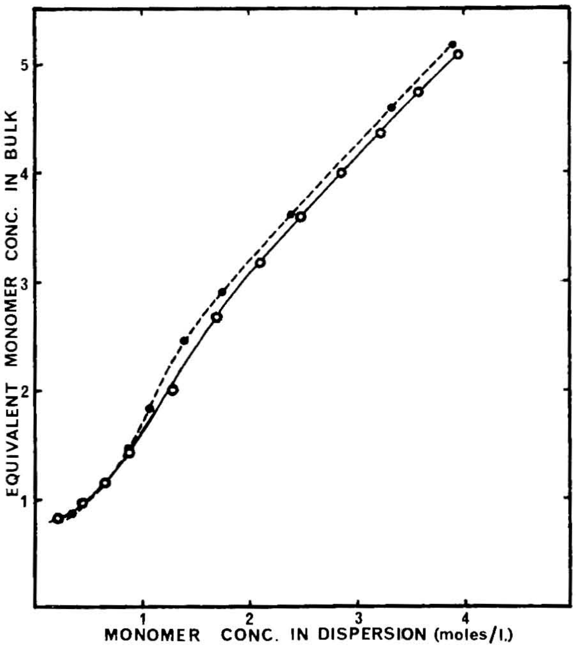

Fig. 5. Monomer concentrations giving equivalent rate constants at 80°C in bulk and dispersion polymerization. (from Figs. 3 and 4): (——) by use of eq. (6); (- - -) by use of fully corrected eq. (23).

As shown in Figure 5 (full line), the resulting graph is a good approximation to a straight line except at very high conversions, where the additional plasticizing effects in dispersion contrast most strongly with the approach to the glassy state in bulk polymerization. The slope of the line gives a first estimate of the partition coefficient, which in this case is 1.04.

This estimate of α using the approximate eq. (6) can then be used in the fully corrected eq. (23) (Appendix) to give an improved estimate. The dotted line in Figures 3 and 5 shows the result. The discrepancy is obviously small when α is near unity.

As shown below, the curves obtained in both bulk and dispersion polymerization are very slightly displaced by altering the initiation rate. The best estimate for α taking this into account is 1.02. For simplicity, a rounded value $\alpha = 1.00$ is taken and the fully corrected eq. (23) used in all further calculations unless otherwise stated.

Direct Estimation of Partition Coefficient

Equilibration of monomer with dispersions of poly(methyl methacrylate) particles at 80°C, followed by centrifugation and analysis of the diluent phase by GLC, gave estimates of α in the range 1.2 ± 0.3 with cyclohexane as diluent. Equilibration of bulk polymer with monomer in petroleum ether (bp 100–120°C) at 60°C resulted in an estimate[17] of $\alpha = 0.8$.

While these values were obtained with the use of different hydrocarbon diluents from those used to obtain the kinetic data, they are in agreement with the estimate of approximately 1 obtained from dispersion polymerization runs in *n*-dodecane.

Estimation of Apparent Initiator Efficiency in Dispersion Polymerization

The peak value of $\alpha(2f)^{1/2}\, k_p/k_t^{1/2}$ found in Figure 3 by using the corrected eq. (23) is 7.6 at 80°C. The corresponding peak value of $k_p/k_t^{1/2}$ in bulk polymerization at 80°C is 7.4, obtained by combining the interpolated peak value of 48 for Trommsdorff acceleration factor from Schulz's curves with the value of $k_p/k_t^{1/2} = 0.155$ in dilute solution at 80°C calculated from the equation given in Revzin's recent review.[18]

If we put $\alpha = 1$, the resulting value of the initiation efficiency f is 0.52. This appears a reasonable figure, bearing in mind the overall experimental error in the values used in the calculation, and is fully consistent with the proposed mechanism.

Dependence of Rate on Initiator Content

Pseudo-first-order rate constants for a series of runs at 80°C with 50% initial monomer, 2.5% stabilizer and varying initiator contents are given in Table III. A square-root relationship fits the data approximately, though if the lowest result is excluded an initiator exponent of 0.4 gives a much closer fit.

The dependence on initiator content is shown in more detail in Figure 6, where derived curves are plotted against conversion by using the fully corrected equation, which implies a square-root relationship. It is now apparent while the general shape of the curves is the same throughout, there is a progressive displacement of the rising portion to higher values as the initiator content falls.

This behavior runs closely parallel to a similar displacement observed by Schulz with falling initiator content, illustrated in Figure 7 covering a range

TABLE III
Rates with Varying Initiator Content[a]

AIBN content, %	Rate constant $k \times 10^3$, sec^{-1}
0.05	1.5
0.10	4.1
0.20	4.9
0.30	6.5
0.50	8.1
1.00	9.8

[a] Runs at 50% initial monomer, 2.5% stabilizer, 80°C.

from 0.125% to 2% benzoyl peroxide content at 70°C. The effect is explained by Schulz as arising from the higher average mobility of the smaller radical chains produced at higher initiation rates. In dispersion polymerization at 80°C the effect is magnified partly because the whole run occupies only a portion of the bulk conversion curve and partly because of the much higher initiation rates used.

At such high initiation rates, it is probable that termination by primary radicals[19] also plays an increasingly significant part as polymerization proceeds, due to immobilization of macroradicals and decreasing monomer content. However, it has not been possible to disentangle this effect from the more general effect of increasing viscosity on the macroradicals, whose mobility will be greater the lower their molecular weight. In this context k_t must be regarded as an empirical parameter, characterizing the resultant of all these simultaneous effects.

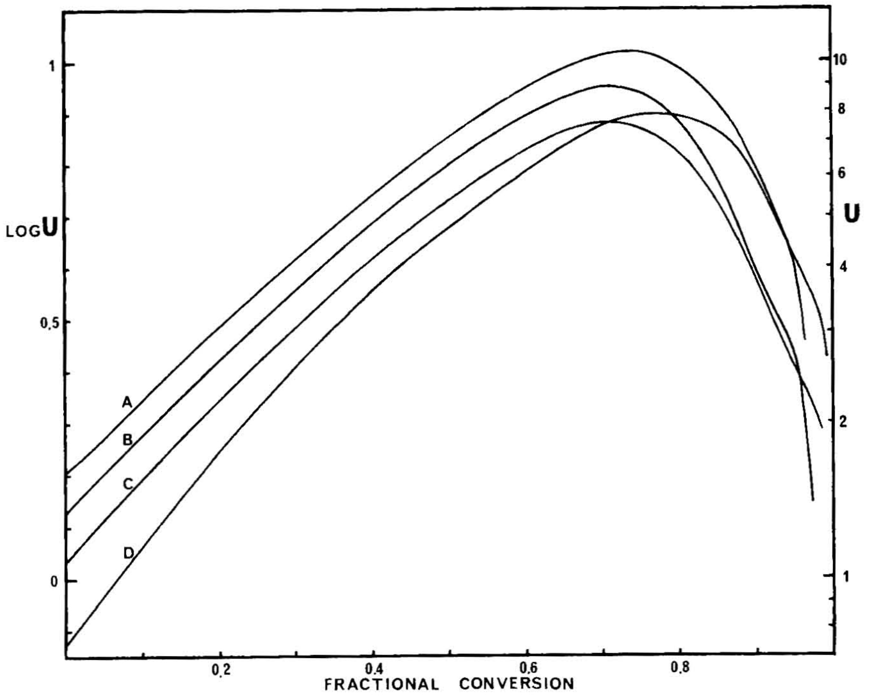

Fig. 6. Effect of varying initiator (AIBN) content in dispersion polymerization at 80°C: (*A*) 0.05% AIBN; (*B*) 0.1% AIBN; (*C*) 0.2% AIBN; (*D*) 1.0% AIBN. All with 50% methyl methacrylate, 2.5% stabilizer, in *n*-dodecane. *U* calculated by using fully corrected eq. 23.

The effect of the displacement is that at lower initiator levels, rates are faster than would be expected from a square root law, especially at low conversions. The resulting initiator exponent is therefore slightly less than 0.5 even at the peak rate and falls much lower (0.2–0.3) at very low conver-

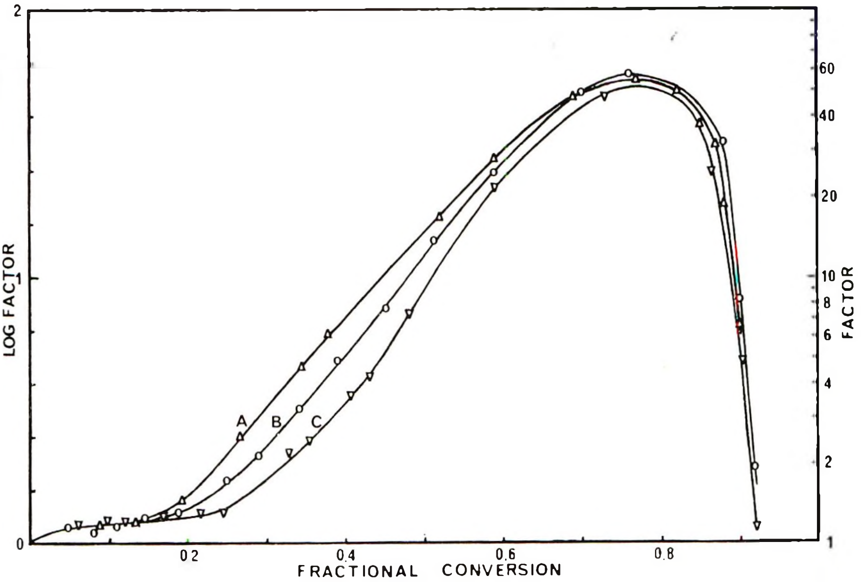

Fig. 7. Effect of varying initiator (benzoyl peroxide) content in bulk polymerization at 70°C: (*A*) 0.125%; (*B*) 0.5%; (*C*) 2%. Adapted from Schulz.[4]

sions. For this reason the overall time taken to reach a given conversion is not an informative kinetic index of the comparative rates of reaction.

Dependence of Rate on Monomer Content

Changes in initial monomer content produce changes not only in overall rate but in the form of the time–conversion curve. The maximum rate is displaced to lower conversions and the initial acceleration period progressively shortened as the initial monomer content is lowered.

Pseudo-first-order rate constants k (for a series of runs at 80°C and 0.5% AIBN) show pronounced changes with a drastic fall at low monomer contents, but no simple relation (Table IV).

However if the derived values of $\alpha(2f)^{1/2} k_p/k_t^{1/2}$ according to eq. (23) are plotted against the monomer concentration remaining in the dispersion (which is also that in the particles if $\alpha = 1$) for each of the runs, a consis-

TABLE IV
Rates with Varying Monomer Content[a]

Initial monomer content, %	Rate constant $k \times 10^3$, sec^{-1}
20	0.4
30	2.5
40	5.4
50	3.5

[a] Runs at 0.5% AIBN, 2.5% stabilizer, 80°C

tent picture emerges. As shown in Figure 8, all the experimental results fit well into a single curve relating $k_p/k_t^{1/2}$ to monomer content.

As monomer content falls, the initial acceleration period shortens because the run starts nearer the peak of the curve. Equation (5) predicts proportionality of rate of conversion to square root of initial monomer concentration, but superimposed on this is the combined effect of the factor $x^{1/2}(1 - x)$, which has a maximum at one-third conversion, and the position and magnitude of the peak of the curves for the Trommsdorff acceleration factor. In particular, at low initial monomer content the whole of the run is on the rapidly falling part of the curve, so that the overall rate is low.

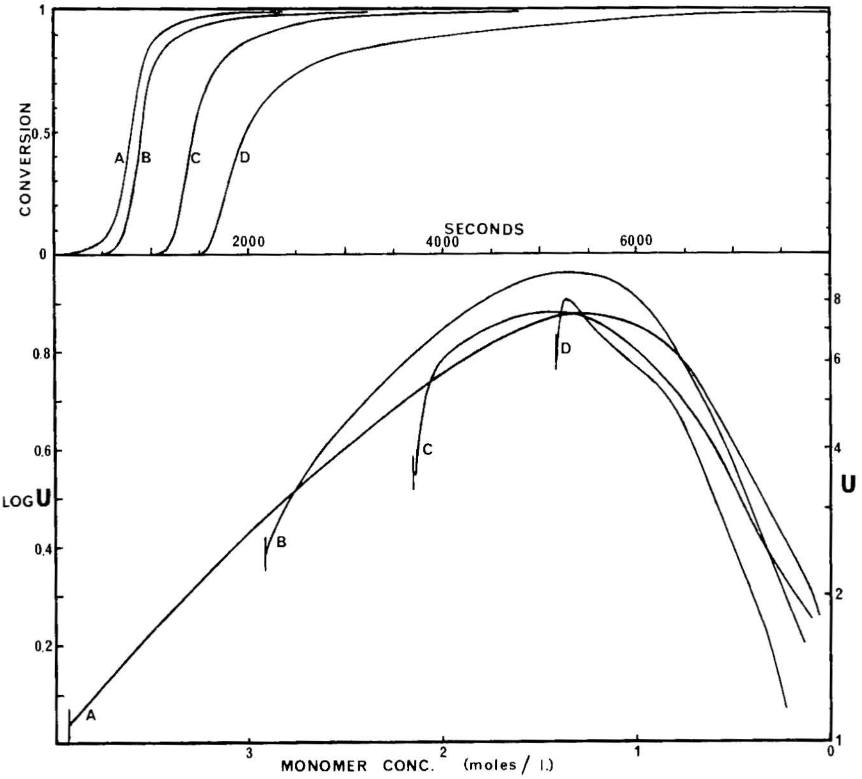

Fig. 8. Effect of varying monomer content in dispersion polymerization at 80°C: (*A*) 50%; (*B*) 40%, (*C*) 30%, (*D*) 20%. All with AIBN 0.5%, stabilizer 2.5%, in *n*-dodecane. *U* calculated by using fully corrected eq. (23); time–conversion curves displaced successively by 500 sec for clarity.

Effect of Added Solvent

Additions of strong solvents slow down the polymerization and markedly distort the shape of the time conversion curve. The experimental results can be readily explained on the basis of uptake of solvent by the particles resulting in plasticizing action and less hindered termination of radicals.

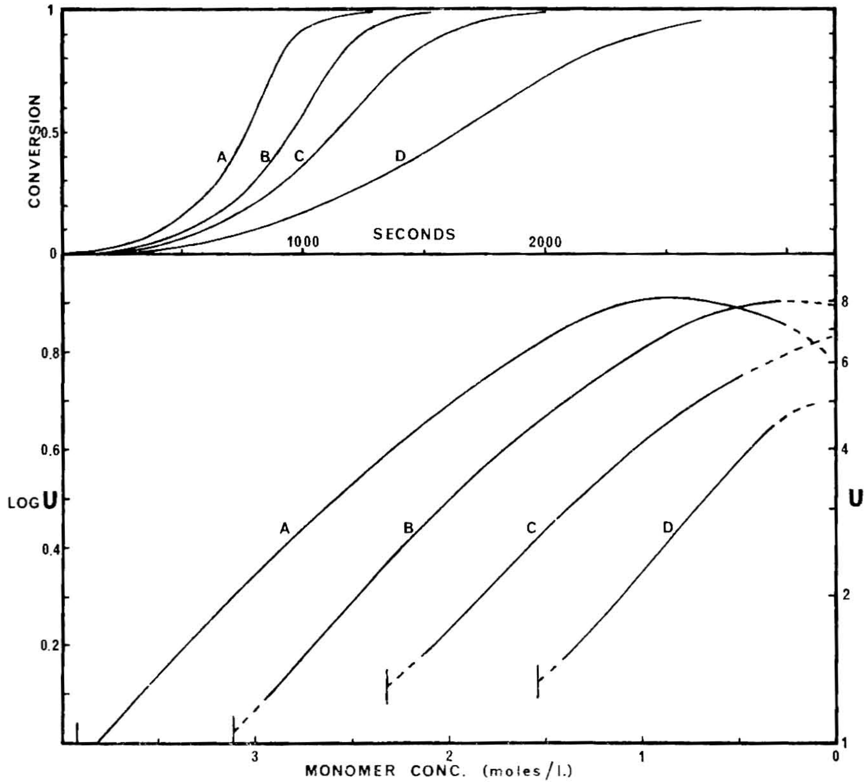

Fig. 9. Effect of replacing monomer by butyl acetate in dispersion polymerization at 80°C: (*A*) monomer 50%; (*B*) monomer 40%, BuAc 10%; (*C*) monomer 30%, BuAc 20%; (*D*) monomer 20%, BuAc 30%. AIBN 0.5%, stabilizer 2.5% in each case.

An exact treatment taking into account the partition of solvent and monomer between diluent and particles and the increase in volume due to this would be very complex, but to a good approximation the results are well represented by a simple displacement of the Trommsdorff acceleration curves towards lower monomer concentrations by an amount proportional to the initial solvent concentration. In a typical case, for example, 1 g of *n*-butyl acetate is equivalent to approximately 0.85 g of methyl methacrylate in its effect on $k_p/k_t^{1/2}$.

This is illustrated in Figure 9, showing results of runs with successive replacement of monomer by butyl acetate.

Figure 10 shows runs with successive replacement of diluent by butyl acetate, at 50% initial monomer. Here curve *1* corresponds to normal dispersion polymerization and curve *4* to solution polymerization. In the intermediate runs *2* and *3*, the first part of the curve represents solution polymerization, followed by a more or less sharp transition to dispersion polymerization, since the polymer is soluble in a combined monomer and butyl acetate content greater than about 55%. This transition leads to coarse particle size, with some distortion in the curves, but it is clear that

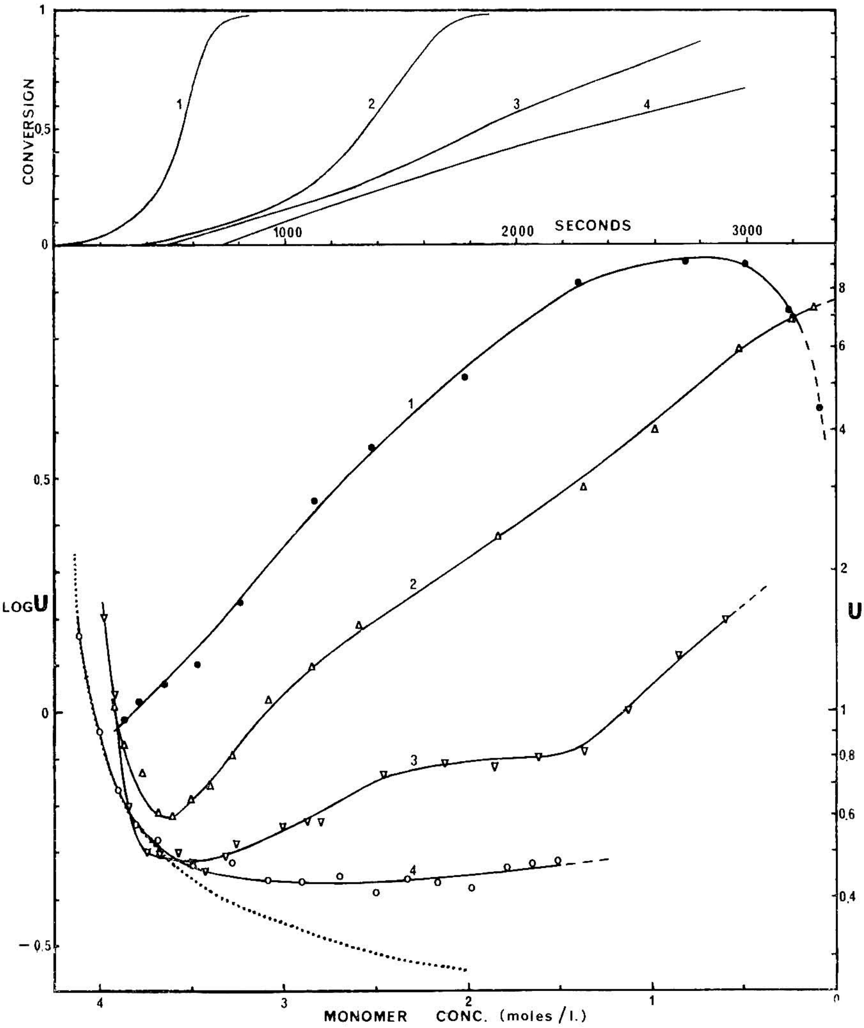

Fig. 10. Effect of replacing diluent by butyl acetate in dispersion polymerization at 80°C: (*1*) no BuAc; (*2*) BuAc 10%; (*3*) BuAc 20%; (*4*) BuAc 45%. AIBN 1%, monomer 50%, stabilizer 2.5% in each case. Dotted line shows theoretical first-order solution polymerization with constant k_p, k_t; time–conversion curves displaced successively by 200 sec for clarity.

the sections corresponding to dispersion polymerization again show sideways displacement due to plasticization similar to Figure 9.

Similar results have been obtained with benzene as added solvent.[17]

Effect of Added Polymer Seed

In some experiments a preformed polymer dispersion was added at the start of a run. To minimize the effects of residual initiator, the original dispersion was centrifuged, the polymer particles washed twice with cyclohexane and redispersed for use in these runs.

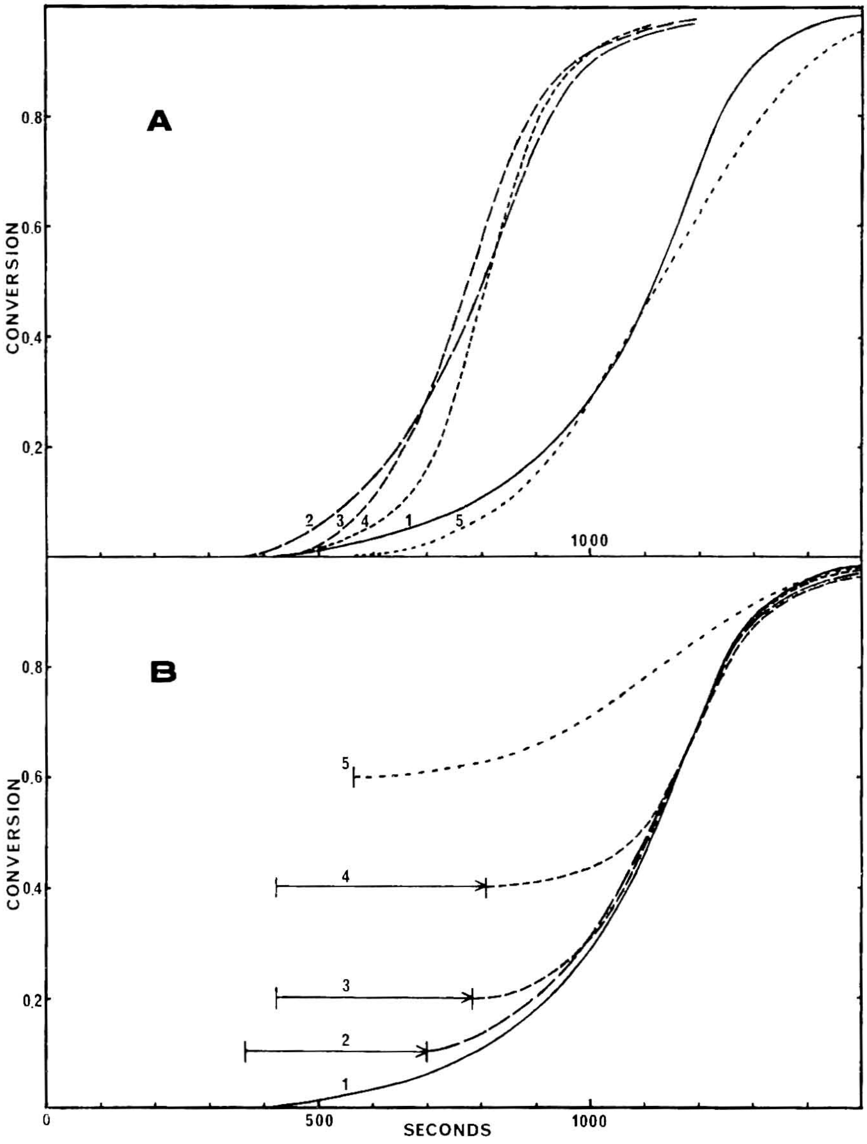

Fig. 11. Effect of replacing monomer by polymer "seed" in dispersion polymerization at 80°C: (*A*) original time–conversion curves; (*B*) conversions recalculated to include polymer seed as converted monomer. Polymer "seed" added: (*1*) 0; (*2*) 5%; (*3*) 10%; (*4*) 20%; (*5*) 30%. AIBN 0.5%, stabilizer (total) 2.5%, monomer + polymer 50% in each case. Curves *2*, *3*, *4* displaced as indicated in (*B*) to coincide with curve *1* at 70% conversion.

Figure 11 shows some typical results. As indicated, the time–conversion curves approximate closely to the curves which would have been obtained if all the polymer had started as free monomer, after an "approach curve" which is longer the more polymer is present. This approach curve presumably represents the time required to establish pseudo-steady-state conditions, not only of radical flux (which would be much briefer) but also of radical molecular weight distribution and penetration into the particles of monomer, initiator, and radicals.

For the same total content of monomer plus polymer, the maximum rate of polymerization will therefore remain essentially constant (at all but the very highest concentration of polymer seed). This will be given by the maximum rate of conversion of monomer multiplied by initial monomer content, as shown in Table V.

TABLE V
Rates with Varying Seed Polymer Content

Initial monomer, %	Initial polymer, %	Maximum conversion rate, %/sec	Maximum polymerization rate, %/sec[a]
50	0	0.265	0.13
45	5	0.267	0.12
40	10	0.315	0.13
30	20	0.375	0.11
20	30	0.175	0.035

[a] Obtained as maximum conversion rate × initial monomer content/100.
Runs at 0.5% AIBN, 2.5% stabilizer, 80°C.

Effect of Temperature: Anomalous Activation Energy

A series of dispersion polymerization runs at 70, 80, and 90°C gave the pseudo-first-order rate constants shown in Table VI.

TABLE VI
Rates at Different Temperatures[a]

Temperature, °C	Rate constant $k \times 10^3$, sec^{-1}
70	4.7
80	8.9
90	11.8

[a] Runs at 1% AIBN, 50% monomer.

The best-fit straight line on a conventional Arrhenius plot corresponds to an overall activation energy of 11.4 kcal/mole. This is lower by 8.1 kcal/mole than the value calculated for solution polymerization from the published activation energies for AIBN decomposition[20] and propagation and termination reactions of methyl methacrylate[21] (30.8, 4.7, 1.2 kcal/mole, respectively)

$$E_{\text{polym}} = (30.8/2) + 4.7 - (1.2/2) = 19.5 \text{ kcal/mole}$$

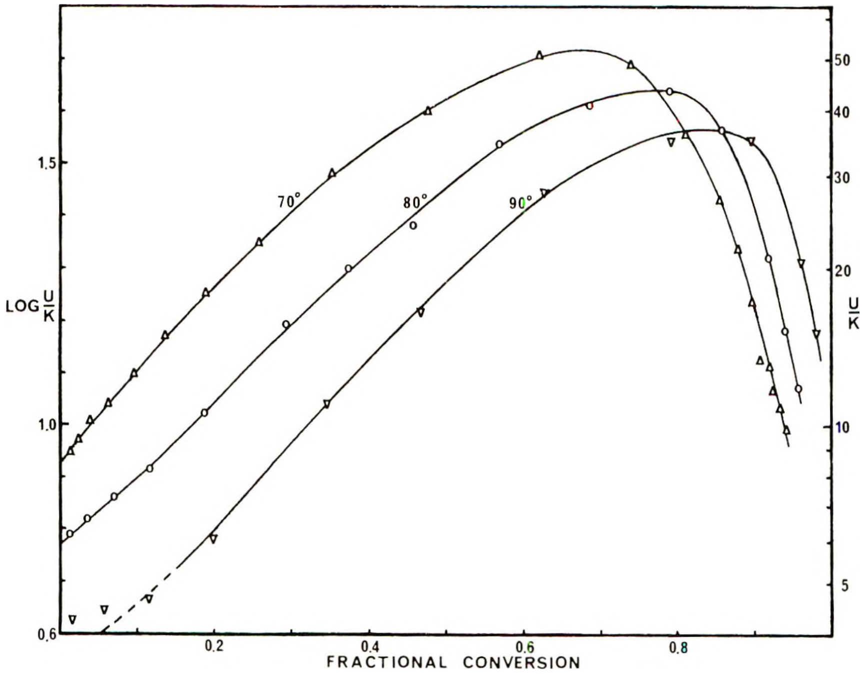

Fig. 12. Effect of temperature: dispersion polymerization at 70, 80, 90°C. Derived curves for runs with 50% monomer, 2.5% stabilizer, 1% AIBN in *n*-dodecane. K = value of $k_p/k_t^{1/2}$ in dilute solution (129, 155, 185 at 70, 80, 90°C). U/K should equal (Trommsdorff acceleration factor) × $\alpha(2f)^{1/2}$.

This anomalous activation energy is explained when the Trommsdorff acceleration curves derived from the kinetic data in dispersion polymerization (Fig. 12) are compared with the corresponding curves obtained by Schulz[4] in bulk polymerization (Fig. 4). In Figure 12 the values of $\alpha(2f)^{1/2}\,k_p/k_t^{1/2}$ have been divided by the values of $k_p/k_t^{1/2}$ found in solution or low-conversion bulk polymerization at the same temperature and therefore represent values of $\alpha(2f)^{1/2}$ × Trommsdorff acceleration factor.

Apart from the more gradual fall in polymerization rate at high conversions, the two sets of curves show very close correspondence. Clearly the polymerizations carried out at lower temperature are faster than would be expected because the viscosity is higher at a given conversion and therefore radical termination is more hindered. In fact, the deficit in activation energy found in dispersion polymerization corresponds very closely to half the activation energy for diffusion (corresponding to square root of k_t) extrapolated back to zero conversion calculated from Schulz's data (8.2 kcal/mole).

The peak values of the curves in Figures 12 and 4 at corresponding temperatures bear a constant ratio within experimental error (Table VII).

The ratio should give values of $\alpha(2f)^{1/2}$ which would be expected to show very little alteration over the experimental range of temperatures. The

TABLE VII
Peak Values from Bulk and Dispersion Curves

Temperature, °C	Peak value		Ratio
	Dispersion	Bulk	
70	53	57	0.93
80	44	48	0.92
90	38	39	0.97

actual values give estimates of initiator efficiency (assuming $\alpha = 1$) ranging from 0.42 to 0.47. This compares well with the value 0.52 estimated from a run at 0.2% AIBN. Both are probably slight underestimates, since the runs were carried out at much higher initiation rates than Schulz's bulk polymerizations, with correspondingly lower molecular weight and slightly reduced Trommsdorff acceleration.

Molecular Weight

On the proposed model the instantaneous molecular weight should run parallel to the rate of reaction, since the kinetic chain length is given by the ratio of polymerization rate to initiation rate. It is therefore very low at the start and finish of a polymerization run, rising to a very marked peak value in the middle.

The peak $\bar{M}_n$ should be half the peak $\bar{M}_w$, assuming ideal molecular weight distribution in the polymer formed at a given moment,[1] but should be roughly equal to the overall $\bar{M}_w$ averaged over the whole run. (Numerical integration on Figure 1 gave theoretical overall $\bar{M}_w$ = peak $\bar{M}_w \times 0.58$ = peak $\bar{M}_n \times 1.16$.)

This approximation is borne out by comparison of values of peak $\bar{M}_n$ calculated from the maximum rate with experimental values of overall $\bar{M}_w$ by light scattering (Table VIII). Data used were obtained earlier by Garden and Wiltshire[17] on dispersion polymerization of methyl methacrylate at 60°C in petroleum ether (bp 100–120°C) with degraded rubber as

TABLE VIII
Estimation of $\bar{M}_w$ from Peak Conversion Rate

Methyl methacrylate, %	Benzoyl peroxide, %	Benzene, %	Peak conversion rate, %/min	Calculated peak $\bar{M}_n$	Overall $\bar{M}_w$ found
33.3	0.417	—	1.4	1.8×10^6	2.1×10^6
40	0.417	—	1.7	2.7×10^6	2.3×10^6
33.3	0.417	12.9	1.1	1.4×10^6	1.6×10^6

stabilizer and benzoyl peroxide initiator. (k_d taken as 2.46×10^{-6} sec^{-1}, f as 0.5; chain transfer and initiator breakdown neglected; rate estimated from total solids on samples).

A corresponding calculation on the run shown in Figure 1 (k_d taken as 1.44×10^{-4} sec^{-1}, f as 0.5; initiator breakdown allowed for) gives estimated values of peak $\bar{M}_n = 0.5 \times 10^6$ and overall $\bar{M}_n$ over the whole polymerization $= 0.13 \times 10^6$. The overall $\bar{M}_n$ is obviously much less affected by the very high peak conversion rates.

Similar comparison of experimental with calculated overall $\bar{M}_n$ values gave fair agreement. In view of the very low expected molecular weight of polymer formed in the final stages of polymerization and probable loss of low molecular weight material in the purification of the polymer by methanol precipitation, the calculations have been based on the time taken to reach 90% conversion in those runs where polymerization proceeded further. Total number of chains initiated in this time was calculated by assuming $k_d = 1.44 \times 10^{-4}$ sec^{-1}, $f = 0.5$. Runs were at 80°C with 10% monomer in cyclohexane (C), benzene (B), or ethyl acetate (EA), and 5% synthetic stabilizer on monomer or none (Table IX). Monomer consumption was followed by gas chromatography.

TABLE IX
Estimation of $\bar{M}_n$ from Reaction Time and Conversion

						$\bar{M}_n \times 10^{-4}$		
System type	Medium	Stabilizer	AIBN, % on monomer	Conversion, %	Time, min	Calcd, overall	Found (VPO)	Found (MO)
Dispersion	C	+	1.0	90	44	4.7	—	6.2
	C	+	0.4	90	80	7.4	—	7.3
	C	+	0.4	90	120	5.7	7.1	8.4
Precipitation	C	−	0.4	80	160	4.4	2.9	4.0
Solution	B	−	0.4	50	120	3.2	2.6	3.3
	EA	−	0.4	46	120	2.9	2.4	3.4

Some confirmation of the very low initial molecular weights was obtained by halting polymerization runs in cyclohexane (10% monomer, 0.4% AIBN on monomer) as soon as visible whitening occurred. $\bar{M}_n$ values by VPO on the isolated polymer were 7 600 (stabilized; stabilizer present as contaminant) and 1 100 (unstabilized).

Change of k_p and k_t with Conversion

Values of k_p and k_t may be calculated for any conversion from kinetic data represented by, for example, Figure 3, if the assumption is made that the peak value of $k_p/k_t^{1/2}$ corresponds to the peak value in bulk polymerization. The method of Schulz[4] was used, which takes the low-conversion value of k_p as constant over the exponentially rising portion of the curve

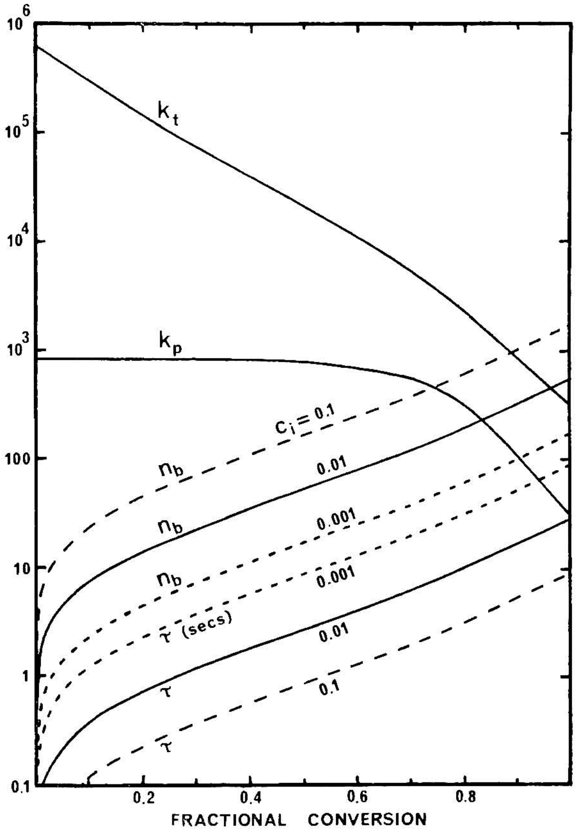

Fig. 13. Variation of parameters during a typical run at 80°C. Conditions as for Fig. 1. τ = mean radical lifetime (seconds); n_b = number of radicals per particle calculated assuming bulk kinetics apply within the particles, for a particle diameter 0.25 μ at full conversion. Dashed lines calculated for 10-fold changes in initiator concentration, using the same values of k_p, k_t.

(only k_t diffusion-controlled). Hence k_t is estimated in this region, and after making allowance for a contribution to the molecular mobility due to chain propagation, the thermal diffusion component of k_t is extrapolated exponentially over the peak and falling portion of the curve in order to estimate k_p in this region.

Typical results calculated from Figure 3 (fully corrected) are given in Table X and Figure 13.

Gardon, in the course of a detailed theoretical study of emulsion polymerization,[22] derived an estimate for the minimum possible value of k_t/k_p in circumstances where the macroradicals are completely immobile and active radical ends can only move into position to react with each other through extension of the molecules by adding monomer units. A value of about 12 times the volume fraction of monomer in the particles was obtained on the basis of a lattice model. (A value about 30% larger follows

TABLE X

Variation of k_p, k_t, Number of Radicals per Particle, Radical Lifetime, and Deviation from Steady-State Kinetics[a]

Conversion, %	k_p	k_t	Radicals per particle[b]	Mean radical lifetime, sec	Underestimation of rate constants, %
1	820	560 000	1.7	0.08	0.02
20	820	140 000	14	0.7	0.14
40	810	40 000	35	1.8	0.52
60	680	10 600	80	4	1.4
70	550	5 400	120	6	1.9
80	320	2 300	190	10	2.4
90	106	860	320	17	1.2
98	39	390	490	25	0.2

[a] Run at 50% monomer, 0.2% AIBN, 2.5% stabilizer, 80°C, in *n* dodecane.

[b] For 0.25 μ final diameter.

from the estimate of the "reaction diffusion" component of k_t made by Schulz[4] from diffusion theory.)

The values of k_t/k_p estimated in the present experiments never fall to less than about four times this theoretical minimum, despite the fact that even monomer diffusion is hindered at high conversions. Termination in these conditions is probably almost entirely by primary radicals which are at least as mobile as monomer molecules.

Radical Concentration and Numbers

Having estimated k_p and k_t, the instantaneous radical concentration is readily calculated on the basis of the proposed model, and hence the number of radicals per particle calculated according to bulk kinetics, which we shall call n_b [Appendix, eq. (9)].

Typical results are given in Table X and Figure 13, for a final particle diameter of 0.25 μ at full conversion. (These can be readily adapted to other conditions at the same temperature and initial monomer concentration, since n_b is proportional to the square root of initiator concentration and cube of particle diameter.)

Stockmeyer[12] has shown that deviations from bulk kinetics only begin to be significant when n_b falls below 1, and only when it falls below about 0.3 does the restriction of termination take on its simplified form where the actual average number of radicals per particle, $\bar{n}$, approximates to 0.5. Clearly, in the present case we should not expect any deviation from bulk kinetics, which fully accords with the experimental results.

A tenfold reduction of initiator would still give no noticeable deviation above 2% conversion at 0.25 μ final diameter, and it would theoretically be necessary to go down to final particle sizes of the order of 0.03 μ to approach ideal Harkins-Ewart-Smith kinetics over the whole conversion range.

Radical Lifetimes and Deviations from Steady State

From k_t the mean radical lifetime can also be calculated (as the ratio of radical concentration to the rate of termination [Appendix, eq. (10)]) and typical results are shown in Table X. The mean lifetime is infinitesimally small initially and increases rapidly due to both increasing particle volume and decreasing k_t, reaching a final value of the order of 20–30 sec at full conversion. At tenfold lower initiator concentration it would be 1–2 min (inversely proportional to square root, see Fig. 13).

It might be thought that the steady-state assumptions used in the derivation of the kinetic equations would be invalidated by these relatively long radical lifetimes. However, the deviation from the rate of reaction calculated on a steady state basis can readily be estimated from the rate of change of radical concentration with conversion (Appendix), and values obtained are shown in Table X. It is clear that rate constants will be under-estimated from the kinetic data throughout the run, but never by more than 2.5%, which is negligible over the eightfold range studied. The extent of deviation is independent of the initiation rate (except in so far as the Trommsdorff curves are slightly displaced).

We can conclude that the steady-state treatment is a valid approximation in the range of conditions studied.

CONCLUSION

The proposed model, based on polymerization within monomer-swollen particles according to bulk kinetics, provides a consistent explanation of the kinetics of free-radical dispersion polymerization of methyl methacrylate in aliphatic hydrocarbon in the temperature range 70–90°C.

APPENDIX

Steady-State Equations

If R_i is the initiation rate in the whole dispersion, all radicals are transferred to particles, and v is the particle volume fraction, then the effective initiation rate in the particles is R_i/v. Putting this equal to the rate of termination in the particles, $k_t c_r^2$, where k_t is the termination rate constant, gives the radical concentration in the particles:

$$c_r = (R_i/vk_t)^{1/2} \tag{7}$$

The rate of polymerization in the whole dispersion, R_p, with a propagation rate constant k_p and monomer concentration in the particles c_p, is given by:

$$R_p = vc_pk_pc_r = c_pk_p\,(R_iv/k_t)^{1/2} \tag{8}$$

The number of radicals per particle assuming bulk kinetics, n_b, for a particle radius r microns, follows from (7):

$$\begin{aligned} n_b &= 10^{-15}\,(4/3)\pi r^3 N c_{\mathrm{r}} \\ &= 10^{-15}\,(4\pi N r^3{}_{\max}/3v_{\max})\,(R_i v/k_t)^{1/2} \end{aligned} \tag{9}$$

where $r_{\max}$, $v_{\max}$ are the radius and volume fraction attained at full conversion, and N is Avogadro's number.

The mean radical lifetime τ is given by:

$$\tau = c_{\mathrm{r}}/R_t = (v/R_i k_t)^{1/2} = R_p/c_{\mathrm{p}} k_p R_i \tag{10}$$

The mean kinetic chain length ν is given by:

$$\nu = R_p/R_i = c_{\mathrm{p}} k_p (v/R_i k_t)^{1/2} \tag{11}$$

Rate of Conversion: Approximate Equation

If c_0 is the initial monomer concentration, x the fractional conversion after time t, v_{p} the molar volume of polymer in liters, α the partition coefficient of monomer between particles and diluent, c_{i} the initiator concentration, f its efficiency, and k_d its decomposition rate constant, we can write the following approximate equations:

$$c_{\mathrm{p}} = \alpha c_0 (1 - x) \tag{12}$$

$$v = x c_0 v_{\mathrm{p}} \tag{13}$$

$$dx/dt = R_p/c_0 \tag{14}$$

Substitution in eq. (8) yields

$$\begin{aligned} dx/dt &= \alpha(1 - x) k_p\,(x c_0 v_{\mathrm{p}} R_i/k_t)^{1/2} \\ &= \alpha x^{1/2}(1 - x)\,(2f k_d c_{\mathrm{i}} c_0 v_{\mathrm{p}})^{1/2}(k_p/k_t^{1/2}) \end{aligned} \tag{15}$$

To allow for breakdown of initiator present in an initial concentration i_0, put:

$$c_{\mathrm{i}} = i_0 e^{-k_d t} \tag{16}$$

Rearranging eqs. (15) and (16) we have:

$$\alpha(2f)^{1/2} k_p/k_t^{1/2} = (dx/dt)/x^{1/2}(1 - x)(c_0 v_{\mathrm{p}} i_0 k_d e^{-k_d t})^{1/2} \tag{17}$$

Rate of Conversion: Corrected Equation

In this derivation, eqs. (12)–(17) are replaced by expressions which allow for the change in volume of dispersion on polymerization, the increased particle volume due to swelling by monomer, and the correct partition relationship. Additivity of volumes is assumed.

If v_{m} and v_{p} are the molar volumes of the monomer and polymer (in liters) then after conversion x the volume of the dispersion will be reduced by a factor v_x, given by:

$$v_x = 1 - x c_0 (v_{\mathrm{m}} - v_{\mathrm{p}}) \tag{18}$$

The concentration of monomer in the whole dispersion, c_m, will be:

$$c_m = c_0(1 - x)/v_x \tag{19}$$

This is related to the concentration c_p in the particles (with volume fraction v) and c_d in the diluent, by:

$$c_m = vc_p + (1 - v)c_d = c_p[v + (1 - v)/\alpha]$$

Hence, replacing eq. (12), we have:

$$c_p = \alpha c_0(1 - x)/v_x[1 + (\alpha - 1)v] \tag{20}$$

The total particle volume fraction v is given by the sum of the polymer volume fraction and the volume of the monomer swelling it at a concentration c_p:

$$v = xc_0v_p/v_x + vc_pv_m$$

Substitution of the expression for c_p of eq. (20) in this gives, after rearrangement, a quadratic equation for v with a single positive root:

$$0 = Av^2 + Bv - C$$

hence

$$v = [(B^2 + 4AC)^{1/2} - B]/2A \tag{21}$$

where

$$A = v_x(\alpha - 1)$$

$$B = v_x + xc_0v_p(1 - \alpha) - \alpha c_0v_m(1 - x)$$

$$C = xc_0v_p$$

We can also replace eqs. (16) and (14) by:

$$R_i = 2fk_di_0e^{-k_dt}/v_x$$

$$dx/dt = v_xR_p/c_0$$

These combined with eqs. (19), (20), and (21) substituted in eq. (8) give:

$$dx/dt = \{v^{1/2}/v_x^{1/2}[1 + (\alpha - 1)v]\}\alpha(1 - x)(2fk_di_0e^{-k_dt})^{1/2}(k_p/k_t^{1/2}) \tag{22}$$

$$\alpha(2f)^{1/2}k_p/k_t^{1/2} = (dx/dt)/(1 - x)(k_di_0e^{-k_dt})^{1/2}\{v^{1/2}/v_x^{1/2}[1 + (\alpha - 1)v]\} \tag{23}$$

These are the fully corrected forms of the rate equations.

In eqs. (22) and (23), the expression in braces replaces $(xc_0v_p)^{1/2}$ in eqs. (15) and (16), with v, v_x as defined by eqs. (21) and (18).

When $\alpha = 1$, eq. (21) simplifies to:

$$v = C/B = xc_0v_p/(1 - c_0v_m + c_0xv_p) \tag{21a}$$

and the expression in braces in eqs. (22) and (23) becomes:

$$(xc_0v_p)^{1/2}[(1 - c_0v_m + xc_0v_p)(1 - xc_0v_m + xc_0v_p)]^{-1/2} \tag{22a}$$

Deviation from Steady State

If the rate of termination falls short of the rate of initiation by a fraction s, we can replace eqs. (7) and (8) by:

$$c_r = (1 - s)^{1/2}(R_i/vk_t)^{1/2} \tag{24}$$

$$\begin{aligned} R_p &= (1 - s)^{1/2}c_pk_p(R_iv/k_t)^{1/2} \\ &= c_0(dx/dt)/v_x \end{aligned} \tag{25}$$

But the difference between the rate of initiation and the rate of termination in the whole dispersion also gives the rate of increase in the number of moles of radicals present in the changing volume of the dispersion:

$$v_xR_is = d(c_rv_xv)/dt$$

hence

$$\begin{aligned} s &= [d(c_rv_xv)/dt]/v_xR_i \\ &= (dx/dt)[d(R_pv_x/c_pk_p)/dx]/v_xR_i \\ &= (R_p/c_0R_i)d(R_pv_x/c_pk_p)/dx \end{aligned} \tag{26}$$

All the quantities involved here can be readily calculated from the experimental data. $(1 - s)^{1/2}$ then represents the factor by which the observed rate is slower than would be expected from the steady state equations, that is the factor by which the overall rate constants are underestimated from the experimental rate data.

Provided that s is small, the steady-state equations (8) for R_p can be substituted in eq. (26) to obtain a good estimate of s. Then, taking R_i as constant:

$$s = (k_pc_p/c_0)(v/k_t)^{1/2}d(v/k_t)^{1/2}/dx \tag{27}$$

Thus the rate of initiation cancels out, so the extent of deviation from steady-state kinetics is independent of initiation rate (except in so far as the diffusion-controlled value of k_t is slightly dependent on molecular weight).

The fully corrected equation in terms of the conversion x is very complicated, but the approximate form corresponding to eqs. (12) to (15) reduces to:

$$s = \alpha c_0v_pk_p(1 - x)(1 - xd\ln k_t/dx) \tag{28}$$

Values Taken for Numerical Data

TABLE XI

Value	70°C	80°C	90°C	Ref.
Density of methyl methacrylate	0.884	0.872	0.859	23
Density of poly(methyl methacrylate)	1.173	1.170	1.167	23[a]
Density of n-dodecane	0.714	0.706	0.699	24[b]
Density of n-butyl acetate	0.827	0.815	0.804	24,[c] 25
Density of stabilizer (in solution)	0.965	0.959	0.952	c
k_p in dilute solution	674	819	985	18
k_t in dilute solution $\times 10^{-7}$	2.75	2.80	2.84	18
k_d for azobisisobutyronitrile $\times 10^4$	0.403	1.44	4.83	20
k_d for benzoyl peroxide $\times 10^4$	—	0.31	—	26

[a] Extrapolated by using quadratic expression.

[b] Interpolated from decane and tetradecane.

[c] Temperature variation by analogy with similar esters.

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Reaction Mechanism of the Alternating Copolymerization of Aziridines with Cyclic Imides

TSUTOMU KAGIYA, TERUHO ADACHI, and KENICHI FUKUI,
Faculty of Engineering, Kyoto University, Kyoto, Japan

Synopsis

The copolymerizations of *N*-substituted aziridines and cyclic imide were studied. *N*-Ethylsuccinimide copolymerized with ethylenimine, but *N*-ethylethylenimine did not copolymerize with succinimide and *N*-ethylsuccinimide without catalyst. The effect of additives on the copolymerization of ethylenimine with succinimide and that of *N*-ethylethylenimine with succinimide and *N*-ethylsuccinimide was also examined. The rate of copolymerization of ethylenimine with succinimide was accelerated by the addition of *N*-acetylethylenimine or water. The copolymerization of *N*-ethylethylenimine with succinimide was initiated only by water, but *N*-ethylethylenimine did not copolymerize with *N*-ethylsuccinimide in the presence of water. Gas evolved on heating the copolymer of ethylenimine and succinimide was analyzed and confirmed to be ammonia. On the basis of these results the reaction mechanisms of the copolymerization of ethylenimine with succinimide or *N*-ethylsuccinimide and of *N*-ethylethylenimine with succinimide initiated by water are discussed.

INTRODUCTION

In the previous paper,[1] the structures of copolymers of aziridines with cyclic imides were clarified and a mechanism for the initiation reaction in the copolymerization of ethylenimine with succinimide was discussed.

The present research was undertaken to elucidate the reaction mechanism, especially that of propagation of the copolymerization and that of copolymerization of *N*-ethylethylenimine with succinimide initiated by water.

EXPERIMENTAL

Materials

The methods of preparation and purification of monomers were described in the previous paper.[1] Benzene, *n*-propylamine, and ethanol were purified by usual method.[2] Acetamide and ethanolamine were obtained commercially (G. R. grade) and used without further purification. Succinamic acid was prepared from succinic anhydride and aqueous ammonia according to the literature,[3] mp 157.7–158.0°C (reported[3] mp 157°C).

Copolymerization Procedure

The method of the copolymerization was described in the previous paper. Solid material was placed in a reaction ampoule with imide. Liquid monomer and solvent were distilled into the ampoule under vacuum.

Analysis of Gas Evolved by Heating the Copolymer

A 0.3-g portion of the copolymer of ethylenimine with succinimide was heated in a glass ampoule under a nitrogen atmosphere at 110°C for 16 hr.

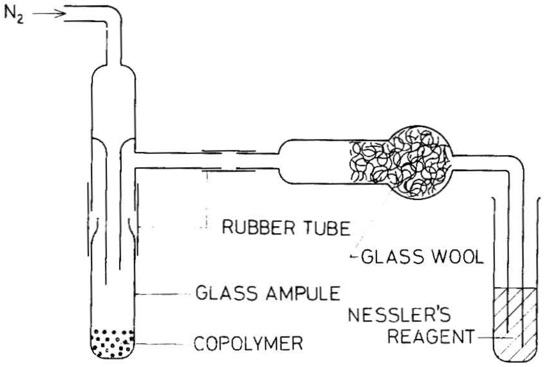


Fig. 1. Analysis of gas evolved by heating the copolymer.

Then the ampoule was broken and placed in the arrangement shown in Figure 1. The gas evolved on heating was analyzed with Nessler's reagent.

RESULTS AND DISCUSSION

Reactivities of *N*-Substituted Monomers

In the previous paper, it was shown that the copolymer of ethylenimine with succinimide had *N*-substituted succinimide and *N*-acylethylenimine (both of which have no hydrogen attached to nitrogen) as endgroups. From this result, it was considered that the hydrogens attached to nitrogen in the monomers had migrated during the reaction. To verify this, copolymerizations of *N*-substituted monomers (having no *N*-hydrogen) were carried out; results are shown in Table I.

N-Ethylsuccinimide copolymerized with ethylenimine. On the other hand, *N*-ethylethylenimine (no *N*-hydrogen) did not copolymerize with either succinimide or *N*-ethylsuccinimide, even at 100°C. *N*-Acetylethylenimine, which was a model compound of the endgroup, did not also copolymerize with succinimide.

These results indicate that the *N*-hydrogen of succinimide is not necessary for this copolymerization, but that hydrogen migration of ethylenimine plays an important part in the copolymerization.

TABLE I
Reaction of N-Substituted Monomers[a]

Expt. no.	Monomers, g (mole)[b] Imine	Imide	Solvent (Benzene), ml	Time, hr	Yield, g
1	EI 0.86(0.02)	ESI 2.54(0.02)	—	65.0	0.887
2	EEI 0.71(0.01)	SI 0.99(0.01)	—	170.5	0.000
3	EEI 0.71(0.01)	ESI 1.27(0.01)	—	48.0	0.000
4	EI 0.86(0.02)	ESI 2.54(0.02)	5.0	95.5	1.457
5	EEI 0.71(0.01)	SI 0.99(0.01)	2.5	170.5	0.000
6	EEI 0.71(0.01)	ESI 1.27(0.01)	2.5	18.0	0.000
7[c]	EEI 2.13(0.03)	SI 2.97(0.03)	—	7.5	0.000
8	AEI 0.85(0.01)	SI 0.99(0.01)	—	119.0	0.000

[a] Without catalyst, at 70°C.

[b] EI = ethylenimine, SI = succinimide, EEI = N-ethylethylenimine, ESI = N-ethylsuccinimide, AEI = N-acetylethylenimine.

[c] At 100°C.

Effect of Additives on the Copolymerization of Ethylenimine with Succinimide

It was shown clearly that the copolymer of ethylenimine with succinimide had the *N*-acylethylenimine and primary amide endgroups. Moreover, it may be considered that there is an amine end. In order to determine the endgroup which reacts with monomer in the propagation reaction, acetamide, *n*-propylamine, and *N*-acetylethylenimine as model compounds were added to the system of ethylenimine and succinimide. The results are shown in Table II. Acetamide and *n*-propylamine scarcely affected the rate of copolymerization, but the rate was remarkably accelerated by addition of *N*-acetylethylenimine. The composition of the copolymer obtained, as determined by elementary analysis, was succinimide 46.5 mole-%, ethylenimine 41.8 mole-%, *N*-acetylethylenimine 11.7 mole-%.

TABLE II
Effect of Additives on the Rate of the Copolymerization of Ethylenimine with Succinimide[a]

Expt. no.	Additive Type	Amt, mole	Time, min	Yield, g	Rate, g/min[b]
1	—	—	21.5	2.19	0.102
2	Acetamide	0.003	18.0	2.01	0.112
3	*n*-Propylamine	0.003	23.5	2.15	0.092
4	*N*-Acetylethylenimine	0.003	9.2	2.32	0.252

[a] Ethylenimine 0.03 mole, succinimide 0.03 mole, at 70°C.

[b] Reaction was stopped at almost the same yield, and the reaction rate was expressed by the yield divided by time.

This result indicates that the *N*-acylethylenimine endgroup produced by acylation of ethylenimine with succinimide is an active species and the propagation of the copolymerization proceeds from this endgroup.

On the other hand, water was reported to catalyze polymerization of ethylenimine.[4] Water did accelerate the copolymerization, as shown in Table III. The molar ratio of ethylenimine and succinimide units in this copolymer was unity. Therefore, homopolymerization of ethylenimine did not occur, but the copolymerization of ethylenimine with succinimide occurred.

TABLE III
Effect of Water on the Rate of the Copolymerization of Ethylenimine with Succinimide[a]

Expt. no.	Water, g (mmole)	Time, min	Yield, g	Rate, g/min	η_{sp}/c[b]	Composition Imine, mole-%	 Imide, mole-%
1	—	21.5	2.19	0.102	0.085	—	—
2	0.01(0.6)	20.5	2.19	0.107	0.085	—	—
3	0.03(1.7)	16.0	2.19	0.137	0.084	—	—
4	0.05(3.0)	15.0	2.84	0.189	—	49.7	50.3
5	0.16(10.0)	8.0	3.12	0.390	0.079	—	—

[a] Ethylenimine 0.03 mole, succinimide 0.03 mole, at 70°C.
[b] 0.5% solution of formic acid at 35°C.

Effect of Additives on the Copolymerization of *N*-Ethylethylenimine with Succinimide or *N*-Ethylsuccinimide

As shown in Table I, *N*-ethylethylenimine did not copolymerize with succinimide, but in the presence of water (Table IV), copolymerization

TABLE IV
Effect of Additives on the Copolymerization of *N*-Ethylethylenimine (EEI) with Succinimide (SI) and *N*-Ethylsuccinimide (ESI)[a]

Expt. no.	Monomers, g (mole) EEI	 Imide	Additive[b] Type	 Amt, mole	Time, hr	Yield, g
1	0.57(0.008)	SI 0.99(0.01)	H_2O	0.002	118.5	0.143
2	2.13(0.03)	SI 2.97(0.03)	H_2O	0.01	24.0	0.616
3	2.13(0.03)	SI 2.97(0.03)	AEI	0.003	37.5	0.000
4	2.13(0.03)	ESI 3.82(0.03)	H_2O	0.003	29.0	0.000
5	2.13(0.03)	SI 2.97(0.03)	EtOH	0.006	22.0	0.000
6	2.13(0.03)	SI 2.97(0.03)	SAA	0.006	24.0	0.000
7	2.13(0.03)	SI 2.97(0.03)	EA	0.006	22.5	0.000

[a] Temp. 70°C.
[b] AEI = *N*-acetylethylenimine; SAA = succinamic acid; EA = ethanolamine.

occurred. It was reported in the previous paper that this copolymerization proceeded alternately and the endgroups of the copolymer were not *N*-acylethylenimine, but *N*-substituted succinimide and secondary amine. These results suggest that water initiates the copolymerization in a different way not involving migration of the ethyl group of *N*-ethylethylenimine. On the other hand, the copolymerization of *N*-ethylethylenimine with succinimide did not occur with *N*-acetylethylenimine, which was an active species in the copolymerization of ethylenimine with succinimide. *N*-Ethylethylenimine and *N*-ethylsuccinimide which have substituents on nitrogen, did not copolymerize in the presence of water. To elucidate the action of water, ethanol, which has a hydroxyl group, was added to the system of *N*-ethylethylenimine and succinimide, but reaction did not occur. The possibility of hydrolysis of monomers was considered; however, when ethanolamine and succinamic acid, which are reaction products of hydrolysis, were added, copolymerization did not occur.

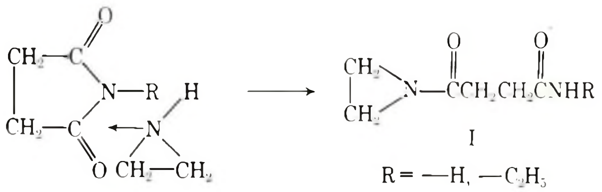
Analysis of Gas Evolved by Heating the Copolymer

It is known that polyamides containing the succinic acid are unstable on heating, and undergo degradation. In the previous paper, it was considered that the *N*-substituted succinimide ring endgroup was not formed by initiation reaction, but might be formed by another reaction, such as degradation or cyclization. To confirm the mechanism of formation of the *N*-substituted succinimide ring, the copolymer of ethylenimine with succinimide was heated at 110°C and the gas evolved was qualitatively analyzed. After heating, the pressure in the ampoule was slightly elevated. The evolved gas smelled of ammonia, and it was positive for Nessler's reagent.

Reaction Mechanism

Alternating Copolymerization of Ethylenimine with Succinimide or N-*Ethylsuccinimide*

Initiation. The initiation reaction for the alternating copolymerization of ethylenimine with succinimide or *N*-ethylsuccinimide was as shown in eq. (1):[1]

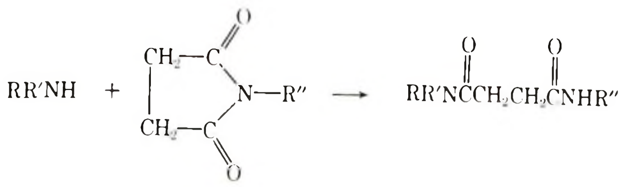


I

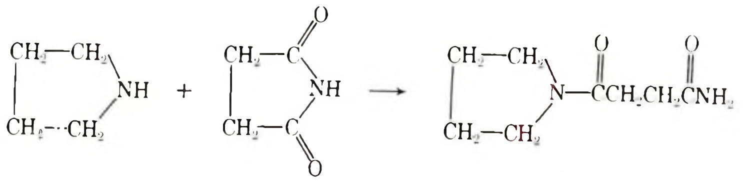
R = —H, —C_2H_5

(1)

N-Acylethylenimine and amide end were formed by this initiation reaction. This reaction is similar to reactions (2)[5] and (3).[6]

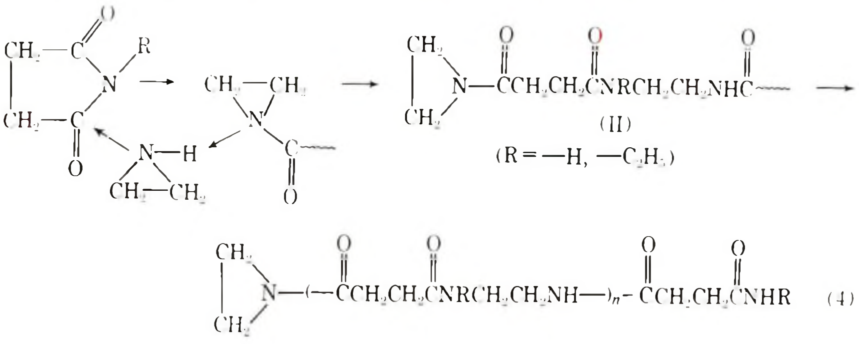


(2)



(3)

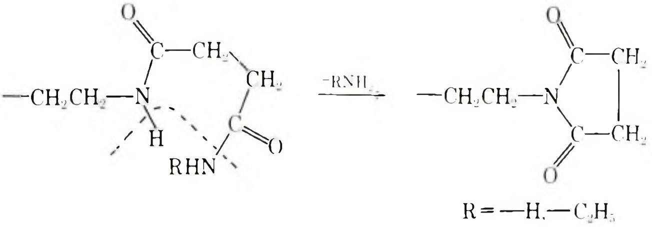
Propagation. Compound I did not polymerize by polyaddition,[7] but propagates by alternating addition of monomers. From the effect of additives, it was determined that the active species of this copolymerization was the *N*-acylethylenimine end. Thus, propagation proceeds from this endgroup. Because of alternating copolymerization, succinimide (or *N*-ethylsuccinimide) attacks *N*-acylethylenimine end. If it is supposed that succinimide alone attacks this end, the *N*-hydrogen of succinimide must migrate to the nitrogen of the *N*-acylethylenimine end, and the ring-opening reaction of *N*-acylethylenimine occurs. The *N*-hydrogen of succinimide, however, did not migrate, because *N*-ethylsuccinimide which has no *N*-hydrogen, copolymerized with ethylenimine. As shown in experiment 3 of Table IV, *N*-ethylethylenimine did not copolymerize with succinimide by addition of active species, that is, *N*-acylethylenimine. From this result, it was confirmed that hydrogen migration of ethylenimine also occurred in the propagation reaction. It is therefore considered that the hydrogen of ethylenimine migrates to the nitrogen of *N*-acylethylenimine. As shown in eq. (4), the nucleophilicity of the nitrogen of succinimide (or *N*-ethylsuccinimide) increases on coordination of ethylenimine to the carbonyl group of imide, and the nitrogen of the imide attacks the *N*-acylethylenimine end. Then, via a six-membered ring, the hydrogen of ethylenimine migrates, and the succinimide ring opens without hydrogen migration of succinimide to yield II, which also has an *N*-acylethylenimine



(4)

end. This reaction is repeated to give a polyamide having *N*-acylethylenimine and an amide as endgroups.

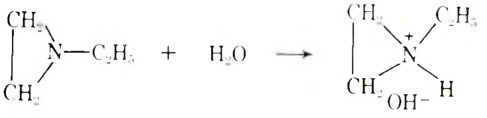
Cyclization. On the other hand, the copolymer of ethylenimine with succinimide had an *N*-substituted succinimide ring as an endogroup, as mentioned in the previous paper.[1] Since the copolymer of ethylenimine with *N*-ethylsuccinimide also has this endgroup, this end is not formed by hydrogen migration of succinimide. The fact that the formation of ammonia occurred on heating shows that evolution of ammonia gas or $C_2H_5NH_2$ also occurs at the amide end in the copolymerization, and an *N*-substituted succinimide end is given by cyclization [eq. (5)].



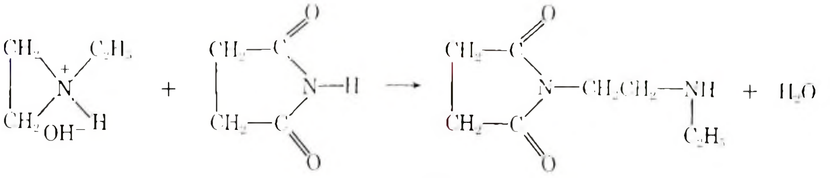
(5)

Alternating Copolymerization of N-Ethylethylenimine with Succinimide Initiated by Water

Initiation. *N*-Ethylethylenimine copolymerized with succinimide in the presence of water, whereas *N*-ethylethylenimine and *N*-ethylsuccinimide did not (Expt. 4 in Table IV). This fact indicates that hydrogen migration of succinimide occurs in this copolymerization. The copolymer did not have an *N*-acylethylenimine endgroup, but *N*-substituted succinimide and secondary amine ends, as mentioned in the previous paper.[1] The fact that ethanolamine and succinamic acid did not catalyze the copolymerization (Expts. 6 and 7, Table IV) leads to the conclusion that the hydrolyzed products of monomers do not initiate the copolymerization. On the other hand, it was reported that water catalyzed the polymerization of ethylenimine[4] and the active species of the polymerization was immonium ion.[8] A reaction mechanism is proposed in consideration of the facts mentioned above.


(6)

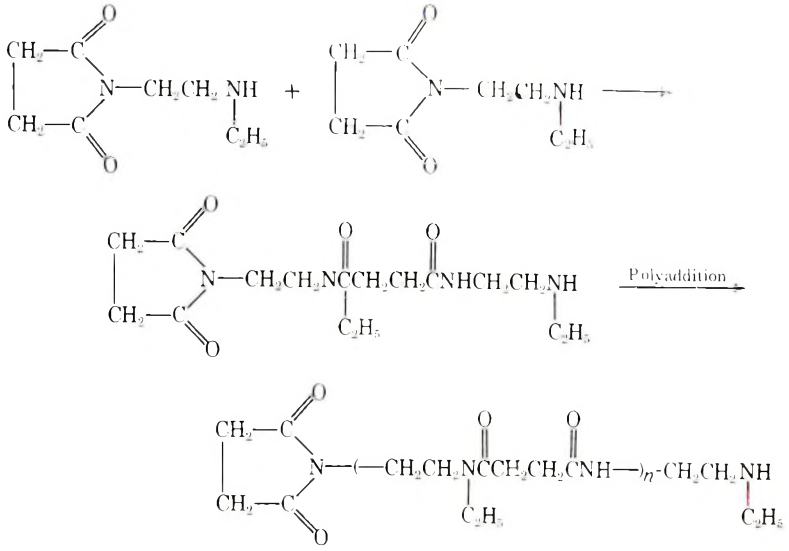
III


(7)

IV

As shown in eqs. (6) and (7), an immonium ion (III) is produced by the action of water, and III attacks succinimide to give compound IV.

Propagation. *N*-Ethylethylenimine does not attack the imide end of IV, because *N*-ethylethylenimine has no *N*-hydrogen, and the *N*-acylethylenimine end is not present in the copolymer. As mentioned before, ring opening of succinimide occurs by the reaction with amine. The amine end of IV is deactivated by the reaction with monomeric succinimide to give an amide end. So it is concluded that propagation reaction proceeds by the reaction shown in eq. (8).



(8)

The copolymer which has *N*-substituted succinimide and secondary amine endgroups is produced by polyaddition, that is, the amine end of IV attacks the succinimide end of IV.

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Structural Study of Alternating Copolymerization of Aziridines with Cyclic Imide

TSUTOMU KAGIYA, MASATSUGU IZU, TERUHO ADACHI, and KENICHI FUKUI, *Faculty of Engineering, Kyoto University, Kyoto, Japan*

Synopsis

The structures of copolymers of aziridines with cyclic imides were determined by means of infrared spectrometry, paper electrophoresis of the hydrolyzate, and NMR spectrometry. The structure of the repeating unit in the copolymer of ethylenimine with succinimide was $\text{+}CH_2CH_2NHCOCH_2CH_2CONH\text{+}$. The endgroups of the copolymer were *N*-acylethylenimine ring, *N*-substituted succinimide ring, and primary amide group. The copolymer of ethylenimine with *N*-ethylsuccinimide had the repeating unit of $\text{+}CH_2CH_2NHCOCH_2CH_2CON(C_2H_5)\text{+}$ and the endgroups of *N*-acylethylenimine and *N*-substituted succinimide ring. *N*-Ethylethylenimine did not copolymerize with succinimide, but in the presence of water, the reaction occurred to give an amorphous polymer. This copolymer had the repeating unit $\text{+}CH_2CH_2N(C_2H_5)COCH_2CH_2CONH\text{+}$ and the endgroups were *N*-substituted succinimide ring and amine group but not *N*-acylethylenimine ring. On the basis of this structural information, the initiation reaction was discussed.

INTRODUCTION

In recent years, Kagiya et al.[1] and Grundschober[2] reported that aziridines copolymerized alternately with cyclic imides to give crystalline polyamide. For example, ethylenimine copolymerized with succinimide to yield nylon 24, $\text{+}CH_2CH_2NHCOCH_2CH_2CONH\text{+}_n$, melting near 300°C.

Two different mechanisms of this copolymerization were proposed by the two groups mentioned above. Kagiya et al.[1] proposed a reaction mechanism via *N*-ethylenesuccinamide, $\overline{CH_2CH_2N}COCH_2CH_2CONH_2$, while Grundschober proposed a mechanism via *N*-(β-aminoethyl)succinimide, $\overline{C(O)CH_2CH_2C(O)N}{-}CH_2CH_2NH_2$. In order to clarify the mechanism, the present research was undertaken to identify the structure of the copolymers, especially those of endgroups.

EXPERIMENTAL

Materials

Ethylenimine was obtained commercially, dried over potassium hydroxide pellets, and then fractionated. *N*-Ethylethylenimine[3] and *N*-acetylethylenimine[4] were prepared according to the literature. Physical constants were: ethylenimine, bp 55.9°C; *N*-ethylethylenimine, bp 51.0–51.2°C (reported[3] bp 51.0°C); *N*-acetylethylenimine, bp 36.4–36.6°C/11 mm Hg (reported[4] bp 41.5–43.5°C/20.2 mm Hg).

Succinimide was obtained commercially, recrystallized from ethanol, and dried *in vacuo;* mp 126–127°C. *N*-Ethylsuccinimide was prepared from succinic acid and ethylamine according to the literature[5,6] and distilled under reduced pressure; bp 126.5–128.0°C/21 mm Hg (reported[6] bp 122–132°C/20 mm Hg).

Copolymerization Procedure

A measured amount of cyclic imide was placed in a glass ampoule. The ampoule was evacuated for drying. In order to dry aziridine, potassium hydroxide pellets were added to a reservoir where aziridine was placed. A measured amount of aziridine was distilled from the reservoir into the glass ampoule under vacuum. The glass ampoule was then sealed and kept in a constant-temperature bath for a definite period. The reaction products were washed with acetone to remove the residual monomers and then dried *in vacuo.*

Characterization of the Copolymer

The composition of the copolymer was determined by elementary analysis. The molecular weight was measured by a cryoscopic method with water as solvent. The infrared spectrum was obtained by the potassium bromide pellet technique or the liquid film method on a Shimadzu infrared spectrophotometer, Model IR-27, with a sodium chloride prism. The NMR spectrum was recorded with a JEOL instrument, Model JNM-3H-60 at 60 MHz.

Hydrolysis of the Copolymer

A 0.5-g portion of the copolymer dissolved in 5 ml of 6*N* HCl was heated in a glass ampoule under a nitrogen atmosphere at 110°C for 36 hr. The hydrolyzate was identified by paper electrophoresis with the use of a ninhydrin–*n*-butanol solution for the coloration. The conditions of electrophoresis were: voltage, 1500 V; time, 48 min; buffer solution, *M*/15 KH_2PO_4, pH 4.5; filter paper, Toyo Filter Paper No. 51-A.

RESULTS AND DISCUSSION

Copolymerization of Aziridines with Cyclic Imides

The results of the copolymerization of aziridines with cyclic imides are shown in Table I.

The molar ratio of aziridine and cyclic imide units in the copolymer was almost unity in every case, as has been reported by previous workers. Without catalyst, *N*-ethylethylenimine did not copolymerize with succinimide, but copolymerization occurred in the presence of water.

TABLE I
Copolymerization of Aziridines with Cyclic Imides[a]

Expt. no.	Monomers, g (mole)[b]		Time, hr	Yield, g	Composition[c]	
	Imine	Imide			Imine, mole-%	Imide, mole-%
1	EI, 3.88(0.09)	SI, 2.97(0.03)	0.75	0.98	55.3	44.7
2	EI, 1.29(0.03)	SI, 2.97(0.03)	0.45	2.40	52.9	47.1
3	EI, 1.29(0.03)	SI, 2.97(0.03)	0.33	1.79	51.7	48.3
4	EI, 0.65(0.015)	SI, 2.97(0.03)	0.43	0.90	50.5	49.5
5	EI, 0.86(0.02)	ESI, 2.54(0.02)	65.0	0.89	45.7	54.3
6	EEI, 0.71(0.01)	SI, 0.99(0.01)	170.5	0.00	—	—
7[d]	EEI, 2.13(0.03)	SI, 2.97(0.03)	24.0	0.62	50.4	49.6

[a] Without catalyst, at 70°C.

[b] Monomers: SI = succinimide, ESI = *N*-ethylsuccinimide, EI = ethylenimine, EEI = *N*-ethylethylenimine.

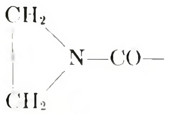
[c] The composition was determined by the elementary analysis.

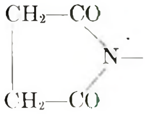
[d] 0.01 mole of water was added to the system.

Structure of the Copolymer

Copolymer of Ethylenimine with Succinimide. The copolymer obtained was a white or light yellow powdery polymer and soluble in formic acid and water. The number-average molecular weight of the copolymer measured by a cryoscopic method was about 400–500.

The infrared spectra of the copolymers shown in Figure 1 displayed the characteristic peaks of secondary amide at 1643 and 1553 cm^{-1}, regardless of the composition of monomers. These peaks are assigned to the amide group of the repeating unit, $+CH_2CH_2NHCOCH_2CH_2CONH+$. The peak at 1705 cm^{-1} may be attributed to an endgroup. Considering the structures of the monomers, two plausible structures of endgroups, *N*-acylethylenimine (I) and *N*-substituted succinimide (II), may be proposed.


I


II

The infrared spectra of succinimide and *N*-acetylethylenimine are shown in Figure 1d and 1e; both exhibited an absorption peak near at 1705 cm^{-1}.

TABLE II
Paper Electrophoresis of Hydrolyzate[a]

Sample	Relative mobility		
Hydrolyzate	1.00	0.815	0.605
NH_4OH	1.00	—	—
Ethylenediamine	—	0.815	—
Ethanolamine	—	—	0.601

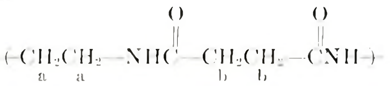
[a] Conditions given in experimental section.

Fig. 1. Infrared spectra of copolymers of ethylenimine with succinimide, with various compositions of monomers. (*a*) ethylenimine: succinimide molar ratio = 1:1; (*b*) molar ratio = 1:2 (*c*) molar ratio = 3:1; (*d*) succinimide; (*e*) *N*-acetylethylenimine.

From this result, it was suggested that one of these rings or both were present in the polymer as endgroups.

To confirm the existence of an *N*-acylethylenimine ring which must yield ethanolamine by hydrolysis, the copolymer was hydrolyzed with 6*N* HCl. The result of the paper electrophoresis of the hydrolyzate is shown in Table II. Besides the spot of ethylenediamine formed from the repeating unit, two spots which are considered to originate from the endgroups were observed. The first spot agreed with that of NH_4OH from the amide end, $-CONH_2$, and the second one was in agreement with that of ethanolamine from the *N*-acylethylenimine ring.

The NMR spectrum measured with D_2O as a solvent is shown in Figure 2*A*. Peaks at τ = 6.85(a), 7.57(b) were assigned to the methylene proton of the repeating unit,



$$\left(\!-\underset{a}{CH_2}\underset{a}{CH_2}-NH\overset{O}{\overset{\|}{C}}-\underset{b}{CH_2}\underset{b}{CH_2}-\overset{O}{\overset{\|}{C}}NH-\right)$$

The NMR spectra of *N*-ethylsuccinimide and *N*-acetylethylenimine, as the model compounds of the endgroups, were measured under the same conditions and are shown in Figure 2(*B* and *C*). The methylene proton of *N*-ethylsuccinimide ring showed a peak at τ = 7.34, which was in agreement with that of the copolymer at τ = 7.35. The methylene proton of the *N*-acetylethylenimine ring showed only one peak at τ = 7.70, which was nearly equal to the peak of the copolymer at τ = 7.66. Accordingly, the

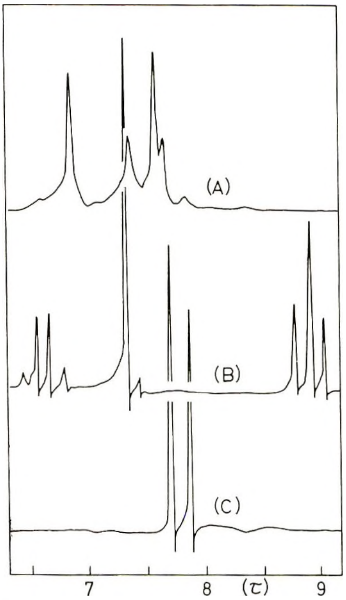


Fig. 2. NMR spectra of (*A*) copolymer of ethylenimine with succinimide; (*B*) *N*-ethylsuccinimide; (*C*) *N*-acetylethylenimine. Solvent D_2O, standard DSS.

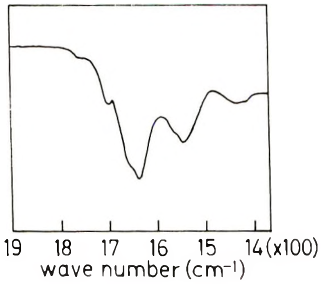


Fig. 3. Infrared spectrum of the copolymer of ethylenimine with *N*-ethylsuccinimide.

peaks of the copolymer at τ = 7.35 and 7.66 were assigned to the methylene protons of *N*-substituted succinimide and *N*-acylethylenimine ring, respectively.

From the results of the infrared spectra, the analysis of the hydrolyzate, and the NMR spectra of the copolymer, it was concluded that the structure of the copolymer of ethylenimine with succinimide was $+CH_2CH_2NHCO-CH_2CH_2CONH+_n$ having *N*-acylethylenimine ring, *N*-substituted succinimide ring, and primary amide as endgroup.

Copolymer of Ethylenimine with *N*-Ethylsuccinimide. The copolymer obtained was a light-brown amorphous polymer which was partly soluble in water. As shown in Table I, the molar ratio of ethylenimine and *N*-ethylsuccinimide units in the copolymer was almost unity. The infrared spectrum of the copolymer shown in Figure 3 showed the characteristic

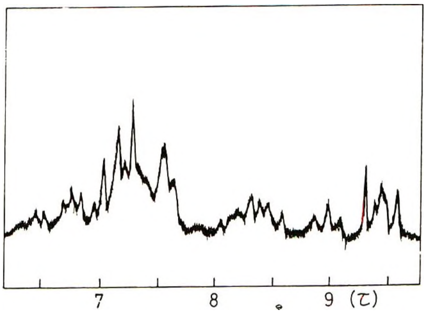


Fig. 4. NMR spectrum of the copolymer of ethylenimine with *N*-ethylsuccinimide. Solvent D_2O, standard DSS.

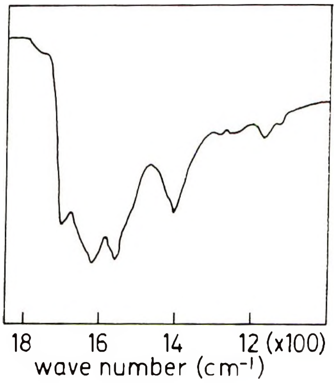


Fig. 5. Infrared spectrum of the copolymer of *N*-ethylethylenimine with succinimide.

peaks of secondary amide at 1640 and 1545 cm^{-1}. From these results, it was considered that this copolymer had the repeating unit $\leftarrow CH_2CH_2NH\text{-}COCH_2CH_2CON(C_2H_5)\rightarrow$. The infrared spectrum showed a peak at 1705 cm^{-1} assigned to *N*-acylethylenimine and *N*-substituted succinimide ring, as mentioned in the case of the copolymer of ethylenimine with succinimide. The NMR spectrum of the copolymer is shown in Figure 4. The spectrum is not clear owing to the noise of the NMR instrument; this noise could not be avoided because of the low solubility of the copolymer. Peaks at $\tau = 7.31$ and 7.65 were assigned to the methylene protons of *N*-substituted succinimide and *N*-acylethylenimine ring at the polymer end, respectively. Peaks at $\tau = 6.75$(a) and 7.57(b) were assigned to the methylene protons of the repeating unit,

$$\leftarrow \underset{a}{CH_2}\underset{a}{CH_2}NHCO\underset{b}{CH_2}\underset{b}{CH_2}CON(C_2H_5)\rightarrow$$

Other peaks might be assignable to the *N*-ethyl substituents which attached to the repeating unit or to the polymer end.

From the results of the infrared and NMR spectra, it was concluded that the structure of the copolymer of ethylenimine with *N*-ethylsuccinimide

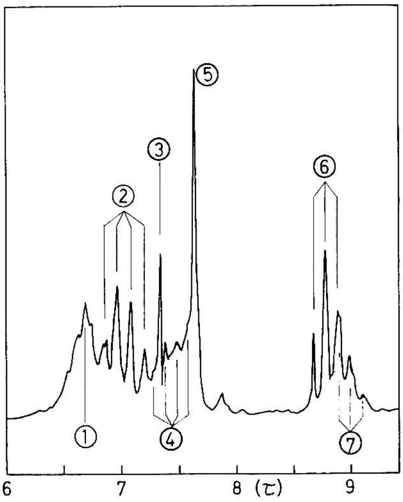


Fig. 6. NMR spectrum of the copolymer of *N*-ethylethylenimine with succinimide. Solvent D_2O, standard DSS.

was $\text{+}CH_2CH_2NHCOCH_2CH_2CON(C_2H_5)\text{+}_n$, having also the *N*-acylethylenimine and *N*-substituted succinimide rings as end groups.

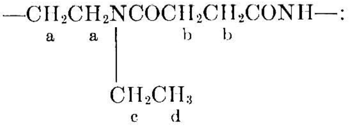
Copolymer of *N*-Ethylenimine with Succinimide Initiated by Water. The copolymer obtained was a white, amorphous polymer which was soluble in water. As shown in Table I, the molar ratio of *N*-ethylethylenimine and succinimide units in the copolymer was almost unity. The infrared spectrum of this copolymer, shown in Figure 5, displayed the characteristic peaks of secondary amide at 1635 and 1555 cm^{-1} and that of the *N*-acylethylenimine end group or *N*-substituted succinimide ring at 1700 cm^{-1}. From these results, it was considered that this copolymer had the

TABLE III

Assignment of the Peaks in Figure 6[a]

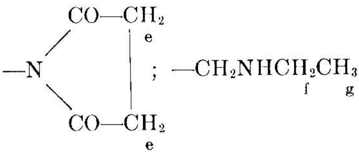
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7
τ value	6.68	7.03	7.34	7.43	7.62	8.78	8.99
Assignment	a	c	e	f	b	d	g

[a] Repeating Unit,



$$-\underset{a}{CH_2}\underset{a}{CH_2}\underset{\underset{c\quad d}{CH_2CH_3}}{N}CO\underset{b}{CH_2}\underset{b}{CH_2}CONH-:$$

end groups,



$$-N\begin{matrix}CO-\underset{e}{CH_2}\\ \\ CO-\underset{e}{CH_2}\end{matrix}\ ;\ -CH_2NH\underset{f}{CH_2}\underset{g}{CH_3}.$$

repeating unit $+CH_2CH_2N(C_2H_5)COCH_2CH_2CONH+$. Assignment of the peaks of the NMR spectrum shown in Figure 6 is summarized in Table III. With the use of a spin–spin decoupling method, the triplet (No. 6) and quartet (No. 2) were confirmed to be assigned to the *N*-ethyl group of the repeating unit. The peak at $\tau = 7.34$ assigned to the methylene proton of the *N*-substituted succinimide ring at the polymer end was also observed; however, no peak assignable to the *N*-acylethylenimine ring was found. Triplet (No. 7) and quartet (No. 4) were assigned to the *N*-ethyl group by the use of a spin–spin decoupling method. This ethyl group was therefore considered to belong to the terminal amino group.

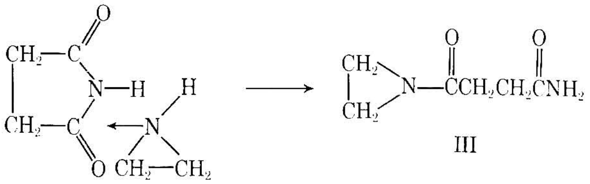
From the results of the infrared and NMR spectra, it was concluded that the structure of the copolymer of *N*-ethylethylenimine with succinimide initiated by water was $+CH_2CH_2N(C_2H_5)COCH_2CH_2CONH+_n$ having the *N*-substituted succinimide ring and the secondary amino group as the endgroups, but not the *N*-acylethylenimine ring.

Reaction Mechanism

In the previous paper, we proposed a mechanism of the copolymerization of ethylenimine with succinimide according to which *N*-ethylene-succinamide, $CH_2CH_2—N—COCH_2CH_2CONH_2$, was formed first in the copolymerization and gave a polyamide by polyaddition. But Grundschober synthesized this intermediate and showed that this compound did not polymerize under the condition of the copolymerization. Therefore, he suggested a mechanism by way of *N*-(β-aminoethyl)succinimide, $C(O)CH_2CH_2-C(O)—N—CH_2CH_2NH_2$.

The results of the present paper show clearly that the copolymer had the *N*-acylethylenimine and *N*-substituted succinimide endgroups. In respect to the existence of *N*-substituted succinimide, the latter mechanism proposed by Grundshober is plausible, but it is impossible to elucidate the fact that *N*-ethylsuccinimide, having no hydrogen attached to nitrogen, copolymerized with ethylenimine, and that *N*-ethylethylenimine did not copolymerize with succinimide.

In consideration of the existence of *N*-acylethylenimine end and the reactivity of the *N*-substituted monomers, the following initiation reaction proposed in the previous paper is considered to be preferable:



III

N-Ethylenesuccinamide (III) does not propagate by polyaddition but may propagate by addition of monomers. The *N*-substituted succinimide ring may be formed by another reaction, such as cyclization or degradation reaction.

Detailed studies concerning the reaction mechanism, especially propagation mechanism, and that of the copolymerization of *N*-ethylethylenimine with succinimide initiated by water will be reported in subsequent papers.

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Interfacial Syntheses of Polyphosphonate and Polyphosphate Esters. I. Effects of Alkaline Medium

F. MILLICH and C. E. CARRAHER, JR.,* *Chemistry Department, Polymer Section, University of Missouri-Kansas City, Kansas City, Missouri 64110*

Synopsis

The effects on polymer yield and viscosity in the interfacial condensation of hydroquinone with phenylphosphonic dichloride as a function of the pH of the aqueous medium are reported. Reactions competing with polymer formation are discussed. The beneficial advantages in the use of soluble buffers or bases of limited water solubility to control pH are contrasted with results of conventionally used sodium hydroxide. The results of investigations of other comer pairs for which reaction conditions have not been optimized are also reported; desoxyribose and the diols: thymidine, resorcinol, 2,5-dichlorohydroquinone, 1,3-dihydroxyacetone, 1,4-butanediol, tartaric acid, ethylene glycol, and 2,2-dimethyl-1,3-propanediol are tabulated.

INTRODUCTION

The first nonbiological synthesis of a polyphosphonate or polyphosphate ester was reported by Arvin[1] in 1936, wherein he reported the formation of a resinous material by refluxing phosphorus oxychloride in the presence of 2,2-bis(4-hydroxyphenyl)propane. It was not until about 1950 that much polyphosphate and polyphosphonate ester synthesis was reported. Sander and Steininger[2] recently have written a review of phosphorus-containing polymers including polyphosphonate and polyphosphate esters.

The first extensive reference to interfacial polymerization was made at the 134th American Chemical Society meeting in Chicago by chemists of the duPont Pioneering Research Laboratories.[3] Since then, extensive work has been done concerning the use of the interfacial technique in the production of polymers.[4]

The first reported use of the interfacial technique in the synthesis of polyphosphonate esters was by Kuznetsov et al.[5] and Aufderhaar[6] in 1961. The first reported synthesis of polyphosphate esters by interfacial polymerization was made by Rabek and Prot[7] in 1963. Previous nonbiological syntheses were all accomplished either by solution polymerization or (chiefly) by high temperature fusion of the reactants. The results of these methods have been comprehensively reviewed by Gefter.[8]

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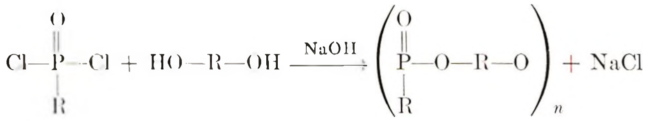
* Present address: Department of Chemistry, University of South Dakota, Vermillion, S. D. 57069.

Attempts at nonenzymatic syntheses of polynucleotides have been made by methods differing from the above. Oligomeric products have been reported by Schramm and co-workers,[9] who used polyphosphoric acids as a condensation medium, and by Khorana and co-workers,[10] who used condensing agents such as carbodiimides.

There have been other reported examples of the production of polyphosphonate and polyphosphate esters by the interfacial technique.[11–17] These synthetic preparations generally have utilized bisphenols in a Schotten-Baumann like esterification involving an acid chloride and sodium hydroxide as a scavenger of hydrogen chloride, as shown in eq. (1).



$$\mathrm{Cl{-}\overset{\overset{O}{\|}}{\underset{\underset{R}{|}}{P}}{-}Cl + HO{-}R{-}OH \xrightarrow{NaOH} \left(\overset{\overset{O}{\|}}{\underset{\underset{R}{|}}{P}}{-}O{-}R{-}O\right)_{n} + NaCl} \qquad (1)$$

The reaction of phenylphosphonic dichloride with bisphenol A with the simultaneous use of phosgene gives polycarbonate phosphates of bisphenol A,[11] or the simultaneous use of an aromatic dicarboxylic chloride yields the corresponding carboxylic mixed esters.[12]

There has been no reported study in depth concerning phosphoryl-containing polyesters produced either by the interfacial polycondensation or other methods. For instance, information is lacking on the subjects of molecular weight distribution of the polymers, nature of the polymer end groups, the mechanism of reaction, or the effects of temperature, nature of the reactants, stirring rate, comer molar ratio, solvent polarity and viscosity, etc.

The comer pair that was chosen in this work for detailed study is that of phenylphosphonic dichloride (PPD) and hydroquinone (HQ), because of the availability of the comers, and because preliminary experiments showed the evolving reaction system to be very rapid and sensitive to many variables. Further, since esters of aryl diols are intrinsically less stable to alkaline media than the esters of aliphatic alcohols, the choice of hydroquinone presented a more demanding test case in determining parameters for successful polymer synthesis. For perspective, the condensation of several other comer pairs were also investigated, but only in the briefest manner, and the results are tabulated in this first paper.

Shuto[15] and others[8] have synthesized by the "high-melt" polycondensation method a polymeric product from hydroquinone and phenylphosphonic dichloride. There is no report of polymer synthesis by the interfacial technique with this comer pair.

As part of an investigative program of studies of chemical evolution, it has been the desire of one of the authors (F.M.) to develop synthetic control of poly(phosphate ester) reactions. Two starting points are investigations of (a) nonenzymatically catalyzed rapid polycondensations, and (b) nonenzymatically catalyzed rapid hydrolyses and transesterifications. Progress has been achieved on the latter subjects.[18–21] The present series of papers undertakes to identify influential factors in polycondensations for the purpose of developing a rapid polycondensation system which might be applied to the preparation of natural or unusual analogs of polynucleotides.

EXPERIMENTAL

Materials

Phenylphosphonic dichloride (Eastman Organic Chemicals, practical grade) was vacuum-distilled, and the fraction boiling in the range 104.0–104.5°C/4 mm; (lit.[22] bp 104.0°C/4 mm). Hydroquinone (Mallinckrodt) was recrystallized from boiling water, mp 171.0–172.5°C (lit. mp 170.5°C). Other reagents, usually of analytical reagent grade, were obtained commercially and used without further purification.

Apparatus

Stirred polymerizations were carried out in a Waring Blendor (Model 1001; rotor speed 15000 rpm), fitted with a 1-pt Kimax emulsifying jar, having a screw cap through which three $^3/_4$-in. steel tubes were fixed. One tube was used for the introduction of N_2, a second tube was used for venting the system to a scrubbing column, and a third tube was connected to a separatory funnel (500 ml) which was used for rapid introduction of first the aqueous and then the organic, water-immiscible phase. The bore of the stopcock had a 4-mm diameter, for rapid liquid flow.

Viscometry was conducted at 25 ± 0.1°C in micro-Ubbelohde viscometers (Cannon Inst.) in which the flow time for dimethyl sulfoxide is about 200 sec. Limiting viscosity numbers (LVN) were obtained by serial dilution of solutions of 4 g/ml and less and graphical extrapolation.

All buffer systems calculated to give values of pH of 12 or less, were checked with a Coleman pH-Electrometer (Model 18) and a Calomel electrode, and calibrated by using several standard buffer solutions (Hellige Inc.), except that values for the KCl–NaOH buffer system were taken from the literature.[23]

Polymerization Procedure

A representative procedure is given as follows. Hydroquinone (HQ, 2.32 g, 0.021 mol) was added to the reaction jar before capping and connecting the tubes. Only in the case of $Ba(OH)_2$ (granular solid) was base introduced with HQ. The system was flushed with N_2 for 5 min before the aqueous medium (deaerated by boiling, 100 ml) was introduced; see Table I for description of the different aqueous solutions. After the jar contents were stirred for 1 min, CCl_4 (100 ml), containing phenylphosphonic dichloride (PPD, 4.10 g, 0.021 mole), was run in quickly. After 30 sec, more than sufficient 1*N* aqueous HCl was added to reduce the pH to below 7 (about 1.2 times the theoretical amount of HCl needed to neutralize the original amount of base).

Polymer separates from solution as a tacky, coherent mass, adhering to the container surface. Most often the liquid phases could be separated by decantation without the need for filtration. (Rarely was residue found dissolved.) Acetone (75 ml) was added to the blender and stirred for 1 min, producing a solution, designated as original acetone-soluble portion (OAS), and a granular solid, designated as original acetone-insoluble (OAI), which was easily poured on a suction filter and separated. An aliquot of the acetone solution was evaporated on a steam bath, yielding a clear film, and was weighed for estimation of the total yield of OAS fraction. The solid was washed with 50-ml portions of water and acetone, and dried and weighed (OAI). Alternatively, all of the original polymer may be dissolved in *tert*-butyl alcohol, since the higher molecular weight material (OAI) is effectively solubilized by the OAS fraction.

RESULTS

The per cent yields and values of LVN in dimethylsulfoxide of (HQ-PPD) polymer is given in Table I for various values of pH of the polymerization media. Figure 1 illustrates the relations of yield and of concentra-

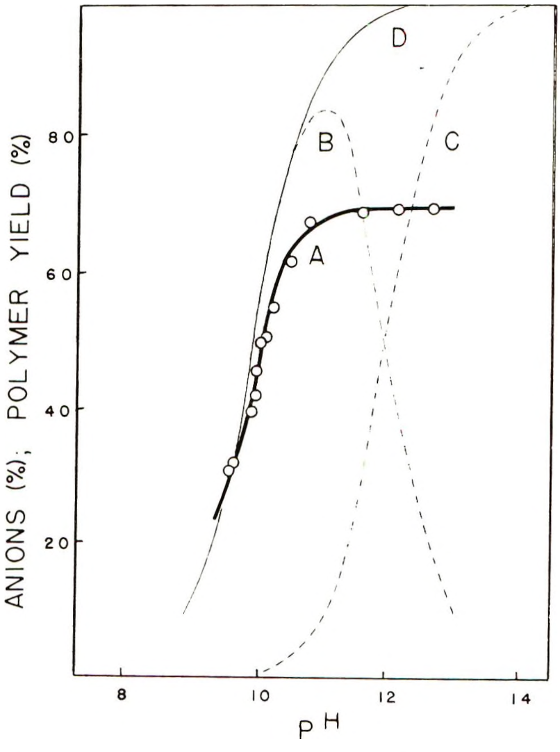


Fig. 1. Plots of (*A*) variation of polymer yield with pH in the equimolar polycondensation of HQ with PPD by interfacial polymerization; (*B*) variation with pH of the per cent of total HQ of HQ monoanions and (*C*) of HQ dianions. Curve *D* represents the sum of curves *B* and *C*.

tions of ionized species of HQ with pH. The fractions of HQ ions were calculated by using eqs. (2) and (3),

$$\text{Fraction of monoionized hydroquinone} = K_1[\mathrm{H}^+]/([\mathrm{H}^+]^2 + K_1[\mathrm{H}^+] + K_1K_2) \quad (2)$$

TABLE I

Base-Catalyzed Interfacial Polycondensation of Hydroquinone with Phenylphosphonic Dichloride: Yield and Product Viscosity as a Function of pH of the Aqueous Medium[a]

Buffering system (moles)	pH initial–pH final[b]	pH average	OAS, %	OAI, %	Total yield, %	LVN of unfractionated product, ml/g[c]
$NaHCO_3$ (0.084)	8.2–7.4	7.8			0	
$Na_2HPO_4\cdot 2\ H_2O$ (0.084)	8.8–8.0	8.4			0	
$NaHCO_3$ (0.056) + $Na_2CO_3\cdot 7\ H_2O$ (0.028)	9.4–9.2	9.3	19	2	21	17
$Na_2HPO_4\cdot 2\ H_2O$ (0.068) + $Na_3PO_4\cdot 12\ H_2O$ (0.017)	9.8–9.4	9.6	28	3	31	15
$NaHCO_3$ (0.042) + $Na_2CO_3\cdot 7\ H_2O$ (0.042)	9.8–9.6	9.7	28	4	32	15
$NaHCO_3$ (0.028) + $Na_2CO_3\cdot 7\ H_2O$ (0.056)	10.0–9.8	9.9	35	6	41	15
$Na_3PO_4\cdot 12\ H_2O$ (0.028) + $Na_2HPO_4\cdot 2\ H_2O$ (0.056)	10.1–9.9	10.0	41	5	46	13
$Na_2HPO_4\cdot 2\ H_2O$ (0.062) + NaOH (0.022)	10.1–10.0	10.05	44	6	50	13
$Na_2HPO_4\cdot 2\ H_2O$ (0.051) + NaOH (0.034)	10.3–10.2	10.25	48	7	55	13
$Na_3PO_4\cdot 12\ H_2O$ (0.042) + Na_2HPO_4 (0.042)	10.6–10.7	10.5	54	8	62	15
$Na_3PO_4\cdot 12\ H_2O$ (0.051) + $Na_2HPO_4\cdot 2\ H_2O$ (0.034)	10.9–10.7	10.8	59	9	68	15
NaOH (0.080) + $Na_2HPO_4\cdot 2\ H_2O$(0.020)	11.7–11.5	11.6	53	15	68	20
KCl (0.080) + NaOH (0.020)	12.2–12.0	12.1	49	20	69	24
KCl (0.040) + NaOH (0.060)	12.8–12.6	12.7	49	21	70	24
$Ba(OH)_2$ (0.040), heterogeneous aqueous phase	12	12	38	28	66	28
$NaHCO_3$ (0.056) + $Na_2CO_3\cdot 7\ H_2O$ (0.112), heterogeneous aqueous phase	10.0–9.9	9.95	36	6	42	

[a] Reaction conditions: 0.021 moles PPD in 100 ml CCl_4 added to 0.021 mole HQ in 100 ml aqueous buffer solution, with stirring at 15000 rpm, room temperature, N_2 atmosphere, reaction time 30 sec.

[b] The initial pH is that of the buffer solution which contains HQ; the final pH is that of the aqueous phase following reaction.

[c] Viscometry was performed in dimethyl sulfoxide at 25.0 ± 0.1°C.

TABLE II

Results of the Condensations of Equimolar (0.021 mole) Comer Systems with 50 ml of Carbon Tetrachloride

Acid chloride	Diol	Base	Moles base	Volume water, ml	Blender stirring time, sec[a]	Total yield, %	[η] (25°C in Me_2SO), ml/g	Product melting point, °C
Phenylphosphonic dichloride	Hydroquinone	$Ba(OH)_2$	0.040	100	10	69	29	92–101
	Hydroquinone	NaOH	0.050	25	10	84	10	62–75
	Resorcinol	NaOH	0.050	25	10	80	8	63–78
	1,4-Cyclohexanediol	$Ba(OH)_2$	0.030	100	30	20	8	61–77
	2,5-Dichlorohydroquinone	NaOH	0.050	25	10		8	72–79
	1,3-Dihydroxyacetone	$Ba(OH)_2$	0.030	100	10	6	11	95–105
	1,3-Dihydroxyacetone	NaOH	0.500	100	30	0		
	1,3-Dihydroxyacetone	Na_3PO_4	0.040	100	30	0		
	1,4-Butanediol	$Ba(OH)_2$	0.030	100	10	28	17	>300
	Tartaric acid	$Ba(OH)_2$	0.051	100	10	90	12	100–110
	Ethylene glycol	$Ba(OH)_2$	0.030	100	10	10	15	278–292
	Ethylene glycol	NaOH	0.500	100	30	0		
	Ethylene glycol	Na_3PO_4	0.040	100	30	0		
	2,2-Dimethyl-1,3-propanediol	$Ba(OH)_2$	0.030	100	10	26	9	110–118
	2,2-Dimethyl-1,3-propanediol	Na_3PO_4	0.040	100	10	0		
	2,2-Dimethyl-1,3-propanediol	NaOH	0.500	100	10	0		
Phenyl phosphorodichloridate	Hydroquinone	$Ba(OH)_2$	0.030	100	360	50	10	
	Hydroquinone	$Ba(OH)_2$	0.030	100	10	10	9	67–75
	1,4-Butanediol	$Ba(OH)_2$	0.030	100	10	11	8	103–115
	1,4-Butanediol	$Ba(OH)_2$	0.030	100	360	2	4	43–50

[a] This is the period of time that stirring at 15000 rpm was continued following the addition of the organic phase and prior to the addition of acid.

Fraction of diionized hydroquinone

$$= K_1K_2/([H^+]^2 + K_1[H^+] + K_1K_2) \quad (3)$$

where $[H^+]$ is the hydrogen ion concentration. K_1 and K_2 are the first and second ionization constants for hydroquinone, the values being taken[24] as 0.99×10^{-10} and 1.2×10^{-12}, respectively, at 30°C. The total ionized HQ is taken as the sum of these two fractions.

In separate experiments the pH at the conclusion of stirring, just prior to acidification, was determined to insure that base had not been exhausted. These determinations are recorded in Table I. The initial pH value is that of 100 ml of buffer solution containing 2.31 g of HQ, protected by a nitrogen atmosphere.

The results of other briefly investigated comer pairs are listed in Table II. The yields by no means represent optimal values.

DISCUSSION

It is well known that the reaction of diols with diacid halides takes place especially rapidly when the diol is in a deprotonated form,[25] although there are few experimental data available on rates and mechanisms for this type of reaction[4] in interfacial systems.

A plot of per cent total yield of polymer as a function of the pH of the aqueous phase (Fig. 1) shows the same general shape as the plot of per cent ionized hydroquinone versus pH. Both parameters approach plateau values in the same general pH region (i.e., 10.7–11.0). This suggests what has been known for noninterfacial acid chloride–alcohol systems[25]—that yield (and rate) of reaction is heavily dependent on the concentration of phenoxide ion, acting as a nucleophilic agent. This is among the first yield–pH profiles reported in interfacial polymerization work.* Profiles relating pH to yield, rate, or molecular weight have not been published for polyphosphonate interfacial polymerizations.

The yield–pH relationship found in Figure 1 allows the following interpretations: (1) production of polymer is independent of the chemical nature of the buffer system, but is dependent on the pH of the aqueous solution; (2) in the system under examination, no polymer formation is found below a pH of approximately 8.8, i.e., much below the pK_{a1} of the diol, at which the diol is less than 10% ionized; (3) the leveling off of the yield at about 70% in the pH range 12–14 probably indicates that the monoanion of HQ is comparable in reactivity either to the dianion of HQ (except for a statistical factor of two) or (more probably) to the monoanions of the instantaneously produced monoester derivatives of HQ. Thus, the acidity of the first ionizable phenolic hydroxyl group of HQ is probably similar to that of monoesters of HQ, as it is similar, for instance, to that of $p\text{-HOC}_6\text{H}_4\text{PO}_3^{-2}$ (i.e. $pK_{a3} = 9.9$).[27]

* Sokolov and Kudim[26] have given polyamide yields and intrinsic viscosities as a function of aqueous phase acidity.

The apparent correlation of the yield–pH profile with the concentration of anionic species should be taken with reservation. Although this may be a dominant relation, the profile is not uniquely dependent on phenoxide concentration. The polymer yield is dependent on many factors, which are discussed in subsequent papers, combinations of which determine rate of polymer formation relative to rates of competing reactions. Thus, a good yield is obtained when conditions are established in which polymer formation is favored relative to alkaline or solvolytic attack upon the condensing agents—phosphonic dichloride and phosphonic monochloride endgroups of polyphosphate ester oligomers. This side reaction can be easily demonstrated in the present system by delaying the addition of HQ for fractions of a minute, during polymerizations in the presence of sodium hydroxide, in which case polymer yield is drastically reduced. Base attack upon the phosphonic dichloride is probably more serious than attack upon phosphonyl monochloride end groups because of the greater reactivity of the P—Cl bond in the former. In general, oligomers of very low $\overline{DP}$ have not been isolated in this study.

If it can be assumed that none of the competing nucleophiles, (i.e. water, hydroxide ion, phenoxide endgroups) is favored by solubility differences in the organic phase (wherein concentrations are indeed very small in carbon tetrachloride), then successful polycondensation to high degree of polymerization may be attributed to intrinsically high, outstanding rates of reaction of phenoxide anions with phosphonyl groups bearing chlorine atoms. (There is evidence that the aqueous phase is the locus of the chain

TABLE III
Results of the Polycondensation of Hydroquinone (0.021 mole) and Phenylphosphonic Dichloride (0.021 mole) with High-Speed Stirring at 25°C

Base	Blender stirring time, min	OAS, %	OAI, %	Total yield, %	LVN of total product in dimethyl sulfoxide, ml/g
$Ba(OH)_2$[a]	1/2	22	45	67	37
	1	22	43	65	36
	2	20	44	64	37
	4	21	45	66	35
	5	20	44	64	32
	7	20	40	60	27
	10	26	31	57	25
	15	26	21	47	23
NaOH[b]	1/6	—	—	85	15
	1/2	—	—	70	10
	2	—	—	3	3

[a] 50 ml CCl_4, 50 ml H_2O, 0.040 mole $Ba(OH)_2$.
[b] 25 ml CCl_4, 25 ml aqueous 5*N* NaOH solution.

propagation reaction.) In the presently employed system polymer formation is also disadvantaged by decrease in phenoxide concentration as conversion progresses, by separation of the polymer from solution as a tacky, solid phase, and by the need of a very rapid supply of phosphonylating agent from the organic phase to the aqueous reaction phase. Nevertheless, on a very brisk time schedule, high polymer can be achieved in good, if not quantitative, yields.

Another important competing reaction is that of degradative attack by base upon the high polymer product. Control against base degradation of the polymer product is accomplished in the present system by means of control of pH with either soluble buffers or bases of limited water solubility. These can provide a relatively constant concentration of hydroxide ion and yet provide any desired base capacity to neutralize acids being liberated during reaction from the condensing agents or from base degradation of the polyphosphate ester product. That polymer saponification is a serious detrimental alternative can be seen from the contrast of the results of yield and viscometry as a function of reaction time, shown in Table III, carried out with a partially soluble base [$Ba(OH)_2$] to control pH, on the one hand, and a completely soluble strong base (NaOH), on the other. Examples in the patent literature have invariably shown the employment of a soluble strong base, and most frequently it is used in stoichiometric amount such that the final pH of the reaction is found to have decreased to a value of 7. Other contrasting features between the use of strong base vs. a system in which pH is controlled are given in subsequent papers in this series. Table III offers some examples contrasting the use of $Ba(OH)_2$ and NaOH.

In the spectral region 3700–650 cm^{-1} the infrared spectra of the HQ–PPD polymer samples produced in this study agree in peak shape, intensity, and location with reported spectra of the polymer made by the high-temperature fusion method.^{15}

The authors have used barium hydroxide and buffer solutions to advantage over the use of sodium hydroxide in condensations of phenylphosphonic dichloride, phenyl phosphorodichloridate, and phosphorus oxychloride with alkylene- and arylenediols, including thymidine and trifunctional desoxyribose.

This paper is taken in part from the Ph.D. thesis of C. E. Carraher, University of Missouri-Kansas City, Kansas City, Missouri, 1968.

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Condensation of Benzyl Chloride Catalyzed by Group II Metals

EDWARD J. SPANIER and FRANK E. CAROPRESO, *Chemistry Department, Seton Hall University, South Orange, New Jersey 07079*

Synopsis

The polymerization of benzyl chloride in the presence of various group II metal salts has been investigated. The extent of reaction and the relative activities of various salts were determined by measurement of the evolved HCl as a function of time. Formation, *in situ*, of an active catalyst is proposed.

INTRODUCTION

The formation of polymer from benzyl chloride, with the evolution of hydrogen chloride, is a well known example of a condensation process initiated by Friedel-Crafts catalysts. Various benzyl derivatives (fluoride,[1] chloride,[2,3] bromide,[4,5] alcohol[6]) are known to give rise to polymers. A recent synthesis of polybenzyl has been given by Haas,[7] while much of the earlier work has been summarized by Shriner,[6] Haas,[7] and Valentine.[8]

In our investigation of reactions of calcium carbide a nucleophilic displacement with benzyl chloride was attempted; however, only polybenzyl was formed. Since the calcium carbide used in our studies contains significant amounts of oxide, the investigation was extended to include this species and related group II oxides and chlorides. Since the literature contains references predominately to the polymerization of benzyl chloride with the use of conventional Friedel-Crafts catalysts[1-8] we were prompted to investigate the reaction further, particularly as there is no report of the polymerization of benzyl chloride by group II metal oxides.

EXPERIMENTAL

Materials

Calcium oxide, magnesium oxide, barium oxide, and anhydrous calcium chloride were reagent grade and were used as received, after sieving. Commercial calcium carbide (~85% purity) was ground with the use of a vibrating ball mill. Since redistillation prior to use had no effect on the reaction, benzyl chloride (Matheson, Coleman and Bell) was used without further purification. All solvents were reagent grade and were used as received. Elemental analyses were carried out by the Alfred Bernhardt

Microanalytical Laboratories, Ruhr, Germany and the F.M.C. Corporation, Princeton, N. J. Molecular weights were determined with a Mechrolab vapor pressure osmometer, Series 300, with benzene as a solvent; however, consistent and reproducible molecular weights could not be obtained. Infrared spectra were run as films from $CHCl_3$ solution with the use of a Beckman IR-5 or IR-10 spectrophotometer. The NMR spectra were obtained with a Varian Associates A-60-A spectrometer. The spectra were recorded for CCl_4 or $CDCl_3$ solutions containing 10–20% by weight of sample. The polybenzyl polymer used for the NMR study was first washed free of benzyl chloride and inorganic salts. In those cases where the reaction was followed by NMR spectroscopy, a sample of the reaction mixture was suspended in CCl_4 and filtered to remove the inorganic salts, prior to determining the spectrum. The reaction could be readily followed in this manner until the system became too viscous to sample representatively.

All the spectra were run with the use of the Varian A-60-A nuclear magnetic resonance spectrometer, a sweep width of 0–500 Hz and a sweep time of 250 sec with tetramethylsilane as an internal standard being used. Gas chromatographic analyses were carried out with a Beckman 2A instrument with a 3-ft silicone rubber column. Melting points were determined on a Mel-temp melting point apparatus and are uncorrected.

Procedure

Method of Following the Reaction

The reaction was followed by measuring the amount of HCl evolved, which is assumed directly proportional to the amount of benzyl chloride consumed.[8] Polymerizations were carried out in 100-ml three-necked round bottomed flasks fitted with a condenser and gas inlet. The measured quantity of metal oxide was introduced into the flask and the benzyl chloride (10.7 g, 85 mmole) added. Dry nitrogen (8 cc/min) was immediately passed over the benzyl chloride and the reaction mixture heated to temperature, with stirring. The nitrogen was used to carry off evolved HCl, which was absorbed in one liter of water contained in two 500-ml gas washing bottles.

At fixed time intervals, 10.00-ml aliquots of water were withdrawn and titrated with standard, 0.0698*N* NaOH to the phenolphthalein endpoint. The efficiency of absorption was verified by titrating a sample from the second gas scrubber. At no time did the second sample require more base than a blank, indicating all the evolved HCl was absorbed in the first gas washing bottle.

Purification of Polymer

Two methods were used depending upon the extent of reaction.

Method A. Where the reaction proceeded to more than 50% conversion, benzene (~30 ml) was added to the reaction mixture. The resulting suspension was centrifuged for ~15 min. The supernatant liquid was decanted and centrifuged again to eliminate any remaining suspended solids. The resulting supernate was then evaporated on a Roto-Vac to remove solvent and most of the unreacted benzyl chloride. The resulting tacky solid was placed in anhydrous ethanol (~15 ml) and allowed to stir overnight to dissolve any benzyl chloride still remaining. The ethanol was removed by filtration on a medium-porosity, sintered glass filter. This was repeated until gas chromatographic analysis of the ethanol wash indicated the polymer was free of benzyl chloride. A white to pale yellow product was recovered.

The solids recovered by centrifugation were washed repeatedly with benzene. The washes were combined and held as crude polymer. The resulting insoluble material always had a mass greater than that of the metal oxide initially introduced. This increase is associated with partial conversion of the oxide to chloride and absorption of polymer on the surface of the salt.

After ignition, the insoluble material was shown to be a mixture of metal chloride and oxide. The quantity of polymer absorbed on the surface of the salt, measured by determining the weight loss on ignition, represented about 30% of the insoluble material, by weight. This weight loss could be attributed to either polymer absorbed on the surface of the salt or insoluble high molecular weight polymer. In order to determine which of these possibilities were most likely, 1.00 g CaO was suspended in a benzene solution of polymer. The oxide was recovered in a manner similar to that used in the work-up of polymer. Typical results showed that the recovered calcium oxide increased in weight 28% even after several washings with benzene and chloroform. The fact that polymer in solution can be absorbed to approximately the same extent as observed previously suggests that this is surface absorption rather than the presence of high molecular weight, insoluble polymer. Ignition of this material led to a weight loss corresponding to the amount of polymer initially absorbed.

Method B. Where the reaction proceeded to less than 50%, the above method proved to be unsatisfactory, in that a tacky, essentially intractible mass was recovered from the reaction, since the polymer dissolved partially in unreacted benzyl chloride. The tacky mass was suspended in a small volume (15 ml) of benzene and anhydrous ethanol was added to precipitate the polymer. The supernatant, in which only unreacted benzyl chloride and small amounts of low molecular weight polymer were present, was decanted. This process was repeated several times to remove most of the unreacted benzyl chloride. The partially purified polymer was mixed with ethanol and stirred overnight, as in method A. This washing was repeated until the ethanol showed no trace of benzyl chloride. A white to tan powder was recovered. In each case, the resulting powder was vacuum dried overnight, at room temperature, to remove traces of solvent.

RESULTS AND DISCUSSION

Following Valentine and Winter,[8] the evolved hydrogen chloride was taken as a measure of the apparent reaction rate. Complete (100%) reaction was defined as the theoretical yield of hydrogen chloride in the reaction

$$n\ C_7H_7Cl \rightarrow (C_7H_7)(C_7H_6)_{n-2}(C_7H_6Cl) + (n-1)\ HCl \qquad (1)$$

On the basis of this equation, benzyl chloride (85 mmole) should give approximately 84 mmoles of hydrogen chloride on essentially complete reaction (DP 32). The reaction approached this value as the reaction temperature and quantity of salt were increased. In all cases the evolution of hydrogen chloride was quite reproducible.

In a typical experiment, 1.0 g (18 mmole) CaO of particle size less than 250 mesh was added to 10.7 g (85 mmole) benzyl chloride and the mixture heated to 165°C with stirring. Dry nitrogen was passed over the liquid to facilitate removal of HCl gas. The reaction was continued for 150 min; after this time, 67.6 mmole of HCl was evolved. Analysis of the solid product showed that 0.41 g (3.7 mmoles) of $CaCl_2$ was formed, the formation of which required 7.4 mmoles HCl.

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O \qquad (2)$$

Thus a total of 75.0 mmole of HCl was produced during the reaction. This represents 88% of the chloride initially introduced as benzyl chloride.

The polymer isolated plus that absorbed in the inorganic salts represented a 99% yield based on benzyl chloride introduced [eq. (1)]. The polymer had molecular weight of 1885.

In a similar experiment carried out at 175°C, a yield of 98.1 and 94.1% was obtained for the polymer and HCl, respectively. The molecular weight of this sample was 2360.

All the polymers softened in the range 70–80°C and had infrared spectra similar to those reported by other workers[7,12] using lower temperatures and homogeneous systems. The molecular weights ranged from approximately 1400 to 2500, the highest values being observed with polymers produced with the use of calcium oxide at 175°C and the lowest with barium oxide. The molecular weight data were not readily reproducible, probably due to retained salts and starting material. However, it is interesting to note that the molecular weights of the samples prepared by this route are consistently higher than these reported for polymers obtained by using conventional Friedel-Crafts catalysts, e.g., $SnCl_4$ (MW about 900–1200).[9]

Effect of Varying the Quantity of Metal Oxide and the Reaction Temperature

The effect of varying the quantity of calcium oxide from 0.3 g (5.4 mmole) to 1.4 g (25 mmole) on the amount of hydrogen chloride evolved as a function of time at constant temperature (165°C) is shown in Figure 1. These data suggest there is an optimum concentration of calcium oxide, above which the rate of hydrogen chloride evolution decreases. The optimum amount of calcium oxide is approximately 1.0 g (18 mmole). It is interesting to note that other workers[8,9] using homogeneous systems, in

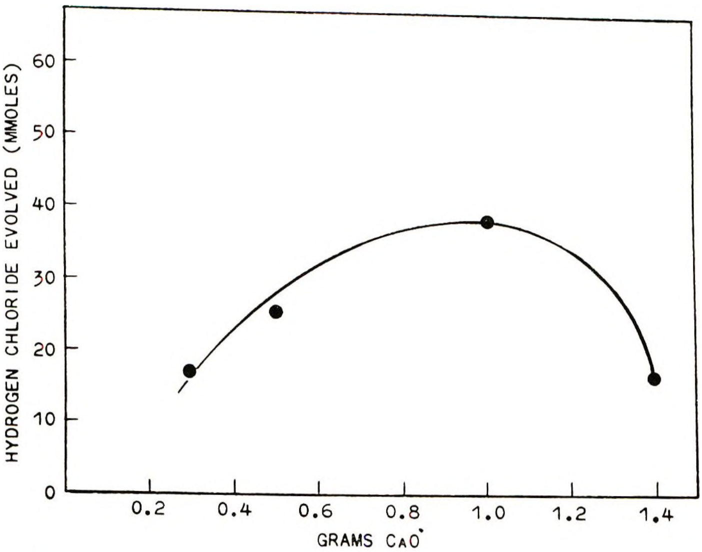


Fig. 1. Total of HCl evolution vs. the quantity of CaO at 165°C.

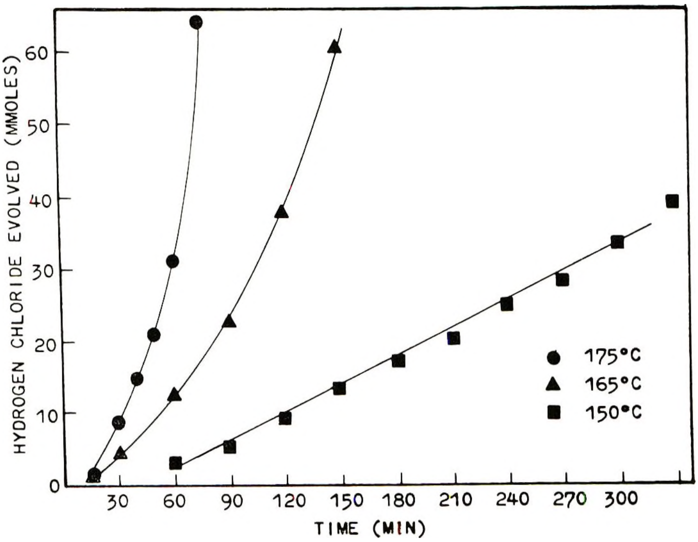


Fig. 2. Total of HCl evolution as a function of temperature with the use of 1 g CaO.

contrast to our heterogeneous system, also observed a maximum in the amount of HCl evolved as a function of the quantity of catalyst.

The effect of temperature on the hydrogen chloride evolution was investigated by using a fixed amount of calcium oxide (1.g, 18 mmole). Typical reaction curves at 150, 165, and 175°C are shown in Figure 2. At temperature greater than 175°C the reaction was too fast to be easily followed, while below 150°C it was too slow. In all cases, there appears to be an induction period, relatively short at the higher temperature and increasing in duration as the temperature is decreased.

Effect of Cation

The effect of different group II cations on the hydrogen chloride evolution was investigated by using MgO, CaO, and BaO. In all cases 150°C was chosen as the operating temperature, and 1.0 g of the metal oxide was used. From the data shown in Figure 3, it is evident that the evolution of hydrogen chloride is dramatically affected by the nature of the cation. Of the three group II cations investigated, MgO has the longest induction period but also exhibits the greatest catalytic activity.

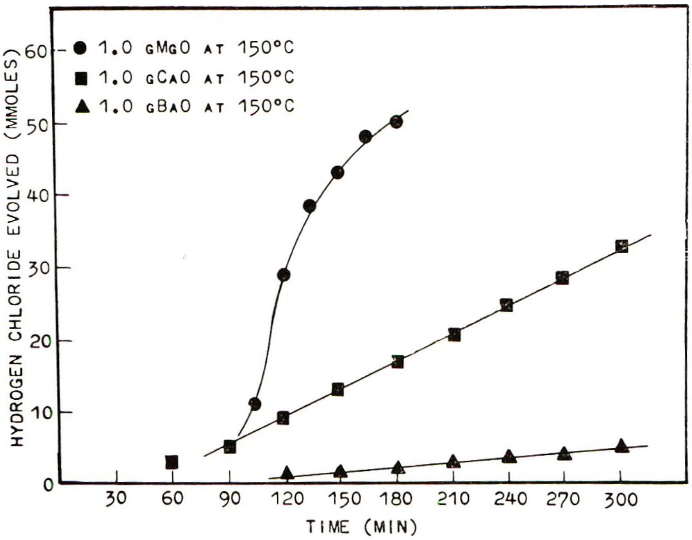


Fig. 3. Total of HCl evolution for various group II metal oxides at 150°C.

The order of effectiveness of the metal ions follows that of their ability to accept electrons and function as Lewis acids. Since these experiments were carried out with the use of fixed masses of metal oxide (1.0 g) and a single temperature, the results are not unequivocal. However, the large difference observed support the above conclusion, suggesting that the polymerization is in many ways a typical Lewis acid catalyzed Friedel-Crafts reaction. In all these reactions, it was found that the metal oxides were partially converted to the corresponding metal chloride. The extent of conversion followed the same trends observed for the relative activity of the different metal oxides, i.e., MgO > CaO > BaO. Apparently, the metal oxide initiates the polymerization reaction and, as the reaction proceeds, the liberated hydrogen chloride reacts with the metal oxide forming active metal chloride. This salt, produced *in situ*, functions as a catalyst for the subsequent polymerization of the bulk of the benzyl chloride.

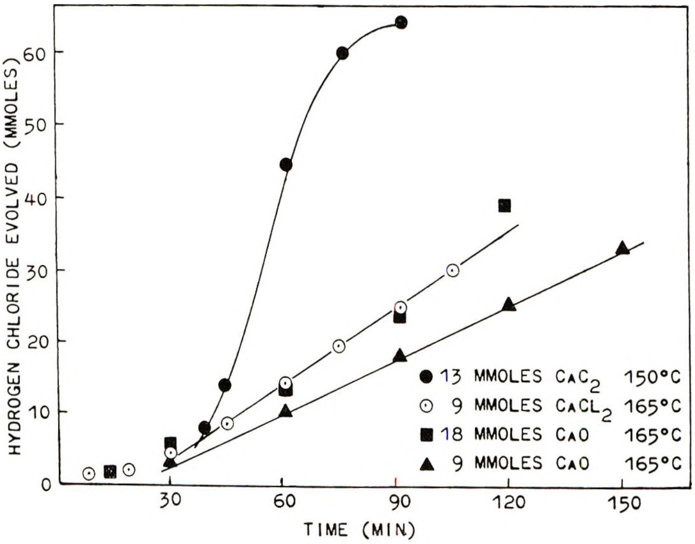


Fig. 4. Total of HCl evolution for CaC$_2$, CaO, and CaCl$_2$.

The polymerization was found to occur at a rate orders of magnitude greater when calcium carbide was used instead of metal oxide. A comparison of the amount of HCl evolved over a period of time for CaO, CaC$_2$, and CaCl$_2$ is shown in Figure 4. These data show that the HCl evolution is greater for CaC$_2$ at 150°C than for the other salts at still higher temperatures. The CaC$_2$ is shown to be even more effective than the quite active MgO. The enhanced reactivity of CaC$_2$ is most certainly due to the rapid and essentially complete reaction of this material with HCl. Complete reaction is favored because of the formation of acetylene [eq. (3)],

$$CaC_2 + 2HCl \rightarrow CaCl_2 + C_2H_2 \tag{3}$$

which drives the reaction to completion. Thus CaC$_2$ undergoes rapid and complete conversion to the chloride, exposing a much greater amount of clean and active surface, whereas with the other materials, reaction is probably limited to the exposed surface. Similar observations have been made by Bryce-Smith and Owen[10] when an extremely active form of magnesium chloride was prepared by the reaction of magnesium and *n*-butyl chloride.

Induction Period

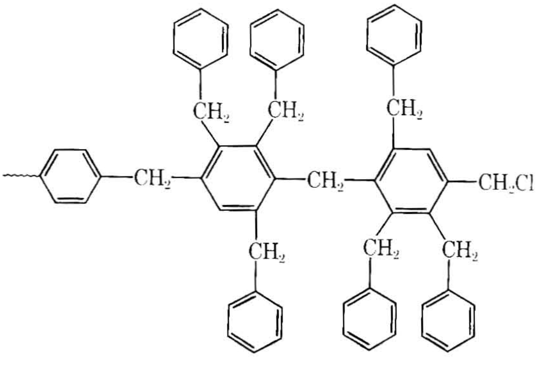
Under all the reaction conditions investigated an induction period was observed. However, since the reaction is followed by the evolution of HCl and since HCl has some solubility in the reaction mixture and also can react with the metal oxide to form the corresponding metal chloride, the observed induction period represents at least these two phenomena. Thus, particularly in the early stages of the reaction, an appreciable quantity of HCl is retained in the reaction system.

Presaturation of benzyl chloride at room temperature with HCl did not eliminate the induction period, despite the fact that it did result in the immediate evolution of HCl. This immediate evolution of HCl has been attributed to desorption of dissolved HCl with increasing temperature.

When the system containing calcium carbide was presaturated with HCl, the induction period appeared real. If the reaction system was rapidly brought up to temperature (in 3–4 min) by using an oil bath, a very slow reaction was observed. However, if the temperature was increased very slowly (over 40–60 min) the polymerization reaction was quite rapid. This was attributed to the formation of calcium chloride *in situ*, which functions as an active Friedel-Crafts catalyst. Where temperature is rapidly increased, the HCl is expelled from the solution much too rapidly to allow for appreciable quantities to react with the CaC_2 to form $CaCl_2$. Thus, the longer induction periods observed with magnesium oxide and calcium carbide can be related to the substantially greater amounts of HCl reacting to form metal halide. This conclusion is supported by the fact that for the various metal oxides, MgO, CaO, BaO, the greatest amount of metal halide was obtained for MgO and the least for BaO. The introduction of calcium carbide clearly led to the formation of the largest amount of chloride. The amount of metal chloride formed is in turn consistent with the observed induction period.

NMR Study

We attempted to gain additional information about the structure of the polymer through nuclear magnetic resonance spectroscopy. The NMR spectrum of the purified polymer shows absorption in the phenyl and methylene proton region. The absorption in the methylene region is a broad yet well defined peak, while the absorption in the phenyl region appears to be a composite of several different phenyl proton absorptions. The ratio of the phenyl protons (integrating as one broad absorption) to the methylene protons is 7:3 (2.33:1). Both peaks are shifted slightly upfield, more shielded, from the peaks of benzyl chloride by 0.3 and 0.7 ppm, respectively.



I

These data appear too consistent with a polymer (I) composed of phenyl rings in several types of environments, as suggested by other workers.[11,12] The methylene group appears to be essentially intact, indicating the proton necessary for HCl formation came primarily from the phenyl ring. The chemical shifts indicate that the phenyl and methylene protons are more shielded than the corresponding protons of benzyl chloride. This is what might be expected if polymerization occurred in such a manner as to replace protons of the phenyl ring with benzyl groups.

If the NMR spectrum of the system is followed during the course of the reaction, the characteristic peaks of benzyl chloride are clearly evident; in addition, several well defined absorption peaks appear in the phenyl region, while only a single, well defined peak is observed in the methylene region. As reaction proceeds the peaks in the phenyl region coalesce to form the observed broad, ill defined peak.

Polymers produced with the use of CaO, CaC_2, MgO, or BaO all give identical spectra. Peaks are observed at 7.10 δ and 3.62 δ, the ratios of the phenyl to methylene protons are all in the region of (2.33 ± 0.05). Several attempts were made to improve the resolution of the phenyl proton region by varying the sweep time, expanding the area and by varying the temperature from ambient to 60°. None of these methods resulted in improved resolution.

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Ferrocene-Terephthalaldehyde Copolymerizations and Analogous Polyferrocenylene Crosslinking Processes

N. BILOW, *Hughes Aircraft Company, Culver City, California 90230*, and H. ROSENBERG, *Air Force Materials Laboratory, Wright Patterson Air Force Base, Ohio 45433*

Synopsis

Ferrocene has been copolymerized with terephthalaldehyde and 1,1′-ferrocenedicarboxaldehyde to produce thermosetting polymers suitable for the fabrication of reinforced structural composites. Both the terephthalaldehyde and 1,1′-ferrocenedicarboxaldehyde were also found to be useful curing agents for polyferrocenylenes formed by other methods. Glass-reinforced laminates have been fabricated from both types of copolymers and from both types of cured polyferrocenylenes. Laminate flexural strengths have been in the range of 35 000 psi.

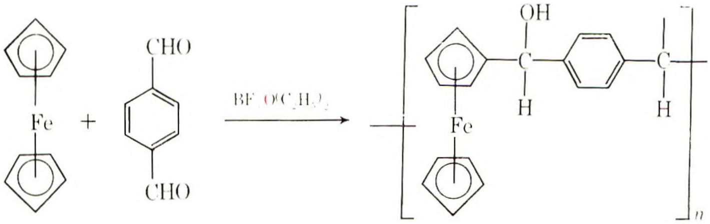
INTRODUCTION

Research on the synthesis of ferrocene-containing polymers has been in progress since approximately 1956. Since that time a wide variety of polymerizations involving ferrocene and ferrocene derivatives has been studied. These include condensations of hydroxyalkyl-substituted ferrocenes,[1] copolymerizations of cinnamoylferrocene with various vinyl monomers,[2] ferric chloride-catalyzed polymerizations of sodium derivatives of α,ω-bicyclopentadienyl alkanes,[3] peroxide-catalyzed polyrecombinations of ferrocene,[4] condensations of 1,1′-ferrocenedicarbonyl chloride with the use of Lewis acid catalysts,[5] addition of 1,1′-bis(hydroxymethyl) ferrocene with diisocyanates,[6] condensation of ferrocene with dimethyldichlorosilane,[7] condensations of ferrocene with aldehydes and ketones,[8] homopolymerizations of vinylferrocenes,[9,10] homocondensation of *N,N*-dimethylaminomethylferrocene,[11] condensations of ferrocene with phenyldichlorophosphine and related compounds,[12] condensations of 1,1′-ferrocenedicarbonyl chlorides with diols and diamines,[5,13] condensations of 1,1′-ferrocenedicarbonyl chloride with hydrazine,[14] and various other methods. Several comprehensive review articles have also been published.[15–18]

The work most closely related to that described in this paper is the work of Neuse.[19,20] Prior to the investigation of Neuse, Graham[21] described the alkylation of ferrocene with benzaldehyde and formaldehyde in the presence of acid catalysts but did no work on synthesizing ferrocene–aldehyde condensation polymers. Neuse, however, studied zinc chloride-catalyzed condensation polymerizations of ferrocene with furfuraldehyde, formaldehyde, benzaldehyde, cinnamaldehyde, 4-cyanobenzaldehyde, and both 2- and 4-carboxyl-substituted benzaldehydes. Neuse also studied other strong Lewis acid catalysts such as sulfuric acid and aluminum chloride, and reported a preference for zinc chloride.

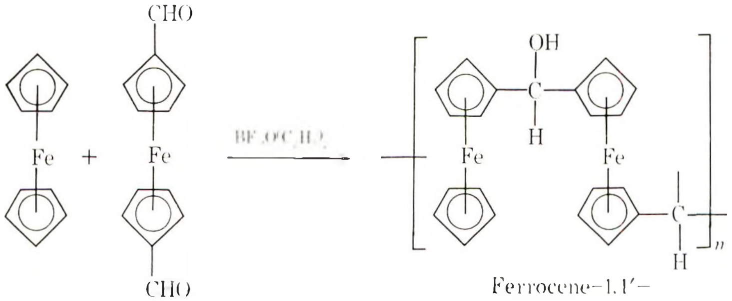
DISCUSSION

In the present work reactions of ferrocene and polyferrocenylenes with aromatic dicarboxaldehydes were studied. Copolymerizations of ferrocene with terephthalaldehyde were found to produce thermosetting copolymers useful as molding compounds and laminating resins. Furthermore, terephthalaldehyde and 1,1′-ferrocenedicarboxaldehyde were both found to be useful curing agents for polyferrocenylenes. These reactions are illustrated in eqs. (1)–(4).



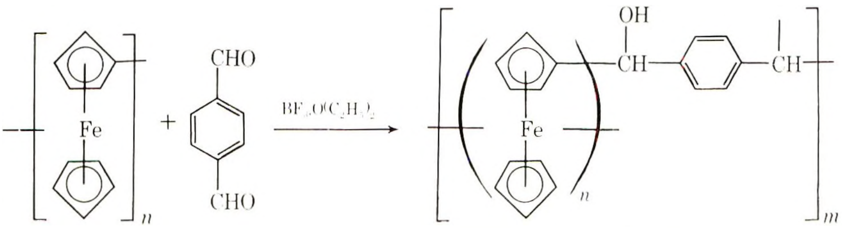
(1)

Ferrocene–terephthalaldehyde copolymer



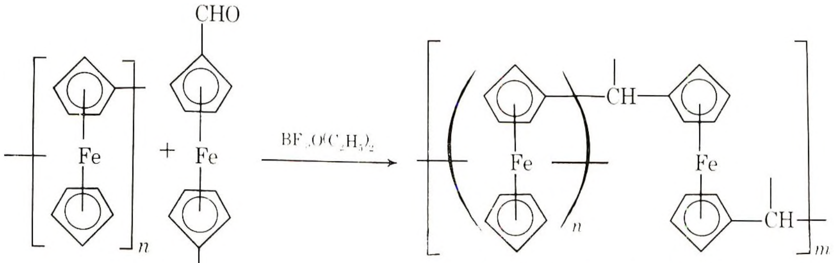
(2)

Ferrocene–1,1′-ferrocenedicarboxaldehyde copolymer



(3)

Terephthalaldehyde-cured polyferrocenylene



(4)

1,1′–Ferrocenedicarboxaldehyde–cured polyferrocenylene

This paper describes ferrocene copolymerizations involving two dialdehydes, namely, terephthalaldehyde and 1,1′-ferrocenedicarboxaldehyde, as well as the use of boron trifluoride etherate as a catalyst. The results of this investigation extend beyond the synthesis of intractable polymers, in that the preparation of thermosetting molding and laminating resins has been achieved, and composite structures have been fabricated.

Melt copolymerizations of ferrocene with terephthalaldehyde were carried out between 120 and 140°C, the former temperature being preferred because of the convenience of terminating the polymerization at that prepolymer stage at which it has optimum processibility. The catalyst boron trifluoride etherate is effective above a concentration of 0.3 mole-%. However a catalyst concentration of 1 mole-% percent was used most frequently in this investigation.

Solution copolymerizations were also carried out in refluxing methylene chloride. However, based upon elemental analyses, the melt phase reactions produced products which withstood thermal postcure with the least adverse effects.

Elemental carbon and hydrogen analyses on cured resins postcured in nitrogen or argon were satisfactory, although samples which were postcured in air often were low in carbon and hydrogen, thus indicating oxidation.

In Table I data on ferrocene–terephthalaldehyde solution copolymerizations are presented. In examining the analytical data (Table II), it is apparent that the cured polymers approach their theoretical structures. For example, in experiment 1, one may compare the observed results with the calculated values as well as with the results on a polymer prepared by melt copolymerization.

The calculated value is based upon a polymer in which only one molecule of water was lost during cure. Theoretically, two molecules of water can be lost for each terephthalaldehyde molecule, although neither the prepolymerization nor cure are dependent upon complete dehydration.

The percentage of iron was determined in only one of these solution polymerization resins, and the value was 2.4% low. However, a known 1,1′-ferrocenedicarboxaldehyde sample analyzed simultaneously by the same procedure was also 2.3% low. Iron analyses performed subsequently on copolymers obtained by melt copolymerizations were significantly better.

TABLE I
Data on Solution Copolymerizations of Ferrocene with Terephthalaldehyde[a]

Experiment	Boron trifluoride etherate, g	Time, hr	Yield, g	Yield, %	Softening range, °C	Molding	Laminate[b]	Cured polymer, % nonextractable with benzene	Analyses of the insoluble portions of cured polymers C, %	H, %	Fe, %
1	0.25	8	12.4	78	50–105	V. good	CCA-1, good	95.0	70.87	4.94	16.08
2	0.25	22	12.2	77	50–90		CCA-1, poor	93.0	70.64	4.93	
3	0.25	30	13.9	87	50–90	Good	CCA-1, poor	80.0	70.60	4.92	
4	0.25	45	16.9	105	45–80	Good	181E, good CCA-1, fair	98.0	70.59	4.85	
5	0.021	6	15.9	99	90–150						
6	0.063	6	16.0	100	60–130						
7	0.19	6	15.7	98	60–130	Poor					
8	0.57	6	15.9	99	45–190	Good		88.0	70.08	4.80	
9	0.021	24	15.0	94	90–160						
10	0.063	24	15.5	97	85–160						
11	0.19	24	15.8	99	60–155						

[a] All of these experiments involved the use of 9.3 g (0.05 mole) of ferrocene and 6.7 g (0.05 mole) of terephthalaldehyde in 25 ml of methylene chloride at 40°C. Molding temperatures differed for the various specimens but were all between 200 and 300°C. Molding pressures varied from 2 500 to 3 000 psi.

[b] CCA-1 carbon cloth and 181E glass fabric. Both carbon cloth and 181E glass fabric are products of HITCO Corp., Gardena, California.

TABLE II
Analytical Data for Ferrocene–Terephthalaldehyde Copolymers[a]

Experiment	Type of Reaction	C, %	H, %	Fe, %
1	Solution polymerization	70.87	4.94	16.08
42[b]	Melt polymerization	71.98	5.31	18.06
Calculated for $-(C_{18}H_{15}OFe)-_n$		71.31	4.99	18.42

[a] Conditions of polymerization as in Table I.

[b] Melt polymerizations are discussed subsequently.

Melt polymerizations of ferrocene with terephthalaldehyde were also attempted with other catalysts. Besides boron trifluoride etherate, these included oxalic acid, *p*-toluenesulfonic acid, benzyldimethylamine, and di-*tert*-butyl peroxide. Of these, the boron trifluoride etherate was the only one which was effective. These experiments were generally started at 120°C, and those which did not proceed were gradually heated to as high as 165°C. Even at the higher temperatures, polymerizations did not occur except with boron trifluoride etherate.

Two subsequent series of melt polymerizations were then carried out. In one of these sets (experiments 17–20), the boron trifluoride etherate concentration was varied and the time required for the reaction to proceed to a high viscosity melt was noted, while in the second series (experiments 21–24) the catalyst concentration was maintained at 0.7 mole-% and the time was varied.

Reaction mixtures which contained 0.3 mole-% boron trifluoride etherate or more polymerized between 120 and 140°C. Reaction periods which were required at 140°C to provide laminating resins with optimum processing characteristics were as given in Table III.

These reactions were carried out by preparing equimolar solutions of ferrocene and terephthalaldehyde in methylene chloride and then adding the boron trifluoride etherate. The methylene chloride was then removed under vacuum and the recovered solids were polymerized as a melt in an oil bath with continuous stirring. Experimental data on the various melt polymerizations are presented in Table IV. Optimum reaction conditions were ultimately selected on the basis of flexural tests using glass fabric-reinforced laminates.

TABLE III

BF_3, mole-%	Time, min
3.5	8–9
1.7	35
0.7	95
0.3	160

TABLE IV
Data on Melt Copolymerizations of Ferrocene with Terephthalaldehyde

Experiment	Reactants[a]	Catalyst				Temperature, °C	Time, hr	Yield, %
		Type[b]	Weight, g	Mole	Mole-%			
12	A	BTE	0.48	0.0034	1.7	140	0.13	98
13	A	OA	0.30	0.0033	1.7	120–165	6.5	—
14	A	PTSA	0.63	0.0033	1.7	120–165	6.5	—
15	A	BDMA	0.45	0.0033	1.7	120–160	12.0	—
16	A	DTBP	0.10	0.0014	0.7	120	3.0	—
17	B	BTE	1.0	0.007	3.5	140	0.14	96
18	B	BTE	0.5	0.0035	1.7	140	0.58	95
19	B	BTE	0.2	0.0014	0.7	140	1.58	89
20	B	BTE	0.1	0.0007	0.3	140	8.0	—
21	B	BTE	0.2	0.0014	0.7	140	1.0	89
22	B	BTE	0.2	0.0014	0.7	140	1.33	90
23	B	BTE	0.2	0.0014	0.7	140	1.66	90
24	B	BTE	0.2	0.0014	0.7	140	2.0	87

[a] Reactants: A = 9.3 g (0.05 mole) ferrocene + 6.7 g (0.05 mole) terephthalaldehyde; B = 18.6 g (0.10 mole) ferrocene + 13.4 g (0.10 mole) terephthalaldehyde.

[b] BTE = boron trifluoride etherate; OA = oxalic acid; PTSA = *p*-toluenesulfonic acid; BDMA = benzyldimethylamine; DTBP = di-*tert*-butyl peroxide.

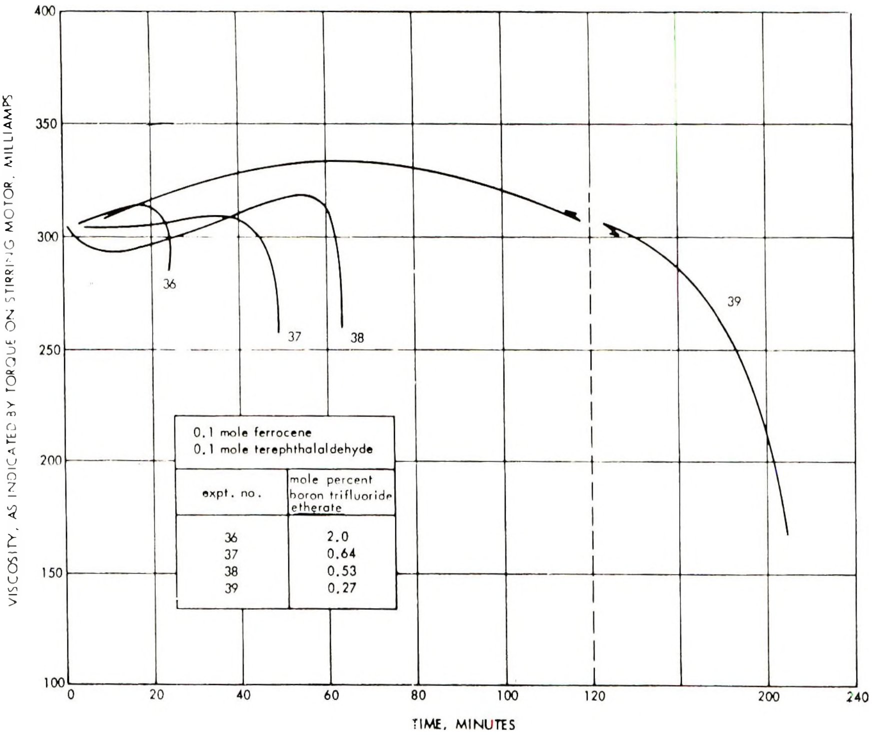


Fig. 1. Effect of catalyst concentration on viscosity of ferrocene–terephthalaldehyde melt copolymerizations at 140°C.

Prepolymer preparations carried out at 140°C generally produced resins whose 181E-glass reinforced laminates had flexural strengths in the range of 15 000–30 000 psi and moduli of about 2.7 × 10^6 psi. When completely analogous reactions were carried out at 120°C, flexural strengths reached 37 000–41 000 psi and flex moduli reached 2.9 × 10^6 psi.

Many of these copolymerizations were followed by viscosity measurements during the course of the reactions. Polymerizations carried out at 120°C with 0.3 mole-% of boron trifluoride etherate were most convenient to terminate at the stage where the prepolymer had optimum processibility. The polymerizations at low catalyst concentrations gave prepolymer which produced laminates with the best appearance; however, these laminates were lower in flexural strength than those containing higher catalyst concentrations.

Postcure studies were carried out in an inert atmosphere (argon) on several sets of ferrocene–terephthalaldehyde laminates. Samples were removed from postcure at the following intervals: 24 hr at 200°C; 24 hr at 200°C and 24 hr at 250°C; 24 hr at 200°C, 24 hr at 250°C, and 8 hr at 300°C; 24 hr at 200°C, 24 hr at 250°C, 8 hr at 300°C, and 8 hr at 350°C. Other samples were removed after 24 hr at 250°C; 24 hr at 250°C, and 16 hr at 300°C; 24 hr at 250°C, 16 hr at 300°C, and 8 hr at 350°C.

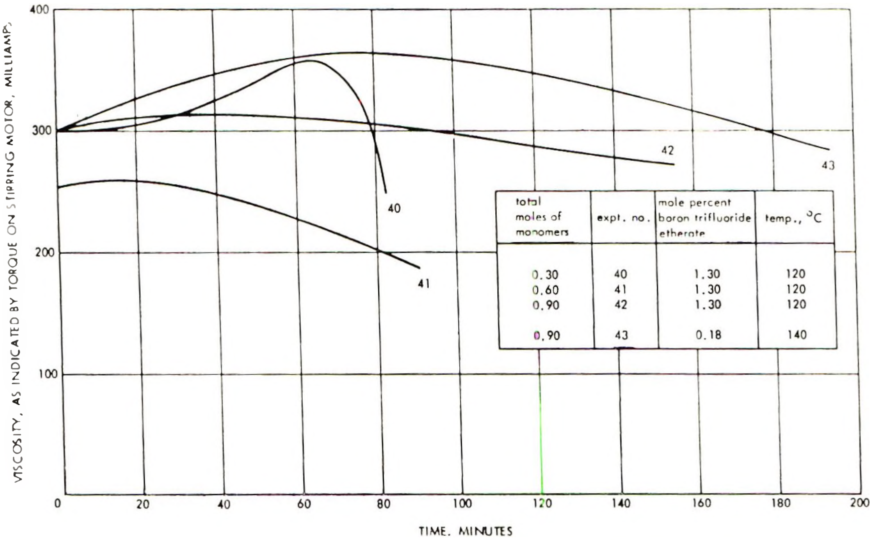


Fig. 2. Viscosity change in various ferrocene–terephthalaldehyde melt copolymerizations.

For each set of specimens, flex strengths were within 10% of the value for the unpostcured specimens and, consequently, it was concluded that the postcures had no significant effect. Apparently, complete cures were achieved in the initial cure. It is interesting to note that under no conditions did the prolonged heating deteriorate the specimens.

Viscosities of the copolymerization mixtures were followed on a milliammeter by measuring current generated by a small dc motor connected to the stirring motor shaft. Examples of these "viscosity" plots are shown in Figures 1 and 2. These results are entirely relative, and no attempt was made to attach conventional viscosity units to these data.

The products of copolymerizations of ferrocene with excess terephthalaldehyde tended to gel very suddenly. Therefore, to determine the importance of excess aldehyde, several experiments were carried out in which equimolar mixtures of reactants were polymerized and excess terephthalaldehyde (10 and 20%) was subsequently added to cooled solutions made therefrom. Laminates were then fabricated and physical tests were conducted. The sample which contained 10% excess terephthalaldehyde could not be evaluated, since it did not provide a satisfactory laminate. However, the flexural strength of the sample which contained 20% excess aldehyde (experiment 42b) was obtained. Since the resin without excess terephthalaldehyde and the resin with 20% excess terephthalaldehyde both produced laminates which were very good in appearance, the failure of the sample containing 10% excess terephthalaldehyde to mold well was attributed to unsatisfactory handling procedures during the molding process. The laminate made from the product of experiment 42b contained 41% cured resin, which is relatively high, indicating that cure occurred before

TABLE V
Results of Physical Tests on 181E Glass Laminates

Resin number	Reaction time, min	Resin on 181E glass, %	Flexural strength, psi × 10³	Flexural modulus, psi × 10⁶	Tensile strength, psi × 10³	Tensile modulus, psi × 10⁶	Notes
28	40	23	31	3.0	34	5.0	No postcure
28	40	23	33	3.2			20 hr postcure in argon at 195°C
29	45	34	33	2.9	17	2.0	No postcure
27	50	38	29	2.8	28	3.3	No postcure

sufficient flow could occur. Its flexural strength was 20 000 psi, which is lower than that generally observed with corresponding laminates having lower resin content (25–30%). Many of the laminates had flexural strengths near 30 000 psi. Thus, it cannot be stated with certainty whether the lower flexural value is due to the presence of excess aldehyde or due to the high resin content of the laminate. The latter would vary considerably with changes in molding temperature and pressure.

Physical properties of 181E glass laminates prepared from these copolymers are presented in Table V. Flexural strengths in each case were $31 \pm 2 \times 10^3$ psi, flexural moduli were $3.0 \pm 0.2 \times 10^6$ psi. These values were on unpostcured laminates, since postcure appeared to have no effect on

TABLE VI
Summary of Copolymerization and Laminate Fabrication Conditions[a]

Experiment	Reaction time, min	Molding parameters		Resin content, %	Laminate appearance
		Temp, °C	Pressure, psi		
25	60	Initial 204 Final 316	4 000	45	1 of 3 very good
26	72	Initial 204 Final 316	1 000	—	Resin too far advanced
27	50	Initial 204 Final 316	1 000	29	Very good
28	40	Initial 204 Final 316	1 000	23	Very good
29	40	316	1 000	34	Very good
34	40	316	500	30	Fair

[a] All experiments involved the use of 55.8 g (0.30 mole) of ferrocene, 40.2 g (0.30 mole) terephthalaldehyde, and 0.85 g boron trifluoride etherate. Experiment 35 was a double batch. All reactions were carried out under argon in the melt phase at 140°C.

physical properties in prior tests. The test specimens were cut from larger laminates and were either 12 × 9 × $^1/_8$ in. or 6 × 9 × $^1/_8$ in. in size. Table VI summarizes the laminate fabrication conditions.

In experiments 30–32, the copolymers obtained initially were found to flow excessively when molded. These resins were removed from solution and polymerized further in the melt phase at 140°C. In each case the gel point occurred suddenly, and the resins were too far advanced for further evaluation.

Terephthalaldehyde Cures

In addition to using terephthalaldehyde in copolymerizations with ferrocene, the crosslinking of polyferrocenylene[22] was also achieved with this compound as illustrated previously. Experiments were carried out using prepolymers with mean molecular weights ranging from 640 (trimers) to 4 000 (22 repeating units). Crosslinking studies were carried out in most cases by dissolving the polymer, crosslinking agent, and catalyst in a common solvent, generally methylene chloride. The solutions were subsequently used as varnishes to coat a reinforcement and, after sufficient weight gain was attained, the dried coated fabrics were cut to size, stacked, and molded under heat and pressure. With polyferrocenylenes having a mean molecular weight below 1 000, the reactants were, in a few cases, melted together and "advanced" for a few minutes until they had a viscosity suitable for molding. In most cases, excellent laminates were obtained. In a few cases, the product specimens were resin-starved, but others made with a somewhat higher resin content were excellent. For example, with a polymer fraction having a mean molecular weight of 2 130, one resin-starved specimen was obtained having a cured resin content of only 34%; however two other laminates of this type containing 41–44% resin were excellent in appearance. Thus, it appears that in this molecular weight range resin contents over 40% are required because such resins tend to exhibit less flow when molded. Thermosetting polyferrocenylenes having mean molecular weights in the range of 1 290 produced excellent appearing glass-reinforced laminates with only 30–36% resin content. The best physical properties achieved with this crosslinking agent were on a polyferrocenylene having a mean molecular weight of only 500. This resin contained three parts by weight of polyferrocenylene per part of terephthalaldehyde. A 181E glass laminate fabricated from this mixture contained 30% cured resin and had a flexural strength, at ambient temperature, of 42 000 psi and a flexural modulus of 2.9 × 10^6 psi. One specimen was postcured at 200°C for 24 hr and then at 250°C for 24 hr, whereas the second specimen was postcured for 24 hr at 200°C, 24 hr at 250°C, 8 hr at 300°C, and 8 hr at 350°C. Here also, as with the ferrocene-terephthalaldehyde copolymer, there was no significant difference in physical properties attributable to postcure. It is very significant, however, that the ferrocene "trimer" ($\bar{M}_n$ = 640) gave better flexural properties when cured than any of the ferrocene-terephthalaldehyde copolymers described previously. Data on

TABLE VII

Composition and Fabrication Parameters on Various Terephthalaldehyde-Cured Polyferrocenylene Laminates

Experiment	Polyferrocenylene			Curing Agent		Catalyst[a]		Lacquer solvent	"Advancing" temperature, °C	Time, hr	Molding temperature, °C	Molding pressure, psi	Reinforcement[b]	Resin content, %	Sample size (diameter), in.
	Wt, g	mole	$\bar{M}_n$	Wt, g	mole	Wt, g	mole								
45	6.0	0.0015	4 000	0.7	0.005	0.20	0.0014	CH_2Cl_2	40	0.50	288	2 500	CCA-1	100	$^3/_4$
46	3.5	0.0026	1 365	1.2	0.009	0.10	0.0007	CH_2Cl_2	140	0.15	288	200	CCA-1	—	$^3/_4$
47	9.0	0.0070	1 290	3.0	0.024	0.50	0.0035	CH_2Cl_2	—	—	200–315	4 000	181E	29	$^3/_4$
48	36	0.0190	1 880	12.0	0.089	1.00	0.0070	CH_2Cl_2	—	—	315	2 000	CCA-1	30	2
49	48	0.0260	1 880	16.0	0.120	1.30	0.0091	CH_2Cl_2	—	—	315	2 000	CCA-1	—	2
50	20	0.0100	2 020	4.0	0.030	0.25	0.0018	CH_2Cl_2	—	—	315	750	181E	27	
51	20	0.0100	2 020	2.7	0.020	0.25	0.0018	CH_2Cl_2	—	—	315	750	181E	44	
52	20	0.0100	2 020	4.0	0.030	0.25	0.0018	CH_2Cl_2	—	—	315	1 000	181E	43	
53	18	0.0090	2 020	6.0	0.045	0.63	0.0044	CH_2Cl_2	—	—	315	1 000	181E	36	
54[c]	18.5	0.0160	1 100	6.0	0.045	0.63	0.0044	CH_2Cl_2	—	—	343	1 000	181E	29	

[a] Boron trifluoride etherate.

[b] CCA-1 = carbon cloth, 181E = 181E glass fabric (HITCO Corp., Gardena, California).

[c] 92% polyferrocenylene by weight ($\bar{M}_n$ = 2 020) + 8% ferrocene by weight.

TABLE VIII
Physical Properties of Polyferrocenylene-Terephthalaldehyde Laminates

Experiment	Polymer/curing agent ratio: Wt. ratio	Polymer/curing agent ratio: Mole ratio	Flexural strength, psi × 10^{-3}	Flexural modulus, psi × 10^{-6}
50	5:1	1:3.1	30	3.1
51	7.4:1	1:2.1	8	3.7
52	5:1	1:3	28	7.0
53	3:1	1:5	19	2.0
54	3:1	1:2.7	31	1.1

the fabrication parameters and composition of various experimental laminates are presented in Table VII.

Physical properties of several of these laminates are shown in Table VIII. Based on the very limited amount of physical test data obtained to date it appeared that the laminate containing resin with the highest polymer: terephthalaldehyde ratio (7.4:1) provided the poorest flexural strength, whereas that with resin having the lowest ratio (3:1) provided the best strength (31 000 psi). Furthermore, at the specific prepolymer: terephthalaldehyde weight ratio of 3:1, it appears that the higher the prepolymer molecular weight the poorer the flexural strength. Thus, polyferrocenylene with a mean molecular weight of 2 020 provided a laminate having a flexural strength of 19 000 psi, where polymer with a mean molecular weight of 1100 produced a laminate with a flexural strength of 31 000 psi and a polymer having a mean molecular weight of 640 yielded a laminate having a flexural strength of 42 000 psi. It may be concluded, therefore, that polyferrocenylene not only can be crosslinked with terephthalaldehyde but that the polymer–crosslinking agent solutions are useful laminating resin varnishes. Glass fabric-reinforced laminates made from these varnishes had flexural strengths between 19 000 and 43 000 psi, with the higher value obtained from a prepolymer which had a degree of polymerization of only 3.5.

1,1′-Ferrocenedicarboxaldehyde Cures

1,1′-Ferrocenedicarboxaldehyde can also function as a polyferrocenylene crosslinking agent in a reaction which was also illustrated previously. Furthermore, in addition to its use as a crosslinking agent, this compound also has been copolymerized with ferrocene.

Prepolymers obtained from boron trifluoride etherate-catalyzed reactions of ferrocene and 1,1′-ferrocenedicarboxaldehyde have been used to prepare laminates reinforced with both 181E glass fabric and CCA-1 carbon cloth. The 181E glass specimens ($^3/_4$ in. diameter, $^1/_2$ in. thick) were excellent in appearance. Carbon cloth laminates were also good in appearance, although they were not of the quality of the fiberglass laminates. In these experiments (44A and 44B), equimolar amounts of comonomers were reacted together in the presence of 1.7 mole-% boron trifluoride etherate. Reactants were dissolved in methylene chloride and were subsequently

TABLE IX
Analytical Results

	C, %	H, %
Ferrocene–1,1′-ferrocenedicarboxaldehyde copolymer	69.45	4.83
Calculated for $\leftarrow C_{11}H_8Fe \rightarrow$ assuming loss of all oxygen as water	67.33	4.11
Calculated for $\leftarrow C_{16}H_{12}Fe \rightarrow$ assuming 1 extra cyclopentadienyl moiety added to each ferrocene molecule	69.10	5.06
Calculated for carbon and hydrogen if 50% of the theoretical amount of H_2O is lost and 1 cyclopentadienyl moiety enters the polymer	68.24	4.88

dried before melt polymerization, which was carried out at 115°C for 2 hr. One sample of cured resin was extracted exhaustively with benzene in a Soxhlet extractor and was found to contain only 0.8% extractable product. Analysis of the insoluble portion of the sample gave the results shown in Table IX.

The elemental analysis does not correspond precisely to the expected structure, and it is possible that some ferrocene cleavage occurs and the resultant cyclopentadiene fragments enter the copolymer molecule. The limited analytical data on these copolymers does not allow definite conclusions to be drawn.

In polyferrocenylene crosslinking studies, solutions of the polymer, 1,1′-ferrocenedicarboxaldehyde, and catalyst were prepared and used as laminating resin varnishes without further reaction prior to cure.

The 1,1′-ferrocenedicarboxaldehyde cured polymers appeared to require pressures of about 4 000 psi to produce laminates which were good in appearance. Specimens molded at 1 000 psi were generally too poor in appearance to test. Those made at 4 000 psi, however, consistently had low flexural strengths in spite of their good appearance, and this probably indicates that during cure the resins became intractable before they could advance to a degree of polymerization sufficient to provide good physical properties.

Although a flexural strength as high as 30 000 psi was achieved in one sample, the flexural strength of most samples were below 10 000 psi. Data on the composition and physical properties of the 181E glass fabric-reinforced laminates prepared for this evaluation are shown in Table X.

Carbon cloth-reinforced laminates were also prepared. Three of these were made with a polyferrocenylene prepolymer having a mean molecular weight of 1 290 and ferrocenedicarboxaldehyde as the cross linking agent and three specimens were prepared with a ferrocene–1,1′-ferrocenedicarboxaldehyde copolymer. Those prepared from the 1 290 $\bar{M}_n$ prepolymer were rated excellent based upon their appearance. These specimens contained

TABLE X

Composition and Physical Properties of 1,1′-Ferrocenedicarboxaldehyde-Cured Polyferrocenylene Laminates

Experiment	Polyferrocenylene			Curing agent		Polymer/curing agent weight ratio	Catalyst[a]		Resin content, %	Molding parameters		Flexural strength, psi × 10^{-3}	Flexural modulus, psi × 10^{-6}
	M_n	Wt, g	Mole	Wt, g	Mole		Wt, g	Mole		Pressure, psi	Temperature, °C		
55	2 020	14.0	0.007	7.0	0.029	2:1	0.40	0.0028	42	1 000	316	32	1.2
56	1 510	13.6	0.009	4.5	0.019	3:1	0.36	0.0025	40	4 000	316	5	0.6
57[b]	848	13.5	0.016	4.5	0.019	3:1	0.36	0.0025	44	4 000	316	6	1.1
58	1 510	10.1	0.0067	5.0	0.021	2:1	0.30	0.0021	44	4 000	316	9	1.0
59[b]	848	10.2	0.012	5.0	0.021	2:1	0.30	0.0021	39	4 000	316	8	1.1

[a] Boron trifluoride etherate.

[b] 89% polyferrocenylene (M_n = 1 510) + 11% ferrocene by weight (50% of each on molar basis).

TABLE XI

Composition of Various 1,1′-Ferrocenedicarboxaldehyde-Cured Polyferrocenylenes

Experi- ment	Polyferro- cenylene		Wt curing agent, g	Wt catalyst, g[a]	Reaction conditions[b]		Lacquer solvent	Rein- forcement	Molding conditions		Quality of part	Laminate resin content, %
	Wt, g	M_n			Temp, °C	Time min			Temp, °C	Pres- sure, psi		
60	9.0	2 130	3.0	0.5	—	—	CH_2Cl_2	181E	204–316	4 000	V. good	44
61	9.0	1 290	3.0	0.5	—	—	CH_2Cl_2	181E	204–316	4 000	V. good	36
62	30.0	1 290	8.5	0.5	—	—	CH_2Cl_2	CCA-1	204–316	4 000	V. good	33, 39, 43
63	12.6	1 290	3.5	0.2	—	—	CH_2Cl_2	181E	204–316	1 000	Poor	—
64	5.0	700	2.5	0.3	100	9	CH_2Cl_2	181E	204–316	4 000	V. good	45
65	6.0	4 000	1.2	0.2	—	—	CH_2Cl_2	CCA-1	204	3 000	V. good	(100)

[a] Boron trifluoride etherate.

[b] Polymer–curing agent–catalyst solutions were prepared at room temperature with no further reaction except where noted.

36–43% cured resin. The three copolymer–carbon cloth-reinforced laminates also were excellent in appearance but not as good as those mentioned previously. Possibly this was due to the inadvertent use of ethylene dichloride rather than methylene chloride as the lacquer solvent.

Various other experimental laminates ($^3/_4$ in. diameter, $^1/_4$ in. thick) were molded and their properties are described in Table XI. In all but one example, solutions of the polymer and crosslinking agent were used without further polymerization prior to cure. Carbon cloth-reinforced specimens suitable for physical tests were not prepared. The physical test data reported previously was on glass-reinforced laminates.

EXPERIMENTAL

Ferrocene-1,1′-Ferrocenedicarboxaldehyde Copolymerizations

Experiment 44A. Ferrocene (1.86 g, 0.01 mole) and 1,1′-ferrocenedicarboxaldehyde (2.42 g, 0.01 mole) were dissolved in anhydrous ether (20 ml) and redistilled boron trifluoride etherate (2 drops, 47% boron trifluoride) was then added. After stirring for $^1/_2$ hr, the ether was evaporated and the reaction mixture was collected and pulverized. It was then heated at 115°C in an oil bath for 2 hr. The viscous polymer weighed 3.8 g, which was about 90% of theory. It melted at about 110–125°C and proceeded to full cure at 220°C.

Experiment 44B. Ferrocene (9.3 g, 0.05 mole) and 1,1′-ferrocenedicarboxaldehyde (12.1 g, 0.05 mole) were dissolved in methylene chloride, and redistilled boron trifluoride etherate (10 drops, 47% BF_3) was then added. After stirring for 1 hr, the reactants were polymerized at 115°C for 2 hr. After cooling, the prepolymer was pulverized. Its molecular weight by vapor-phase osmometry measured in chloroform was 362; however, this undoubtedly is low since the prepolymer contained boron trifluoride and probably even ether as the boron trifluoride etherate, as well as partially hydrolyzed boron trifluoride.

Copolymerization of Ferrocene with Terephthalaldehyde

Ferrocene (41.4 g, 0.223 mole) and terephthalaldehyde (30.2 g, 0.225 mole) were dissolved in methylene chloride (150 ml), and when dissolution was complete, distilled boron trifluoride etherate (0.82 g, 0.72 ml) was added. The solvent then was removed by distillation under reduced pressure. The recovered solids were pulverized and heated at 120°C for 85 min with continuous stirring. The viscous polymer (68 g) was cooled and pulverized. It was redissolved in methylene chloride for use as a thermosetting polymer varnish. Its melting range was 50–90°C.

The authors wish to express their appreciation to Mr. Kenneth L. Rose for his excellent technical assistance in polymer synthesis and to Mr. Arturo A. Castillo for his high degree of competence in molding these new resins and composite structures.

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Effect of Viscosity on Termination Rate Constant in Radical Polymerization at Low Conversion

KATSUKIYO ITO, *Government Industrial Research Institute, Nagoya, Kita-ku, Nagoya, Japan*

Synopsis

By using the expression, $k_t = A_1 D_S$ for the chain termination rate constant (where A_1 is a constant and D_S is the diffusion constant of radical chain end), a familiar chain termination rate constant, $k_t = A_2/\eta_s$ (where A_2 is a constant and η_s is solvent viscosity) was examined with variation of conversion x. It was found that the proportionality of chain termination rate constant and solution viscosity is a valid relation at conversion 0 but is approximate at conversion $x_c \geq x > 0$. Here x_c denotes a critical conversion under the average distance around spherical polymers formed in polymerization solution is zero. At conversions above x_c, the inverse relation between chain termination rate constant and solution viscosity is not correct.

INTRODUCTION

In the past, it has been theoretically and experimentally recognized that the chain termination rate constant k_t is inversely proportional to solvent viscosity η_S;[1-4] that is, this relationship is given by:

$$k_t = A_1 D_S = A_2/\eta_s \tag{1}$$

where A_1 and A_2 are constants and D_S is the diffusion constant of the radical chain end in spherical polymeric radical. The correctness of this equation has not been examined at varying conversions.

The aim of this paper is to find the conversion range over which eq. (1) is precisely or approximately valid. By using Mori and Ototake's equation[5] and Miyama's experimental results,[6] it was found that this conversion range is 0 to x_c, where x_c is the conversion at which the average distance around spherical polymers formed in polymerization solution is zero.

RELATIONSHIP BETWEEN CONVERSION AND SOLUTION VISCOSITY

At low conversion ($x_c \geq x \geq 0$), a polymer or a polymeric radical in polymerization solution can be referred to a sphere with radius r composed of polymer segments and solvent molecules. Viscosity in the spherical polymer is denoted by η_S; viscosity outside of the polymer is equivalent to solvent viscosity. When total spherical polymers in a volume V with average distance λ around spherical polymers accumulates into a volume V_c with $\lambda = 0$, the concentration of spherical polymer in V_c is a limiting concentration and the viscosity in V_c is equivalent to η_S. That is, a distinction between viscosities in and out of spherical polymer is meaningless. According to the above consideration, a critical conversion x_c with $\lambda = 0$ should exist. At conversions above x_c, the polymerization medium is homogeneous solution composed of polymer chains and solvent molecules.

Derivation of a Relationship between Solution Viscosity and Conversion at Low Conversion ($x_c \geq x \geq 0$)

Using the notation of limiting concentration, Robinson[7] derived a relationship between viscosity and the volume of solid particles. On modification of Robinson's treatment, Mori and Ototake[5] derived a relationship between viscosity and average thickness of liquid layer among particles. On the application of their method to polymerization solution, a useful relationship is given by:

$$\eta_{rx} = 1 + 2r/\lambda \tag{2}$$

where

$$\lambda = (2r/3)(1/\phi_v - 1/\phi_{vc})$$

$$\phi_{vc} = W/\rho V_c$$

$$\phi_v = W/\rho V$$

where η_{rx} is the ratio of solution viscosity at conversion x to solvent viscosity, W is total weight of spherical polymers, ρ is density of a spherical polymer, ϕ_{vc} is spherical polymers fraction in limiting concentration, and ϕ_v is volume base of spherical polymers fraction.

In eq. (2), it appears that conversion affects ϕ_v, but the effect of conversion on ϕ_{vc} can be negligible. Furthermore, assuming that the density of a spherical polymer is equivalent to density of polymerization solution, ϕ_v is given by:

$$\phi_v = x(1 + b) \tag{3}$$

where b is the ratio of total weight of monomer to total weight of polymer segments in a spherical polymer. By using eq. (3), eq. (2) becomes:

$$3/(\eta_{rx}\,^{-1}) = [1/(1 + b)](1/x) - (1/\phi_{vc}) \tag{4}$$

Examination of Equation (4)

By using Miyama's results for the bulk polymerizations of methyl methacrylate (MMA) and vinyl acetate (VA),[6] eq. (4) was examined.

The relationship between η_{rx} and x for the bulk polymerization of MMA is shown in Figure 1. Equation (4) becomes valid in the conversion range 0–1.1%. Using this linear relationship, the following values were calculated: $b = 80$, $\phi_{vc} = 1.4$, $x_c = 0.017$ ($\lambda = 0$).

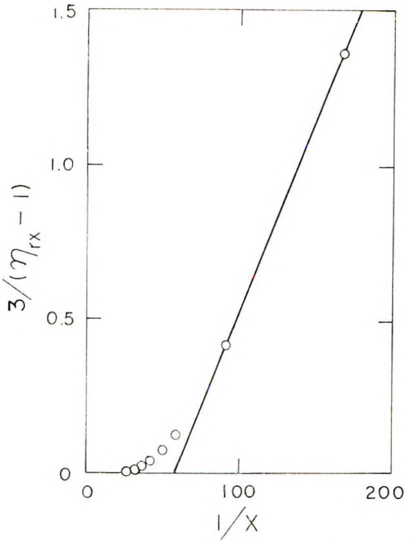

Fig. 1. Relationship between η_{rx} and x for the bulk polymerization of methyl methacrylate at 30°C.[6]

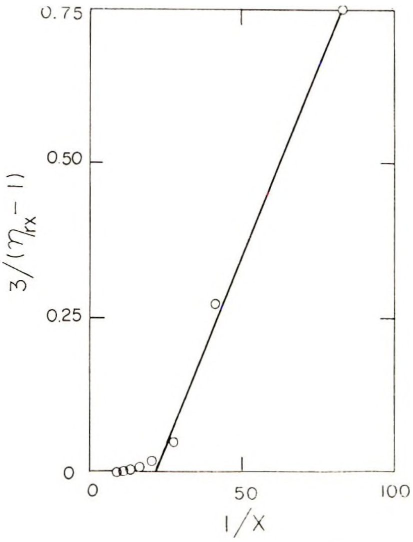

Fig. 2. Relationship between η_{rx} and x for the bulk polymerization of vinyl acetate at 30°C.[6]

The critical conversion x_c was determined from the intercept of the line on the $1/x$ axis.

A relationship between η_{rx} and x for bulk polymerization of VA is shown in Figure 2. Equation (4) becomes valid in the range 0–3.8% and the following values were calculated: $b = 81$, $\phi_{rc} = 3.7$, $x_c = 0.045$ ($\lambda = 0$).

The above investigations indicate that eq. (4) is valid only at very low conversion for bulk polymerization.

DISCUSSION

North and Reed[2] and Ito[4] pointed out that the chain termination rate constant is given by

$$k_t = A_1 D_S \qquad (5)$$

but is independent of solvent viscosity. If we take

$$D_S \eta_S = A_3 \qquad (6a)$$

$$\eta_S = A_4 \eta_s \qquad (6b)$$

where A_3, A_4 are constants, eq. (7) is obtained

$$k_t = A_2/\eta_s \qquad (7)$$

where

$$A_2 = A_1 A_3 / A_4$$

But, because the diffusion constant of the radical chain end increases with the increase of polymer formed in polymerization solution, eq. (6b) is not precise unless conversion $x = 0$. Accordingly, eq. (7) is an approximate relationship at conversions near zero. As stated in the previous discussion, the critical conversion x_c is very small in the bulk polymerization. It thus appears that the chain termination rate constant given by eq. (7) is approximately correct in the conversion range 0 to x_c. For the discussion of this phenomenon, the same experiments to North and Reed's experiments must be carried out.

At conversions above x_c, the behavior of polymeric radical in homogeneous solution of polymer chains and solvent molecules is important. Assuming that the polymeric radical can also be considered a sphere and the collision between two spherical polymeric radicals can be treated by the same method in the conversion range 0 to x_c, the chain termination rate constant given by eq. (5) is still correct; but the chain termination rate constant by eq. (7) is not correct.

Equation (5) will be used in a future paper in which the relation of chain termination rate constant and conversion at conversion above x_c will be theoretically and experimentally treated.

The author thanks Dr. T. Matsuda for the treatment of polymerization reaction.

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Radiation-Induced Polymerization of 1,1,2-Trichlorobutadiene in the Solid State

KATSUKIYO ITO and TATSUO MATSUDA, *Government Industrial Research Institute, Nagoya, Kita-ku, Nagoya, Japan*

Synopsis

Changes in the polymerization and in the structure of the polymer formed during the course of polymerization of 1,1,2-trichlorobutadiene in the solid state were studied. We observed that the rate of polymerization and the molecular weight of the polymers formed increasing conversion. The content of 1,4 units in the polymer also increases with increasing conversion.

In a previous paper,[1] it was reported that, when the radiation-induced polymerization of 1,1,2-trichlorobutadiene was carried out at low conversion, the structure of the resulting polymer showed predominantly 1,4 units with polymerization in the liquid state, but 3,4 units with polymerization in the solid state. The present paper deals with the changes in the polymerization behavior and in the structure of the polymer during the course of the polymerization in the solid state at −78°C. We found that the rate of polymerization and the molecular weight of the polymers formed increase with increasing conversion. Also, the content of 1,4 units of the polymer increases simultaneously.

EXPERIMENTAL

The purified monomer was distilled into a glass ampoule cooled by liquid nitrogen and then sealed under a vacuum of about 10^{-5} mm Hg. The ampoule was then irradiated by γ-rays from a ^{60}Co source at −78°C. After irradiation the contents of the ampoule were diluted with benzene and poured into a large excess of cold methanol. The precipitated polymer was separated by centrifuging, dried *in vacuo*, and weighed. Post-polymerization was not observed.

The polymer samples used for the characterization were purified by repeated precipitation from benzene solution by methanol. The intrinsic viscosity of the polymer was determined in benzene solution at 30°C. The contents of 1,4 and 3,4 units in the polymer were determined by nuclear magnetic resonance techniques as described previously.[1]

RESULTS AND DISCUSSION

Figure 1 shows the course of the polymerization at various dose rates. It is clear that there is an acceleration in the initial rate of the polymeriza-

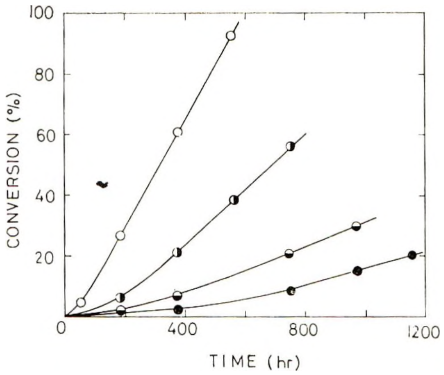

Fig. 1. Relationship between per cent conversion of 1,1,2-trichlorobutadiene and irradiation time at −78°C at various dose rates: (○) 3.16×10^4 rad/hr; (◑) 1.20×10^4 rad/hr; (◒) 0.57×10^4 rad/hr; (●) 0.34×10^4 rad/hr.

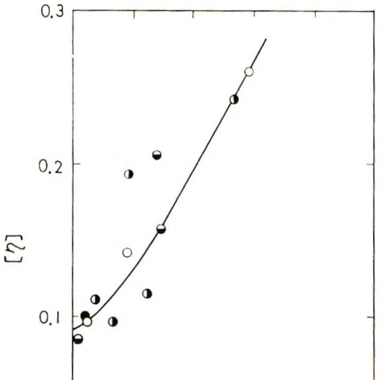

Fig. 2. Relationship between intrinsic viscosity and per cent conversion at −78°C at various dose rates: (○) 3.16×10^4 rad/hr; (◑) 1.20×10^4 rad/hr; (◒) 0.57×10^4 rad/hr; (●) 0.34×10^4 rad/hr.

tion. The data on the molecular weight of the polymer, estimated from intrinsic viscosity, versus conversion at various dose rate is shown in Figure 2. Although the data are scattered, the molecular weight increases with increasing conversion and is independent of the dose rate. Figure 3 shows the dose rate dependence of the polymerization rate at 10% conversion. The data on the initial rate were not given, since they were in good agreement with the results in the previous paper.[1] The following results were obtained: Initial rate, $R_p = 1.6 \times 10^{-6} I^{1.08}$; rate at 10% conversion, $R_p = 6.4 \times 10^{-6} I^{0.98}$; here R_p is polymerization rate (in per cent per hour) and I is dose rate (in rad per hour). In each case, the rates are first-order with respect to the dose rate, and the molecular weight of the polymer is independent of the dose rate. It appears that the reaction mechanism does not change. Figure 4 shows the ratio of 1,4 units to 3,4 units in the polymer, C_{14}/C_{34}, plotted versus the conversion x. The ratio increases with increasing conversion, and a linear relationship was obtained [eq. (1)]:

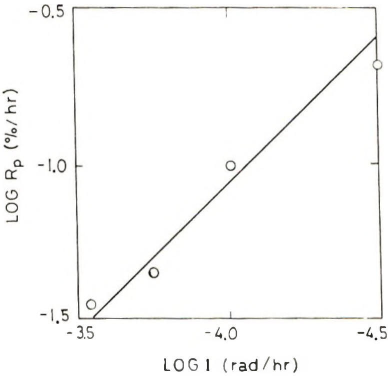

Fig. 3. Dependence of rate of polymerization on dose rate at 10% conversion.

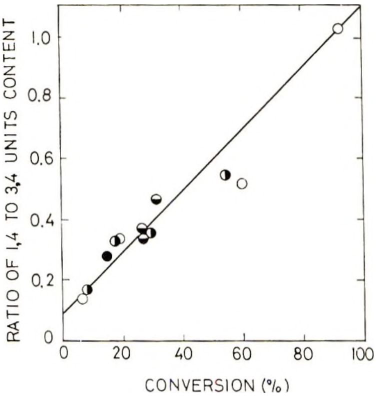

Fig. 4. Relationship between ratio of 1,4 units to 3,4 units in polymer and per cent conversion at −78°C at various dose rates: (○) 3.14 × 10^4 rad/hr; (◑) 1.20 × 10^4 rad/hr; (◒) 0.57 × 10^4 rad/hr; (●) 0.34 × 10^4 rad/hr.

$$C_{14}/C_{34} = 0.1 + 0.01x \qquad (1)$$

The concentrations of 1,4 units and 3,4 units at a given conversion, $x + dx$, may be written

$$c_{14} = \alpha(x)dx/[1 + \alpha(x)]$$

$$c_{34} = dx/[1 + \alpha(x)]$$

where c_{14} and c_{34} are the concentrations of 1,4 units and 3,4 units, respectively, and $\alpha(x)$ is the concentration ratio of two units, c_{14}/c_{34}. Then C_{14}/C_{34} is given by eq. (2):

$$\begin{aligned}\frac{C_{14}}{C_{34}} &= \frac{\int_0^x \alpha(x)dx/[1 + \alpha(x)]}{\int_0^x dx/[1 + \alpha(x)]} \\ &= \frac{x}{\int_0^x dx/[1 + \alpha(x)]} - 1\end{aligned} \tag{2}$$

From eqs. (1) and (2), the material balance is obtained as:

$$\int_0^x dx/[1 + \alpha(x)] = x/(0.01x + 1.1), \tag{3}$$

which yields on integration

$$c_{14}/c_{34} = 0.1 + 0.02x + 0.000091x^2 \tag{4}$$

From eq. (4), the values of c_{14}/c_{34} at conversions of 5.5, 26.5, and 59.5% were calculated to be 0.21, 0.63, and 1.62, respectively. These results show the increase of the concentration of 1,4 units with conversion.

The data in Figures 1 and 2 show that the molecular weight of the polymer is approximately proportional to the yield. It has been suggested that the observed increases in the polymerization rate, in the molecular weight of the polymers, and in the concentration ratio of 1,4 units to 3,4 units, as the reaction proceeds, may be due to an increase of the mobility of the monomer molecule, and this increase results in the rearrangment of the geometry of the monomer crystal lattice to one favorable for 1,4 addition.

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Radiation Chemical Studies of Protein Reactions: Effect of Radiation on the Breaking of Secondary Bonding in Protein

MIZUHO NISIZAWA, *Department of Chemistry, Defense Academy, Yokosuka, Japan*

Synopsis

The effect of radiation on the breaking of secondary bonding in protein was studied by measuring the viscosity change at different radiation doses and urea concentrations. An experimental equation for the viscosity change was obtained, and the observed behavior was explained on the basis of the molecular mechanism. The general equation for the viscosity change is given by $\eta_{\text{red}} = A(X - Be^{-kx}) + C \log R$, where η_{red} is the reduced viscosity of the solution, R is the dose of γ-radiation, X is the concentration of urea, and A, B, C, and k are adjustable constants.

INTRODUCTION

It is well known that many molecules are rendered less stable with respect to the stable form if they are irradiated.[1–3] Since the mechanism of the breaking of secondary bonding in protein is a problem of general interest, it was decided to investigate the effect of radiation on the breaking of secondary bonding in protein. Gelatin was selected as the protein molecule, since it has previously been used in studies of the breaking of secondary bonding in protein.[4] The determination can be followed conveniently by measuring the viscosity change of the solution as a function of radiation dose.[3]

EXPERIMENTAL

Materials

Gelatin and urea used in this work were a commercial materials produced by the Kanto Chemical Co., Inc.

Apparatus and Procedure

An irradiation source containing about 300 Ci ^{60}Co was used. The dose rates in this experiment were 1.0×10^2–1.6×10^4®/hr. The solid gelatin was irradiated in air at room temperature, the irradiated gelatin was dissolved in urea solution, and then the viscosity was measured with the use of Cannon-Fenske Type viscosmeters. The temperature was maintained by a thermostat at 30°C. The results of the viscosity experiments are expressed in terms of the reduced viscosity. Further experimental details were the same as those described in the previous paper.[3]

RESULTS

The changes in reduced viscosity of the gelatin with urea concentration at various radiation doses were studied with a 10% gelatin solution at 30°C. The results are shown in Figure 1.

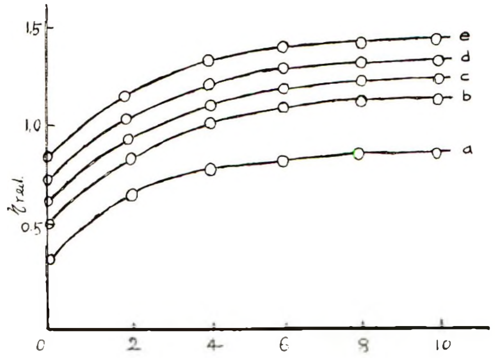

Fig. 1. Reduced viscosity vs. urea concentration for various radiation doses (10% gelatin at 30°C): (*a*) no radiation; (*b*) 10 ®; (*c*) 10^2 ®; (*d*) 10^3 ®; (*e*) 10^4 ®.

From this it is clear that the increase in the reduced viscosity with increasing urea concentration (in molarity) on the linear scale and with increasing radiation dose on the logarithmic scale indicates an accelerating effect of the breaking of secondary bonding in gelatin.

DISCUSSION

As stated above, it is known that many molecules are rendered less stable with respect to the stable form if they are irradiated.[1-3] A discussion of the effect of radiation on the breaking of secondary bonding in protein follows. The viscosity change required for the breaking of secondary bonding is estimated from Figure 1. Thus the relation between the radiation dose and viscosity change is parallel to that between the activation and the breaking of secondary bonding. At constant concentration of gelatin and urea, an increase in the radiation dose results in an increase in the activation required for the breaking of secondary bonds. The reaction mechanism, therefore, depends on the radiation dose. If the main reactions for the breaking of secondary bonds are assumed to be

$$\mathrm{P{-}P} \xrightarrow{h\nu} \mathrm{P^*} + \mathrm{P^*} \tag{1}$$

$$\mathrm{P^*} + \mathrm{U{-}U} \rightarrow \mathrm{P{-}U} + \mathrm{U^*} \tag{2}$$

$$\mathrm{U^*} + \mathrm{U^*} \rightarrow \mathrm{U{-}U} \tag{3}$$

where P—P is the gelatin molecule and U—U is the urea molecule. The activation step may be reaction (1), which means that the observed viscosity change is expressed as a function of radiation dose. Therefore, the response of the gelatin molecule to the radiation dose can be determined by the measuring of the reduced viscosity.

The behavior then, will be treated in terms of a molecular mechanism. In gelatin molecules K^* is the number of activated secondary bonds produced per gram of irradiated gelatin, N is the number of gelatin molecules per gram of irradiated gelatin, M is the number of secondary bonds in irradiated gelatin molecule, R is the radiation dose, and C is an adjustable constant. Then K^* is given by

$$K^* = NM = C \log R \tag{4}$$

Let $(\mathrm{P—P})_{\mathrm{sec}}$ be the number of broken secondary bonds per gram of irradiated gelatin; the breaking rate of secondary bonds $d(\mathrm{P—P})_{\mathrm{sec}}/dx$ will be proportional to the number of secondary bonds M. If the probability of breaking one secondary bond per molecule at unit urea concentration is k_1, one obtains

$$d(\mathrm{P—P})_{\mathrm{sec}}/dx = k_1M \tag{5}$$

As the increase in $(\mathrm{P—P})_{\mathrm{sec}}$ approaches the decrease in M,

$$-dM/dx = k_2M \tag{6}$$

On integrating eq. (6), one obtains

$$M = ae^{-k_2}x + b \tag{7}$$

From eq. (5)

$$M = (1/k_1)\, d(\mathrm{P—P})_{\mathrm{sec}}/dx \tag{8}$$

From eqs. (7) and (8), one obtains

$$d(\mathrm{P—P})_{\mathrm{sec}}/dx = ak_1e^{-k_2x} + bk_1 \tag{9}$$

Now, if the breaking rate of secondary bonds $d(\mathrm{P—P})_{\mathrm{sec}}/dx$ is proportional to the rate of viscosity change η_{red}/dx, one obtains

$$d(\mathrm{P—P})_{\mathrm{sec}}/dx = d\eta_{\mathrm{red}}/dx \tag{10}$$

From eqs. (9) and (10)

$$d\eta_{\mathrm{red}}/dx = ak_1e^{-k_2x} + bk_1 \tag{11}$$

Integration of eq. (11), yields

$$\eta_{\mathrm{red}} = -a(k_1/k_2)e^{-k_2x} + bk_1x + c \tag{12}$$

where c is $C \log R$; otherwise stated eq. (12) becomes

$$\eta_{\mathrm{red}} = A(X - Be^{-kx}) + C \log R \tag{13}$$

where at $R = 0$, $C \log R$ is negligible.

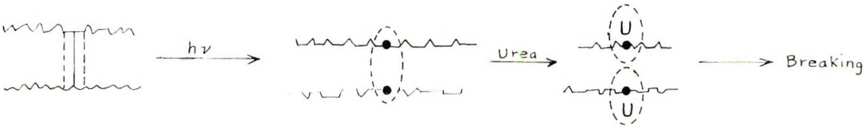

Fig. 2. Mechanism for breaking of secondary bonding in protein.

This formula agrees with the experimental data that describe the curves in Figure 1.

The mechanism considered for the breaking of secondary bonding in protein is shown schematically in Figure 2.

In this mechanism, urea may inhibit the inter- or intramolecular secondary bonding between gelatin molecules.

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Crosslinking Polyferrocenylenes by Polymethylol Compounds

N. BILOW and A. L. LANDIS, *Hughes Aircraft Company, Culver City, California 90230*, and H. ROSENBERG, *Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433*

Synopsis

Polyferrocenylenes with mean molecular weights of 500–4 000 have been converted into thermosetting polymers by reaction with xylylene glycol and telomers thereof. The prepolymers have been used successfully as molding materials and laminating resins. Glass fiber-reinforced laminates have been made with flexural strengths of 63×10^3 psi and flexural moduli of $4–5 \times 10^6$ psi. Ferrocene–xylylene glycol copolymers were also prepared, and 1,1′-bis(hydroxymethyl)ferrocene was used as a polyferrocenylene crosslinking agent. Laminates were also made from the 1,1′-bis(hydroxymethyl)ferrocene-based polymers.

INTRODUCTION

Several years before initiating this research, an extensive investigation of methods for chain extending and crosslinking polyphenylenes was carried out by Bilow and Miller.[1] This earlier research culminated in the development of several polyphenylene cure processes, one of which involved acid-catalyzed crosslinks by polymethylol aromatics such as *p*-xylylene glycol.[2]

The efficacy of crosslinking polyphenylenes and other polyaromatics with xylylene glycol subsequently led to the present study of reactions of quasi-aromatic compounds, namely, ferrocene and polyferrocenylene, with both *p*-xylylene glycol and 1,1′-bis(hydroxymethyl)ferrocene.

Neuse and Trifan[3] have described the synthesis of polyferrocenylene resins from methylol-containing ferrocene intermediates, such as hydroxymethylferrocene, hydroxyethylferrocene and α-hydroxybenzylferrocene. In their work the acid-catalyzed polycondensations which produced the highest molecular weight polymers, i.e., mean molecular weights of 2 500–6 000, were those involving hydroxymethylferrocene. While these polymers could be fractionated to isolate portions having molecular weights of up to 15 000, only low molecular weight polymer ($\bar{M}_n < 3\,000$) was reported to be fusible. Furthermore, whereas strong mineral acid catalysts were reported to produce polymers whose mean molecular weight did not exceed 3 000, catalysts such as zinc chloride and especially aluminum chloride yielded the somewhat higher molecular weight polymer.

DISCUSSION

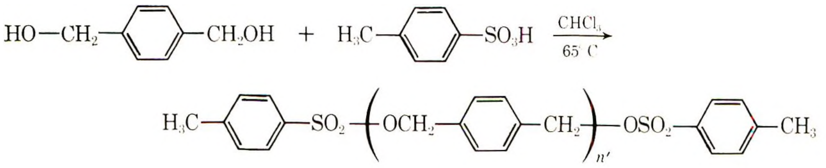
Efforts were directed toward the development of cure processes for ferrocene polymers, the ultimate objective being the synthesis of thermosetting polyferrocenylenes suitable for the fabrication of high strength structural composites. Prior work on ferrocene polymers was limited to the synthesis of new polymer structures; however, none of these had properties which would allow them to be processed into reinforced structures. Generally they were infusible resins or much too low in molecular weight to exhibit desirable physical and mechanical properties. Consequently, ferrocene polymer laminates had previously not been successfully prepared and laminate properties had never been studied.

To achieve the objectives of this investigation, facile polymerizations of ferrocene monomers, capable of producing high molecular weight polymers, were required. Furthermore, catalysts, such as zinc chloride and aluminum chloride used by Neuse,[3] were considered to be undesirable for this application because of the relatively large catalyst concentration required and because they would remain in the thermoset.

Catalysts used in this study included *p*-toluenesulfonic acid, boron trifluoride etherate, and others. The former degrades above 200°C, and consequently vaporizes when the polymer is postcured. In contrast, boron trifluoride is hydrolyzed to innocuous boric oxide or boric acid during cure.

Polymerizations which were studied in the course of this investigation include both copolymerizations of ferrocene with *p*-xylylene glycol or 1,1′-bis(hydroxymethyl)ferrocene, as well as cures of polyferrocenylenes (produced independently by peroxide-catalyzed polymerizations of ferrocene as will be discussed later) with *p*-xylylene glycol, telomeric xylylene glycol, or 1,1′-bis(hydroxymethyl)ferrocene. These reactions are illustrated in eqs. (1)–(5).

With the use of 181-E glass fabric (HITCO, Gardena, California) as a reinforcement with the *p*-xylylene glycol copolymers, laminates having flexural strengths up to 63 000 psi and flexural moduli up to 4.7 × 10⁶ psi



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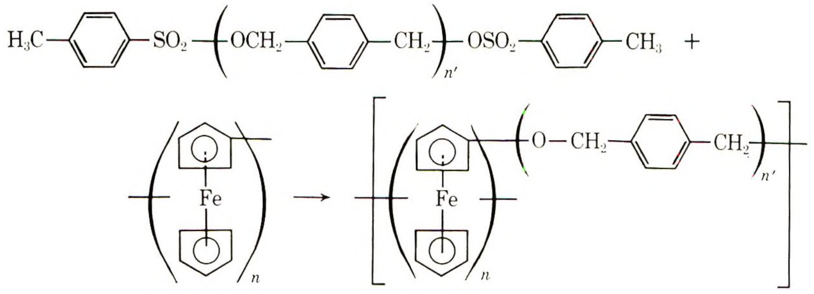

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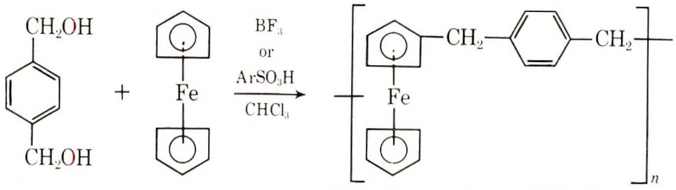
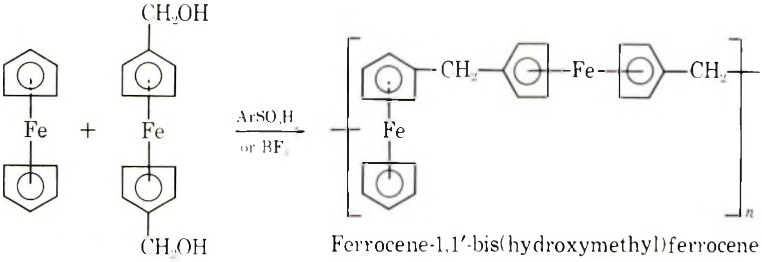


(3)

Ferrocene-*p*-xylylene glycol copolymer



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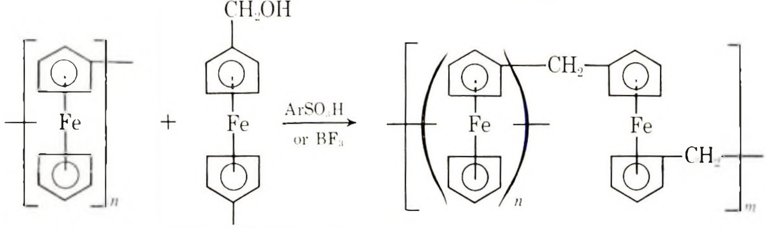
Ferrocene-1,1′-bis(hydroxymethyl)ferrocene copolymer



(5)

1,1′-Bis(hydroxymethyl)ferrocene-cured polyferrocenylene

were obtained. The best physical properties were observed on laminates containing polyferrocenylene cured with the *p*-xylylene glycol telomer. Furthermore, laminates with the best flex strengths were those containing polyferrocenylene prepolymer in the mean molecular weight range of 1 400–1 500.

Polymer content varied between specimens due to the different flow characteristics and wetting characteristics of the prepolymers prior to becoming thermoset. It was, therefore, not possible to produce satisfactory laminates with resin contents as low as 20% when the polyferrocenylene had a mean molecular weight of 2 000 or above prior to cure. Prepolymers in this molecular weight range generally yielded laminates with 30–34% percent cured resin. Similar limitations were observed in studies in which the catalyst concentration was varied. Prepolymers which contained high catalyst concentrations cured too rapidly to allow the preparation of low resin content laminates since excess polymer could not flow out of the laminate before cure. Physical property comparisons made to determine optimum catalyst concentrations thus necessarily were comparisons between laminates of varying resin content. The composition of various *p*-xylylene glycol-cured polyferrocenylenes is shown in Table I; the laminate fabrication parameters and physical properties are shown in Table II.

TABLE I

Composition of *p*-Xylylene Glycol-Cured Polyferrocenylenes

Expt	Polyferrocenylene			Curing agent		Polymer: curing agent	Catalyst		
no.	$\bar{M}_n$	g	mole	g	mole	weight ratio	Type[a]	g	mole
25	1 470	10	0.0068	5.50	0.0400	1.8:1	PTSA	1.93	0.0100
26	186	10	0.054	11.10	0.0800	1:1.1	PTSA	3.85	0.0200
27	2 000	15	0.0075	4.14	0.0300	3.6:1	BTE	0.24	0.0017
28	1 470	10	0.0068	5.52	0.0400	1.8:1	BTE	0.31	0.0022
29	2 000	20	0.010	7.00	0.0510	2.9:1	PTSA	1.00	0.0053
30	1 093[b]	16.4	0.015	8.28	0.0600	2:1	BTE	0.47	0.0033
31	2 000	12	0.0060	3.31	0.0240	3.7:1	PTSA	0.55	0.0290
32	5 300	10	0.0019	2.6	0.0019	4:1	BTE	0.15	0.0010
33	1 140	130	0.114	71.6	0.518	1.8:1	BTE	3.59	0.253

[a] PTSA = *p*-toluenesulfonic acid monohydrate; BTE = boron trifluoride etherate.

[b] 92 wt-% polyferrocenylene (2 000 MW) + 8% ferrocene.

TABLE II

Physical Properties of *p*-Xylylene Glycol-Cured Polyferrocenylene Laminates[a]

Sample no.	Resin content, %	Flex strength, psi × 10^{-3}	Flex modulus, psi × 10^{-6}
25	33	30	3.2
26	28	21	
27	33	36	3.9
28	20	63	4.7
29	31	36	4.0
30	26	53	2.0
31	34	42	3.3
32	33	25	1.3

[a] Specimens molded at 4000 psi and 316°C, reinforced with 181-E glass fabric.

An elemental analysis of a sample of *p*-xylylene glycol-cured polyferrocenylene (exp. 33) gave the following results: C, 67.88%; H, 5.37%; Fe, 20.4% (Theory: C, 70.5%; H, 5.87%; Fe, 20.2%).

The theoretical analysis is based upon a polymer derived from 67.7 wt-% of polyferrocenylene (which contained 65.87% carbon and 5.47% hydrogen), 31.6 wt-% of xylylene glycol pentamer ($C_{40}H_{40}O_4$), and 0.9 wt-% of H_3BO_3 catalyst residue. The observed iron was calculated from ash expressed as FeO.

In addition to promoting crosslinking via telomeric xylylene glycol, crosslinks were also achieved with 1,1′-bis(hydroxymethyl)ferrocene. In these cases the resin content of the laminates ranged from 34 to 45%. Laminates with less than 36% polymer tended to be resin-starved. This was attributed to cure prior to adequate flow of the prepolymer through the reinforcement matrix.

Initially several experiments were carried out in which the 1,1′-bis(hydroxymethyl)ferrocene was copolymerized with ferrocene by using boron trifluoride etherate and *p*-toluenesulfonic acid as the catalysts. In these reactions equimolar amounts of the two comonomers were reacted together in the molten state. In one experiment (no. 23), 8.5 wt-% of *p*-toluenesulfonic acid monohydrate was used as catalyst and the reaction was run at 100°C for 6 min. In a second experiment (no. 24), 5.8 wt-% of the same catalyst was used and the reaction was run at 104°C for 1 hr after the reactants had been slurried in methylene chloride and the product then dried. The latter polymeric product was molded successfully to produce a good, but not excellent quality, glass fiber-reinforced laminate. From these two experiments it was apparent that the prepolymer required polymerization to a lesser extent to achieve better flow characteristics. Shorter reaction periods or lower catalyst concentrations were thus indicated. The tendency was for the 1,1′-bis(hydroxymethyl)ferrocene copolymers to cure too rapidly.

Research on the 1,1′-bis(hydroxymethyl)ferrocene copolymers was terminated to investigate the potential of 1,1′-bis(hydroxymethyl)ferrocene as a curing agent for polyferrocenylene. For these studies solutions of

TABLE III

Composition of Various 1,1′-Bis(hydroxymethyl)ferrocene-Cured Polyferrocenylene Laminates

Experiment no.	Polyferrocenylene		Weight curing agent, g	Catalyst		Quality	Resin content, %
	Weight, g	$\bar{M}_n$		Type[a]	Weight, g		
33	9.0	2 130	3.0	PTSA	0.5	Good	41
34	9.0	2 130	3.0	BTE	0.5	Resin-starved	34
35	9.0	1 290	3.0	PTSA	0.5	Good	36
36	5.0	700	2.5	PTSA	0.2	Good	45

[a] PTSA = *p*-toluenesulfonic acid monohydrate; BTE = boron trifluoride etherate.

polyferrocenylene of various molecular weights were prepared in which 1,1′-bis(hydroxymethyl)ferrocene and the catalyst were dissolved in methylene chloride. The prepolymer solutions were then used as lacquers to coat 181-E glass fabric. Disks, $^3/_4$ in. in diameter, were cut from the fabrics, then stacked and molded at 4 000 psi, initially at 200°C and finally at 316°C. The composition and performance of these resins is shown in Table III.

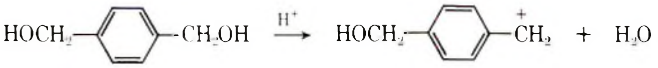
Subsequent efforts were made to prepare a glass reinforced laminate suitable for flexural testing. In this experiment a fraction of polyferrocenylene having a mean molecular weight of 2 020 was used. A 3:1 weight ratio of polymer to curing agent was used along with 1 wt-% of boron trifluoride etherate. The resin did not flow sufficiently well at 600°F and 1 000 psi to yield a satisfactory flexural specimen and due to the lack of additional 1,1′-bis(hydroxymethyl)ferrocene, a second specimen could not be made. Higher pressure, lower catalyst concentration, or lower mean molecular weight prepolymers would be necessary to produce samples suitable for physical tests.

Prior to the discovery that boron trifluoride was an excellent catalyst for the xylylene glycol polymerizations, various experiments were carried out to determine whether acids, such as acetic acid, oxalic acid, trifluoroacetic acid, dichloroacetic acid, or phosphoric acid, were suitable catalysts. Each of these acids was used in various solvents to determine at what temperature, if any, it would be effective.

Solvents used were chloroform, trichloroethylene, tetrachloroethane, chlorobenzene, and in one case a mixture of chlorobenzene with *o*-dichlorobenzene solution. Reactions were run under reflux. Others were carried out in the molten state without solvent. Tetrachloroethane proved to be the worst solvent studied in that it entered into reactions to a major extent. In all cases where this solvent was used the polymer yield was significantly greater than 100%.

In melt polymerizations, with no catalyst (experiment no. 15) or with oxalic acid (experiment no. 16), virtually all of the ferrocene was lost through sublimation, whereas with phosphoric acid only a small portion of the ferrocene sublimed. Reactions catalyzed by *p*-toluenesulfonic acid lost virtually no weight, indicating that all of the ferrocene had reacted.

With a benzylic alcohol such as *p*-xylylene glycol, the formation of carbonium ions is relatively facile in the presence of a strong acid [eq. (6)], and the polymerization undoubtedly proceeds through these intermediates.



(6)

Results of these studies demonstrate that crosslinking polyferrocenylene with *p*-xylylene glycol can be readily achieved provided that boron trifluoride, *p*-toluenesulfonic acid or an equivalent strong Lewis Acid is used as catalyst.

Reactants were melted together, or, when a solvent was used, the stirred slurries were heated at reflux using an azeotropic trap to collect the water

TABLE IV

Data on Ferrocene-p-Xylylene Glycol Copolymerizations

	Catalyst			Solvent					Product						
Expt no.[a]	Type	g	mole	Type	Vol, ml	Reaction time, hr	Reaction temperature, °C	Water collected, ml	Solubility fraction[b]	Weight, g	Mp, °C	Cure temperature, °C	Total, %	Remarks	Naphtha-insoluble portion
1	Trifluoroacetic acid	2.2	0.02	Chloroform	150	24 hr	61	0.3	—	31.5	90–140	—	97	Brown-orange	
2	Acetic acid	1.2	0.02	Chloroform	150	24	61	—	—	32.2	110–150	300?	99	Tan-orange	
3	Acetic acid	1.2	0.02	Trichloroethylene	150	26	87	—	—	31.7	100–140	280?	98	Tan-olive	
4	Acetic acid	1.2	0.02	Tetrachloroethane	150	4	146	4.5	S I	37.0	>400	—	114	Black	
5	Acetic acid	1.2	0.02	Tetrachloroethane	150	7/6	146	3.4	S	26.5	—	150	82	Black	
									I	16.0	—	—	49	Black	
													131		
6	—	—	—	Tetrachloroethane	150	1/2	146	—	S	26.0	Tar	170	80	Black	
									I	7.5	—	—	23	Black	
													103		
7	—	—	—	Trichloroethylene	150	18	87	0.5	—	33	105–150	300?	101	Tan-orange	13.8 g
8	p-Toluenesulfonic acid	3.8	0.02	Chloroform	150	18	61	1.2	—	29	100–150	180	90	Orange-brown	16. g
9	—	—	—	Chlorobenzene	150	4	132	1.5	S	17	145–160	—	52	Orange	0.15 g
									I	12.8	105	—	40	Gray	
													92		
10	—	—	—	Trichloroethylene	150	54	87	—	S	16.0	—	—		Orange	Mp >400°C, 0.1 g
									I	13.2	107	—		Gray	

11	—	—	—	Tetrachloro-ethylene	150	24	121	—	S	14.4	—	—		Orange	Mp 130–190°C, 0.2 g
									I	14.2	103	—		Gray	
12	Trifluoro-acetic acid	2.3	0.02	Trichloroethylene	150	26	87	0.3	S	17.2	—	—		Orange	Mp 104–170°C, 1.0 g
									I	11.1	103	—		Gray	
13	Dichloro-acetic acid	2.6	0.02	Trichloroethylene	150	26	87	—	S	16.3	—	—		Orange	Mp 30–70°C, (Tar), 0.4 g
									I	14.3	105	—		Gray	
14	—	—	—	*o*-Dichlorobenzene Chlorobenzene	43 107	6.5	140	—		31.0	107–150	—		Melt in two phases (orange)	
15	—	—	—	Hot melt, 140–155°C		7	140–155	—		15.0	105	—		Black	
16	Oxalic acid	2.2	0.024 (11%)	Hot melt 140–155°C		5	140–155	—		14.7	Tar	—	55	Black	
17	Phosphoric acid	0.98	0.01 (4.8%)	Hot melt, 140–155°C		6	140–155	—		21.7**	55–85	250 Rubbery	69	c	
18	*p*-Toluene-sulfonic acid	1.9	0.01 (4.8%)	Hot melt, 70–85°C		6.5	70–85	—		31.8	40–90	175	93	Olive paste	
19	*p*-Toluene-sulfonic acid	1.9	0.01 (4.8%)	Chloroform	100	43	61	1.6		32.4	70–100	170	94	Orange tan	
20	Boron trifluoride	0.5	0.0035 (1.8%)	Methylene Chloride	100	6 1.5	40 130								
21	*p*-Toluene-sulfonic acid	2.0		Chloroform	100	4	61					30 sec at 200			
22	*p*-Toluene-sulfonic acid	1.3		Chloroform	100	2	61					30 sec at 200			

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[a] All reactions used 13.8 g *p*-xylylene glycol (0.1 mole) and 18.6 g ferrocene (0.1 mole) except experiments 21 and 22, which used 10 g of ferrocene and 5 g or 3.3 g of *p*-xylylene glycol respectively.

[b] S = soluble; I = insoluble.

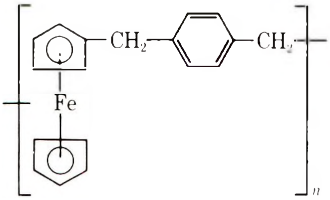
[c] About 1/3 of product was lost through spillage.

formed during the reactions. Products were isolated either by filtering off the insoluble portion and evaporating the solvent from the soluble portion, or were collected by evaporating off the solvent from the total reaction mixture. Pulverized reaction products were used for molding studies.

After demonstrating the need for a relatively strong acid catalyst several thermosetting copolymers of ferrocene and *p*-xylylene glycol were synthesized, molded, and analyzed. Equimolar mixtures of the monomers were catalyzed by *p*-toluenesulfonic acid monohydrate under various conditions, and by boron trifluoride (1.7 mole-%) at 130°C for 1.5 hr (experiment no. 20). Boron trifluoride etherate was most effective, and cured polymer made with this catalyst, when pulverized and extracted exhaustively with benzene, showed no weight loss.

In one set of experiments, four copolymerizations were carried out using *p*-toluenesulfonic acid as the catalyst. In experiment no. 18, 5 mole-% catalyst was used, and the reaction was carried out in the melt phase at 78°C for 6.5 hr. Elemental analysis of the cured molded resin gave the following results: C, 73.32%; H, 5.77%; Fe, 14.50%* (theoretical: C, 75.02%; H, 5.60%; Fe 19.38%).

These analytical results indicate that the polymer has predominantly the structure I, although the low iron content indicates that somewhat more than one mole of xylylene glycol is present per ferrocene moiety.



I

Based on the results of these studies, it is obvious that ferrocene-*p*-xylylene glycol copolymerizations and the cross linking of polyferrocenylene with *p*-xylylene glycol can be carried out successfully. In melt polymerizations the best catalysts were *p*-toluenesulfonic acid and boron trifluoride. Other acid catalysts such as phosphoric acid were less effective. Melt polymerizations have yielded polymers with excellent molding characteristics and elemental analyses have indicated that these polymers have somewhat more than one xylylene glycol moiety per ferrocene moiety. Solution polymerizations proceed well with *p*-toluenesulfonic acid or boron trifluoride, but the weaker acids, such as acetic acid, chloroacetic acid, and phosphoric acid, were not effective. A summary of reaction conditions and other data are shown in Table IV.

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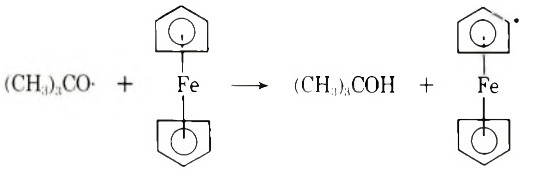
* Atomic absorption analysis used on digested polymer tended to be about 2–2½% low, and thus actual iron content is probably ca. 17%. Low results were also obtained on standard samples.

POLYFERROCENYLENE SYNTHESIS

Polyferrocenylene used in the crosslinking studies described in this work was synthesized by the reaction method of Rosenberg and Neuse,[4] and Korshak et al.[5] Theoretically, this reaction leads to polymeric material via the poly-recombination of ferrocene radicals generated by the thermal decomposition of di-*tert*-butyl peroxide in the presence of ferrocene. The initial step in the reaction involves scission of the oxygen–oxygen bond of the peroxide.

$$(CH_3)_3\,C\text{-}O\text{-}O\text{-}C(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot \qquad (7)$$

These *tert*-butoxy radicals then presumably abstract hydrogen atoms from the ferrocene molecules as shown in eq. (8).

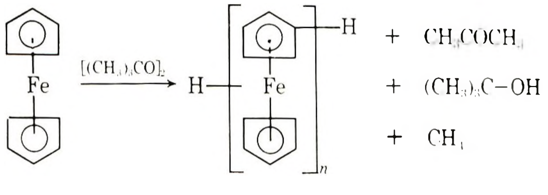


(8)

Besides hydrogen abstractions of this type, dissociation of the *tert*-butoxy radicals also occurs to produce acetone and free methyl radicals:

$$(CH_3)_3CO\cdot \rightarrow CH_3COCH_3 + CH_3\cdot \qquad (9)$$

The resulting methyl radicals may then abstract hydrogen atoms, add to unsaturated bonds, or associate with other radicals. Thus, the poly-recombination reaction of ferrocene can be summarized by eq. (10).



(10)

In actual practice, this reaction is somewhat difficult to carry out. The half-life of the free radicals produced by the thermal decomposition of di-*tert*-butyl peroxide (DTBP) at 200–210°C is quite short. At 145°C it is reported to be 1.3 hr, whereas at 155° it is 0.44 hr. On the basis of these data, it probably would be several seconds at 205 ± 5°C, at which temperature the reactions were run. Because of these competitive side reactions, the polyrecombination reactions are relatively inefficient.

It was found that the yield of fusible polymer was highly unsatisfactory when the di-*tert*-butyl peroxide was introduced just below the surface of the ferrocene. Furthermore, since the ferrocene continuously sublimed during the course of reaction, the level of the molten ferrocene decreased in the reaction chamber and this soon exposed the end of the tube through which the peroxide was being introduced. Oxygen also severely affects the yields so

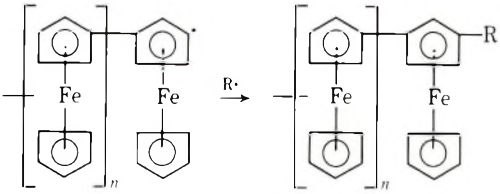
TABLE V
Analyses of Various Polyferrocenylenes

Fraction	Sample number D1510-	C, %	H, %	Fe, %	Ash, %[a]	$\bar{M}_n$	Yield, g	Yield based on peroxide, %	Calculated empirical formula
Precipitated from benzene–isopropyl alcohol	3-1	65.46	5.47		6.40				$C_{10.5}H_{10.5}Fe_{1.0}$
	6-1	66.06	5.44		7.20				$C_{10.8}H_{10.6}Fe_{1.0}$
	12-2	66.69	5.49			3374	4.4	5.8	
	21-1	62.98	5.36	21.59		3900	6.7	5.9	
	22-2	63.57	5.46	21.71 28.20		4030	7.4	6.5	
	39-1						45.2	7.7	
Soluble in benzene-isopropyl alcohol	8-3	66.01	5.52		11.43	240			$C_{10.8}H_{10.6}Fe_{1.0}$
	12-3	64.67	5.45			380	2.7	3.5	
	21-2	65.27	5.88			435	3.0	2.6	
	22-2	64.88	5.88			915	2.5	2.2	
	39-2						11.8	2.0	
Theoretical		64.91	4.90	30.19		370			$(C_{10}H_9Fe)_2$
		65.27	4.38	30.35		∞			$(C_{10}H_8Fe)_n$
		66.71	5.09	28.20		∞			$(C_{11}H_{10}Fe)_n$
		67.96	5.66	26.33		∞			$(C_{12}H_{12}Fe)_n$

[a] Attempts to use ash content as a means of determining iron content appeared to be highly erroneous for uncured polymers. However, such analyses appear to be quite satisfactory for cured polyferrocenes.

that provision must be made to exclude it from the reaction chamber. The best conditions for the polyrecombination reaction were found in experiments in which provision was made to keep the peroxide inlet tube immersed at a constant level in the reaction mixture. From practical considerations one can find an optimum depth of introduction of peroxide into the molten ferrocene to give the maximum yields of soluble polyferrocenylene. It was evident that up to a point (up to $^1/_3$–$^1/_2$ of the depth) the deeper the submersion, the higher the yield of fusible polymer. This has not been reported by Rosenberg and Neuse, and consequently we were unaware of it and used shallow submersion in our earliest experiments. This resulted in yields of less than 5%.

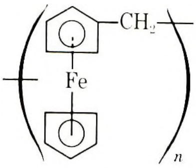
Advantages gained by deep submersion of the peroxide addition tube inlet, however, may be overshadowed by other factors. For example, the increased yield observed was in part due to the formation of an increased amount of alkylated polymer. Such polymers may arise from various free radical chain terminating steps such as the one illustrated in eq. (11),



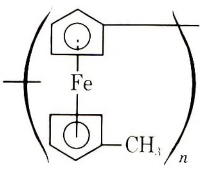
(11)

where R = CH_3 or $(CH_3)_3C\text{-}O$.

From the analyses shown in Table V it is evident that these polymers are partially alkylated and contain one or more methylene groups per ferrocene unit. Thus their structures correspond more closely to either II or III.



II



III

A schematic of the reaction apparatus used in these polymerizations is shown in Figure 1.

Approximately 65 to 70 subsequent polymerizations were carried out and the crude reaction products were mixed together into several groups prior to work up. The clean-up procedure in these cases involved an initial exhaustive pentane extraction using Soxhlet extractors. Pentane-insoluble fractions were then dissolved in benzene and filtered to remove the insoluble portion. Benzene-soluble portions were collected and used in the various cross linking studies. Generally about 80–85% of the ferrocene (and polymer thereof) remained in the reactors, provided that sublimate was constantly pushed back. The useful benzene-soluble, pentane-insoluble

TABLE VI
Data on Polyferrocenylene Preparations Involving Pentane–Benzene Fractionation

Expt. no	$\bar{M}_n$	C, %	H, %	Number of Runs	Ferrocene, g	DTBP, g[a]	Total polymer yield, %[b]	Polymer yield (insoluble in benzene), %	Polymer yield (soluble in benzene), %[c]	Melting range, °C
7	1 290	67.24	5.45	4	540	540	18	0.4	17.6	150–190
8	1 880	67.21	5.51	4	540	540	19	0.4	18.6	145–175
9	560	—	—	5	750	750	29	1.3	27.7	145–180
10	2 000	—	—	11	1 370	1 370	19	1.3	17.7	145–180
11	1 510	67.43	5.69	11	1 375	1 375	13	0.8	12.2	141–190
12	870			10	1 250	1 250	11	1.0	10	
13	1 050			4	1 125	1 125	17	2.0	15	
14a	2 130			4	540	460	11	2.2	8.4	
14b	700									
15a	2 000	65.42	5.63	11	1 650	1 650	12	1.0	11	
15b[d]	1 470								(5.3)	
15c[d]	5 300								(4.7)	

[a] From subfractionation of pentane-insoluble polymer using one part polymer in four volumes benzene and precipitating with 20 volumes of isopropyl alcohol.

[b] Yield based on total ferrocene used.

[c] After an exhaustive pentane extraction.

[d] From subfractionation of 15a using one part polymer in three volumes benzene and precipitating with equal volume of pentane.

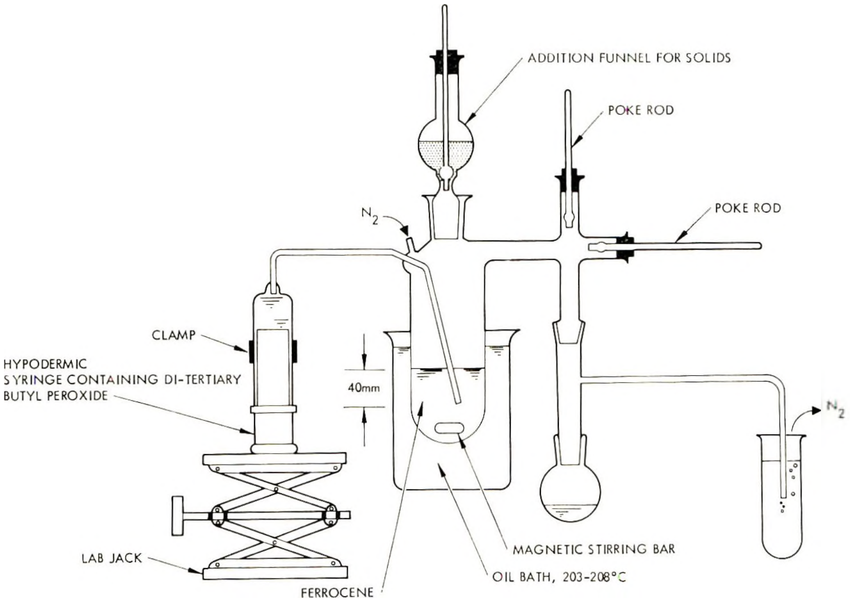


Fig. 1. Apparatus for maintaining constant liquid volume in ferrocene polymerizations.

polymers generally had a mean molecular weight of about 1 500 ± 500. Subfractionation of this material could be achieved readily with benzene-pentane mixtures or benzene-propanol mixtures when desired and, in one case, a fraction having a mean molecular weight of 5 300 was isolated in this manner. Data on these polymerizations are presented in Table VI.

EXPERIMENTAL

Polyferrocenylene

One mole of ferrocene was melted at 200 ± 5°C, and an equal weight of di-*tert*-butyl peroxide was added very slowly through a liquid addition tube immersed to a depth of 75–100 mm below the surface of the ferrocene. The addition required about 3 hr, during which time stirring was continuous. Subliming ferrocene was pushed back regularly into the reactor with appropriate plungers while liquid volatiles were trapped in a reservoir. The reaction was conducted under argon to avoid potential explosions and avoid reactions with oxygen. Upon completion of the addition the reaction mixture was cooled and the product exhaustively extracted with pentane in a Soxhlet extractor. The pentane-insoluble polymer was then dissolved in benzene and the solution was filtered. Upon evaporation of this solution the polymer was recovered. This material generally had a mean molecular weight ($\bar{M}_n$) of 1 600 ± 400, depending upon the efficiency of the exhaustive pentane extraction. Yields of benzene-soluble, pentane-insoluble polymer were generally 15 ± 3% based on the total ferrocene used. The benzene-insoluble fractions were obtained in yields of 0.4–2.0%. Yields calculated on the basis of the ferrocene which had been kept from subliming out of the reactor were 19 ± 4% and 0.5–2.5%, respectively. Melting points of the benzene-soluble polymer generally were in the range of 160 ± 30°C with a 30–40°C spread.

Ferrocene–*p*-Xylylene Glycol Copolymer (Experiment 26)

A copolymer of ferrocene and *p*-xylylene glycol was prepared by heating at reflux a solution containing ferrocene (10.0 g) and *p*-xylylene glycol–*p*-toluenesulfonic acid telomer (equivalent to 11.1 g of *p*-xylylene glycol) in chloroform for 1 hr. The total weight of the solution was 156 g. The *p*-xylylene glycol–*p*-toluenesulfonic acid telomer was prepared by refluxing *p*-xylylene glycol (30 g) and *p*-toluenesulfonic acid monohydrate (10.4 g) in 250 ml of chloroform for 18 hr while removing the water formed (ca 4 ml) with a water trap. Only part of this solution was used in the copolymerization with ferrocene.

Polyferrocenylene–*p*-Xylylene Glycol Copolymer Obtained with *p*-Toluenesulfonic Acid as a Catalyst

Experiment 29. A copolymer of polyferrocenylene and *p*-xylylene glycol was prepared by refluxing for 24 hr a mixture of polyferrocenylene (D1510-57-A, $\bar{M}_n$ 560, 20 g or 0.036 mole), *p*-xylylene glycol (7.0 g, 0.051 mole), *p*-toluenesulfonic acid monohydrate (1.0 g, 0.0059 mole), chloroform (100 ml), and chlorobenzene (100 ml). Approximately 1 ml of water was isolated from the reaction mixture by azeotropic distillation. At the end of the reaction the lacquer was free of insoluble material.

Experiment 25. A copolymer of polyferrocenylene ($\bar{M}_n$ 1470, 10.0 g) and a *p*-xylylene glycol–*p*-toluenesulfonic acid telomer in chloroform (containing 5.5 g of *p*-xylylene glycol as the telomer) was heated at reflux for 30 min. A small amount of chloroform was added to aid dissolution giving a total solution weight of 126 g. The *p*-xylylene glycol telomer was prepared by heating at reflux a mixture of *p*-xylylene glycol (30 g), *p*-toluenesulfonic acid monohydrate (10.4 g), and chloroform(250 ml) for 18 hr. During this period approximately 4 ml of water was obtained. Only a portion of the xylylene glycol telomer was used.

Polyferrocenylene–*p*-Xylylene Glycol Copolymer Obtained with Boron Trifluoride Etherate as a Catalyst

Experiment 27. A mixture of polyferrocenylene ($\bar{M}_n$ 2 000, 15.0 g) and *p*-xylylene glycol–boron trifluoride telomer (55.9 g of solution containing 4.14 g of *p*-xylylene glycol and 0.24 g of boron trifluoride etherate in 30 ml of chloroform) was heated at reflux for 2 hr. The lacquer was clear at the end of this period.

The xylylene glycol telomer was prepared by heating at reflux a mixture of *p*-xylylene glycol (20 grams), boron trifluoride etherate (1 ml), methylene chloride (26 ml) and chlorobenzene (150 ml) while removing water in an azeotropic trap. The reaction took about 1 to 1½ hour at 82°C. The clear hot solution was concentrated in vacuum to a solid which was redissolved in chloroform (200 ml). Portions of the xylylene glycol telomer were used in experiments 27 and 28.

Experiment 28. A mixture of polyferrocenylene ($\bar{M}_n$ 1 470, 10.0 g) and *p*-xylylene glycol–boron trifluoride telomer (prepared in experiment 27, $\bar{M}_n$ 1 470, 90.4 g of solution containing 5.52 g of *p*-xylylene glycol and 0.31 g boron trifluoride etherate) was heated at reflux for 1 hr to yield a clear solution.

Experiment 32. A solution of polyferrocenylene ($\bar{M}_n$ 5 300, 10 g) in chloroform (50 ml) was mixed with a chloroform solution of xylylene glycol telomer (21 g). The latter was prepared from 2.6 g *p*-xylylene glycol, 0.13 ml of boron trifluoride etherate, methylene chloride (3.3 ml), and chlorobenzene (19 ml) by heating the slurry at reflux for 45 min while removing water by azeotropic distillation, taking the solution to dryness, and redissolving the solids in chloroform (13 ml). The mixture of polyferrocenylene and telomer solution was heated at reflux for 1 hr to provide 100 g of lacquer.

Ferrocene–1,1′-Bis(hydroxymethyl)ferrocene Copolymerizations

Experiment 23. 1,1′-Bis(hydroxymethyl)ferrocene (3.7 g, 0.015 mole), ferrocene (2.8 g, 0.015 mole), and *p*-toluenesulfonic acid monohydrate (0.6 g) were ground together and advanced in an oil bath at 100°C. A virtually intractable polymer was formed in only 6 min. The yield was 6.7 g.

Experiment 24. 1,1′-Bis(hydroxymethyl)ferrocene (3.7 g), ferrocene (2.8 g), and *p*-toluenesulfonic acid monohydrate (0.4 g) were slurried in methylene chloride for 1 hr. The mixture was then evaporated to dryness and the reactants were heated at 80°C for 30 min. Since melting had not occurred, the mixture then was heated to 104°C for 1 hr. The resulting product appeared virtually intractable but was moldable under heat and pressure. It produced a very respectable, but not excellent part. A lesser degree of reaction is indicated for subsequent runs.

Experiment 33. *p*-Xylylene glycol (71.6 g), boron trifluoride etherate (3.6 ml), methylene chloride (113 ml), and chlorobenzene (538 ml) were heated at reflux for 2 hr while maintaining the reaction temperature at 80°C. Evolved water was collected by azeotropic distillation. Solvent was removed from the reaction mixture by reduced pressure distillation at 70°C, and the residual solids were redissolved in chloroform (1 000 ml). To this solution was added polyferrocenylene (130 g, $\bar{M}_n$ 1 140, 65.87% carbon, 5.47% hydrogen) and the solution was heated at reflux for 1 hr.

The polymer solution was subsequently used to prepare glass-reinforced laminates by coating pieces of glass fabric; then after drying, molding multilayered stacks of coated fabric at 200°C and 1 000–4 000 psi.

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NOTES

Bubble Formation in Radiation-Induced Grafting of Styrene to Polyethylene

Several laboratories have reported on the formation of bubbles in the radiation-induced grafting of styrene to polyethylene film from the viewpoint of the heterogeneity of the grafting reaction.[1-4] In general, it is found that the grafted film obtained by post-irradiation immersion in styrene is apparently homogeneous, while that obtained by simultaneous irradiation of film and monomer contains bubbles, some of which contain occluded homopolymer.

The purpose of this paper is to present some information on bubble formation in polyethylene film grafted with styrene by the simultaneous irradiation technique. Just after the irradiation no bubbles were observed in the film, and even under examination by optical microscopy it appeared to be homogeneous. After prolonged soaking in benzene, however, bubbles appeared and were observed to grow in size and number with increasing soaking time until the bubbles overlapped and coalesced.

EXPERIMENTAL

DuPont low-density polyethylene film, 0.066 mm thick, was used. Commercial grade styrene was washed three times with an aqueous solution and sodium hydroxide, three times with water to remove inhibitor, and dried over calcium chloride and then calcium hydride. It was then distilled over calcium hydride at 35°C under reduced pressure.

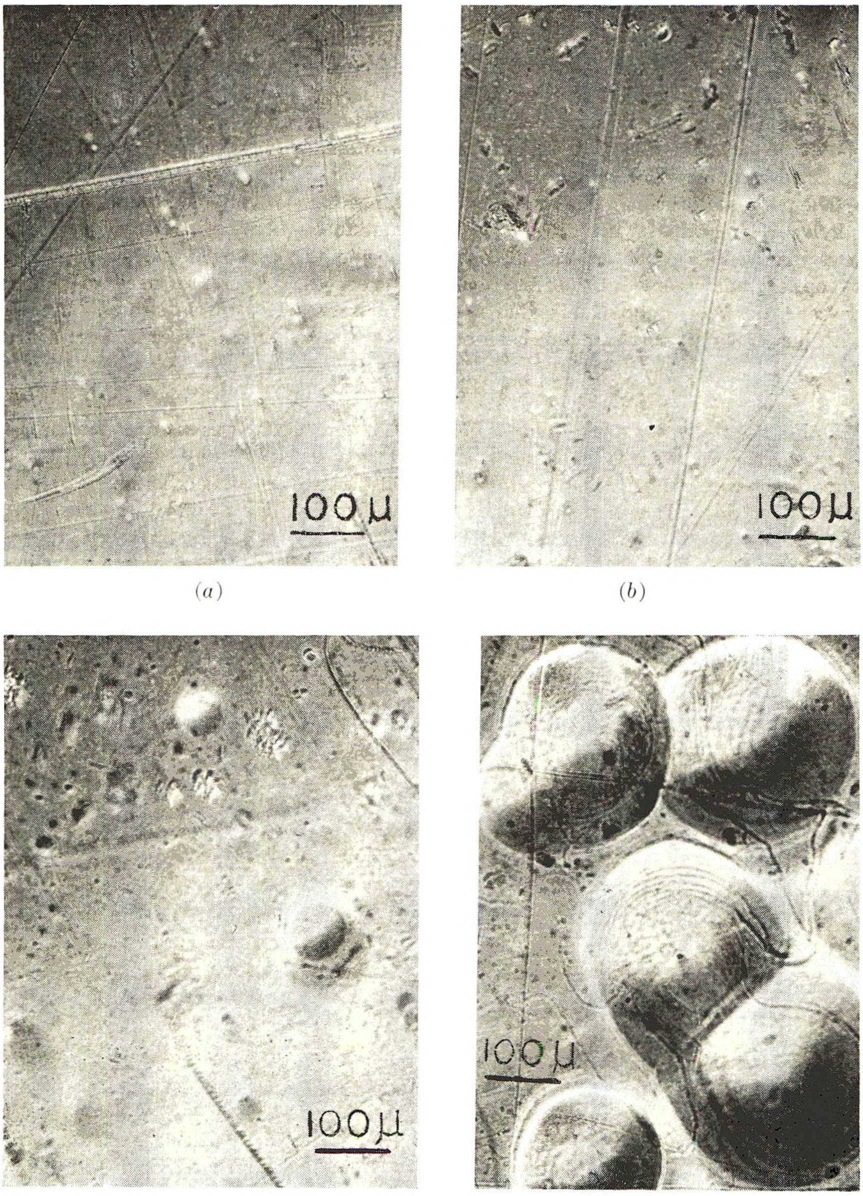
Strips of the polyethylene film, 8 mm × 60 mm in size, were immersed in styrene in a glass tube. The styrene was degassed by four cycles of freezing and melting under high vacuum. The samples were then sealed off from the vacuum manifold at a pressure of 10^{-5} torr. Before irradiation the samples were kept at 5°C for 12 hr and at room temperature for 3 hr. Irradiations were carried out in the ^{60}Co source of University of Maryland. The tube was opened within 20 min after removal from the source. Each strip of film was soaked in benzene for a selected time interval and vacuum-dried. The strip was then examined under an optical microscope. The per cent weight gain of the strip was determined from the weight of the dried film before irradiation and after the soaking.

For some film samples, occluded homopolymer of styrene was separated from the true graft and the polyethylene by the following method. A grafted polyethylene film was dissolved completely in xylene at 100°C. The solution was then poured slowly into large quantities of methanol thereby producing a fine fluffy precipitate. The precipitate was soaked in benzene and filtered to extract the polystyrene. Both infrared and carbon-hydrogen analyses showed that the extract was polystyrene only.

RESULTS AND DISCUSSION

Figure 1 shows the microscopic changes in polyethylene film caused by irradiation of the film in styrene monomer followed by a soaking in benzene. Figure 1*a* is a photomicrograph of the original unirradiated polyethylene. Figure 1*b* is a photomicrograph of the film just after irradiation in styrene for 5 hr at an absorbed dose rate of 1.00 × 10^5 rad/hr. It should be noted there is no significant difference between Figures 1*a* and 1*b* even though the weight gain of the film on soaking is 51%. One interesting observation is that the grafted film (Fig. 1*b*) is more milky in appearance and slightly less transparent than the untreated film. Since no bubbles formed, the film just after irradiation is considered to be homogeneous.

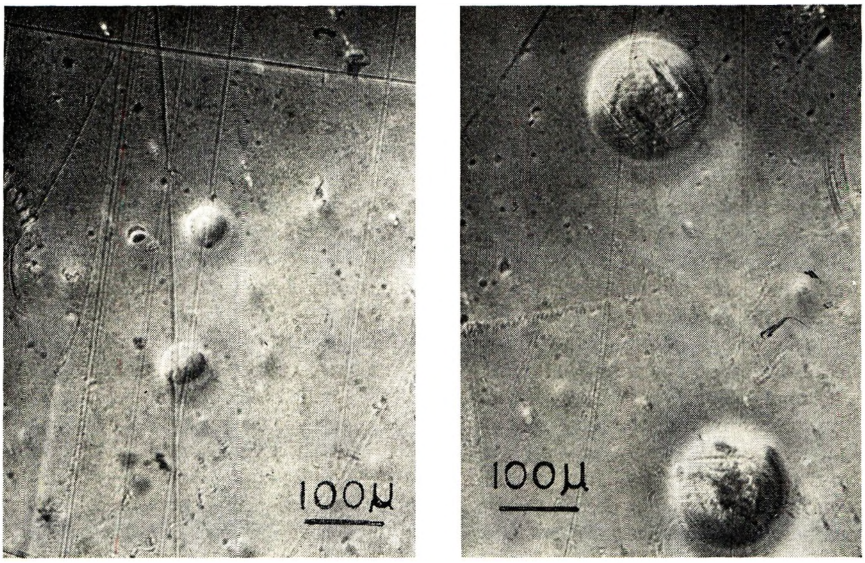
The first clear sign of bubble formation is observed in Figure 1*c*, which is a photomicrograph of the film soaked for 10.8 hr; at this stage, the population and the bubble size are quite small. Examination of Figures 1*c* and 1*d* shows that the number and the size of the bubbles increase with increasing soaking time in benzene. In Figure 1*d*, combination of bubbles is observed. Bubbles grow to as large as 300 microns in diameter, which is much larger than the original film thickness. In addition, on comparing



(*a*) (*b*)

(*c*) (*d*)

Fig. 1 (*continued*)



(e) (f)

Fig. 1. Phase contrast photomicrographs of films: (*a*) unirradiated PE film; (*b*) 10^5 rad/hr for 5 hr, 51% apparent graft, 5 min soaking; (*c*) 10^5 rad/hr for 5 hr, 42% apparent graft, 10.8 hr soaking; (*d*) 10^5 rad/hr for 5 hr, 31% apparent graft, 181 hr soaking; (*e*) 10^4 rad/hr for 5 hr, 27% apparent graft, 136 hr soaking; (*f*) 3×10^4 rad/hr for 5 hr, 28% apparent graft, 144 hr soaking.

Figure 1*d* with 1*e* and 1*f*, it can be seen that the size and number of bubbles decrease very rapidly with decreasing dose rate.

Curves showing the apparent graft as it decreases with soaking time are presented in Figure 2. They summarize data for films irradiated at 1.00×10^5 rad/hr for 5 hr (film A) and for 1.00×10^4 rad/hr for 5 hr (film B). The region where significant bubble formation was first observed is marked with an arrow. Bubble formation is observed

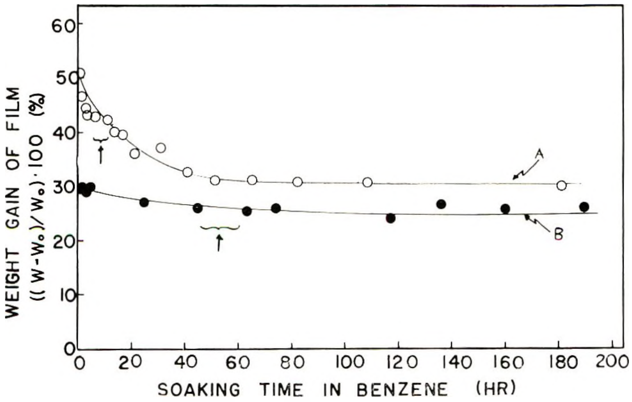


Fig. 2. Weight decrease of grafted polyethylene by soaking in benzene at room temperature. (*A*) irradiated at 10^5 rad/hr at 22°C for 5 hr; (*B*) irradiated at 10^4 rad/hr at 22°C for 5 hr. Arrows indicate the start of bubble formation.

much earlier with the high dose rate samples. The apparent graft on the films with 51 and 30% weight gain before soaking decreases to the almost constant values of 30 and 26%, respectively. The size and number of bubbles increase with the amount of polystyrene that is extractable with prolonged soaking.

The extraction data from the grafted films that were converted to fluff show that the removal of the occluded polystyrene is not achieved even by prolonged extraction; this has been observed in other works.[4-6] The values of per cent weight gain of covalently grafted polyethylene for films A and B are found by this method to be 15.1 and 14.6%, respectively. The ratio of covalent grafting to final apparent grafting are 50.3 and 58.4%; these values are comparable to those obtained by Chen et al.[5] and Matsuda et al.,[5] who analyzed similar samples by dissolution in hot xylene and centrifugal separation at room temperature.

The mechanism of bubble growth can be explained in part. The slight milky appearance of the low dose rate sample (film B) and the more milky appearance of the high dose rate sample (film A) prior to extraction suggests that microcells of occluded ungrafted polystyrene are formed in increasing amounts with increasing dose rate. The occluded homopolymer initially present in film A (51–15 = 36%) is higher than that found in film B (30–15 = 15%). The more rapid growth of bubbles in film A may be due to the formation at the higher dose rate of a greater concentration of microcells containing homopolymer with a shorter chain length. Soaking in benzene permits the polystyrene to diffuse more readily through the film. This effect permits the more rapid coalescence of microcells into increasingly larger bubbles, and also permits a greater rate of homopolymer removal from the film.

The kinetics of microcell formation and buildup of homopolymer in the film during irradiation are more difficult to explain on the basis of our preliminary data. We offer without further comment the interesting observation that our data for the rate of initial homopolymer buildup fit a dose rate dependence of 0.5, while the covalent graft rate is independent of dose rate.

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Sueo Machi*
Joseph Silverman

Laboratory of Radiation and Polymer Science
Department of Chemical Engineering

University of Maryland
College Park, Maryland 20742

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* Permanent address: Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Japan.

Copolymerization of Di(2-cyanoethyl) Fumarate with Several Monomers

We have studied the preparation and chemical reactivity of di(2-cyanoethyl) fumarate (CEF). There is no record in the literature of its reactivity ratios with other monomers. One short patent citation[1] mentions its preparation in low yield. No proper characterization is given.

We have now prepared CEF in 98–100% yield by esterifying fumaric acid and hydracrylonitrile with sulfuric acid catalyst. The samples were identified by comparison with authentic samples prepared by various routes i.e., condensation of the silver salt of fumaric acid with iodopropionitrile and condensation of fumaryl chloride with hydracrylonitrile. The three samples were identified as CEF by analysis (Table I) and infrared spectra which showed no hydroxyl band, but a clear nitrile band at 4.5 μ and carbonyl band at 5.9 μ. The NMR spectrum of sample 2 (Table II), which showed the proper ratio of peak areas for the olefinic and ethylenic hydrogens, gave further evidence to support characterization.

TABLE I
Analysis of Di(2-cyanoethyl) Fumarate Samples

Sample No.	Preparation	Analyses C, %	H, %	N, %	O, %	Melting point, °C
1	Acid + alcohol	54.26	4.58	12.34	28.99	86–87[a]
2	Silver salt + alkyl iodide	54.07	4.81	12.56	28.56	86
3	Acid chloride + alcohol	53.98	4.24	12.47	29.35	86–87
Theory	—	54.05	4.51	12.62	28.82	

[a] Mixed melting point 86–87°C.

TABLE II
NMR Analysis of Di(2-cyanoethyl)Fumarate

σ-value	Peak area ratio	Theoretical ratio	Remarks
3.07 (s)	1.00	1	H *trans*-olefinic
5.51 (t)	1.90	2	CH_2
7.04 (t)	1.93	2	CH_2

We have copolymerized CEF with butyl acrylate, ethyl acrylate, styrene, and vinyl acetate. The reactions were carried out in bulk in evacuated sealed tubes at 90°C and in the presence of di-*tert*-butyl diperphthalate initiator. Reactivity ratios were computed by the curve-fitting method.[2] The results are summarized in Table III. *Q–e* values for CEF were computed from each set of experimental reactivity ratios except for those from the ethyl acrylate experiment. They are in good agreement with each other, and we can report an average value for $Q = 0.80$ and $e = 2.42$. This is shown in the last column of Table III, where the theoretical reactivity ratios calculated with the above *Q–e* values fall within the limits of the experimental data. The large deviation of the ethyl acrylate–CEF pair, however, is disturbing, although a similar observation has been made by Grassie et al.[3] in their studies of the copolymerization of acrylates and methacrylates. Their ethyl acrylate–methyl methacrylate system also showed much larger than theoretical reactivity ratios.

TABLE III
Reactivity Ratios of CEF and Different Monomers[a]

Monomer pair	Experimental		*Q–e* values	
	r_1	r_2	r_1	r_2
Butyl acrylate–CEF	2.65 ± 0.35	0.03	2.64	0.056
Ethyl acrylate–CEF	8.3 ± 0.5	0.03 ± 0.01	1.04	0.008
Styrene–CEF	0.15 ± 0.05	0 ± 0.0005	0.1	0.0004
Vinyl acetate–CEF	0.02 ± 0.02	0.02 ± 0.01	0.02	0.03

Finally, Table IV compares our results with those of analogous pairs which have been reported in the literature. Although the number of similar systems is very limited, it is gratifying to observe that our data are in general agreement with the values of other fumarates.

TABLE IV
Comparison of Experimental Reactivity Ratios with Those of Analogous Pairs as Reported in the Literature

Monomer pair	r_1	r_2	Reaction temperature, °C	Ref.
Styrene–CEF	0.15 ± 0.05	0 ± 0.0005	90	This work
Styrene–Diethyl fumarate	0.3 ± 0.02	0.07 ± 0.007	60	4
Styrene–Dimethyl fumarate	0.21 ± 0.02	0.025 ± 0.015	60	5
Vinyl acetate–CEF	0.02 ± 0.02	0.02 ± 0.01	90	This work
Vinyl acetate–diethyl fumarate	0.011 ± 0.001	0.444 ± 0.003	60	5

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V. Arendt
S. Kaizerman

American Cyanamid Company
Organic Chemicals Division, Rubber Chemicals
Bound Brook, New Jersey

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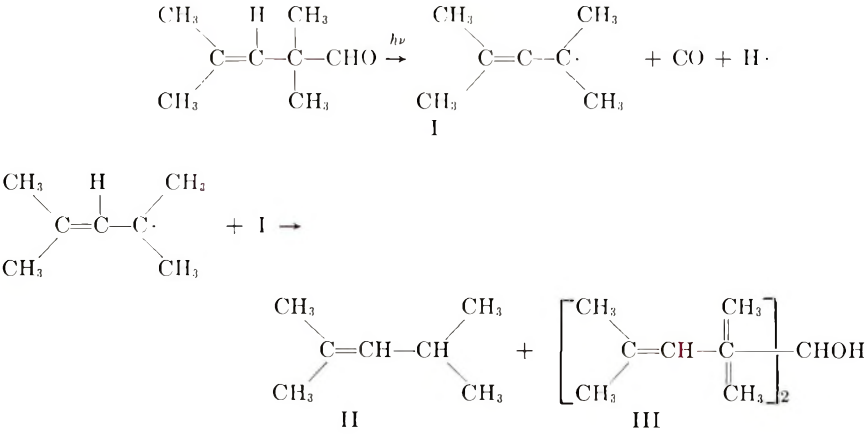
Photochemical Reaction of a Homoallylic Aldehyde

The homoallylic aldehyde, 2,2,4-trimethyl-3-pentenal (I), obtained by the acid-catalyzed decomposition of 2,2,4,4-tetramethylcyclobutane-1,3-diol[1] was photolyzed to determine if products derived from intramolecular reaction could be detected. A solution of 0.2 mole of I in 600 ml dry ether under a gentle nitrogen purge was irradiated 43 hr by a Hanovia 550-W lamp with the use of a Vycor filter. After evaporation of the solvent, the residue was distilled yielding a clearly defined fraction (II), 4.4g, bp 78–83°C, colorless liquid, and a yellow oil (III), 3.8 g, bp 39–79°C/1 mm. Fraction I was readily identified as 2,4-dimethyl-2-pentene, (Calculated for C_7H_{14}: C, 85.63%; H, 14.37%. Found: C, 84.85%; H, 14.57%). The infrared spectrum was identical with that of an authentic specimen.[2] The second fraction had elemental analysis, infrared and NMR spectra consistent with that expected for 2,2,4,6,6,8-hexamethyl-5-ol-2,7-nonadiene. (Calculated for $C_{15}H_{18}O$: C, 80.29%; H, 12.58%. Found: C, 80.33%; H, 12.85%.) The NMR spectrum showed $\tau = 8.94$ singlet, $—C(CH_3)_2—$; τ, 8.30, 8.34, $(CH_3)_2C{=}CHR$; $\tau = 4.84$ multiplet, ${=}CH$; $\tau = 6.7$ broad $(—CH—OH)$ in the approximate ratios of 6:6:1. Identical products were formed by photolysis in the presence of acetophenone.

The formation of these products is most easily accommodated by postulation of a resonance stabilized 2,4-dimethylpent-2-enyl radical of appreciable lifetime. The nonadienyl alcohol (III) arises from reaction of the radical with starting material.



Similarly, a stepwise mechanism for photocyclization of 6-hepten-2-one to 1-methyl-3-cyclohexanol (where an allyl radical can be formed) has been proposed.[3] However, the cyclization of saturated aldehydes to cyclobutanols occurs with partial retention of configuration[4] and requires a different mechanism. The photochemical formation of cyclopropane derivatives from conjugated ketones and the addition of isolated carbonyl groups to olefins to form oxetanes have been observed.[5] In these cases, no product from such a type of intramolecular reaction was observed.

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R. G. Tonkyn*
R. J. Cotter

Research and Development Department
Plastics Division, Union Carbide Corporation
Bound Brook, New Jersey 08805

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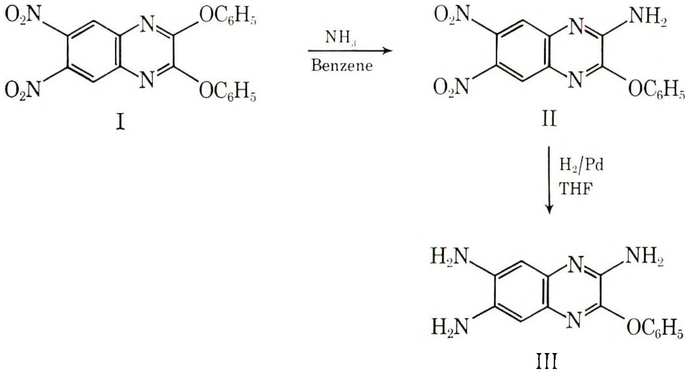
* Present address: Betz Laboratories, Trevose, Pennsylvania 19047.

*Polymers with Recurring Quinoxaline Units. V. Poly(6*H*-imidazo[4,5-*g*]oxazolo[4,5-*b*]quinoxaline-2,7-diyl-*m*-phenylene)*

A difference in reactivity of the apparently identical phenoxy groups is illustrated by the reaction of 2,3-diphenoxy-6,7-dinitroquinoxaline[1] (I) with ammonia. When this compound was treated with gaseous ammonia in benzene solution at room temperature for 24 hr, the product was 2-amino-3-phenoxy-6,7-dinitroquinoxaline (II), which was easily reduced to 2,6,7-triamino-3-phenoxyquinoxaline (III) by catalytical hydrogenation with hydrogen and 10% Pd on charcoal at a pressure of 40 psi with tetrahydrofuran (THF) as solvent.

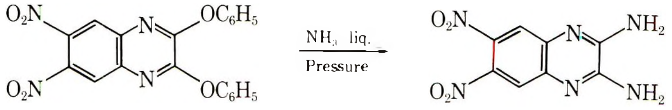


I

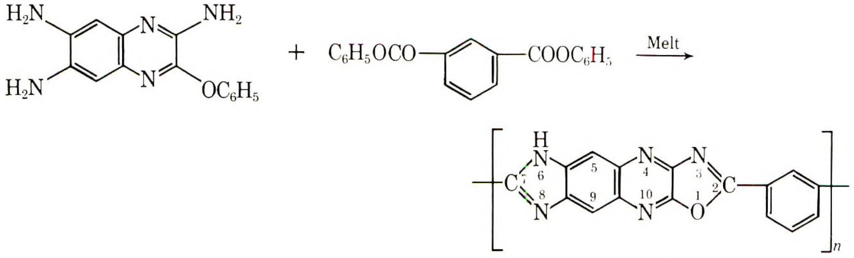
II

III

By carrying out the reaction on the phenoxy derivative in liquid ammonia under pressure at 60°C for 24 hr, it was possible to obtain 2,3-diamino-6,7-dinitroquinoxaline (IV).



An interesting polymer (V) with imidazole quinoxaline and oxazole units was obtained by heating 2,6,7-triamino-3-phenoxyquinoxaline with diphenyl isophthalate.



V

This polymer was not soluble in such solvents as *N,N*-dimethyl acetamide, dimethyl sulfoxide, and hexamethylphosphoramide, but was somewhat soluble in methanesulfonic acid and concentrated sulfuric acid. In the latter solvent it had an inherent viscosity of 0.33. It was quite thermally stable as shown by the TGA curve (Fig. 1).

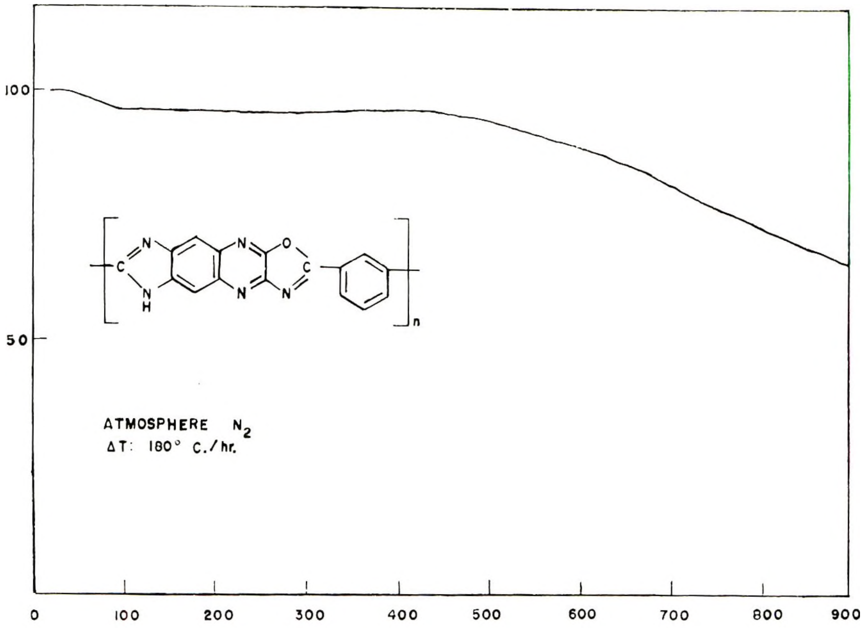


Fig. 1. TGA curve for polymer V.

2-Amino-3-phenoxy-6,7-dinitroquinoxaline

A 10-g portion (0.0495 mole) of 2,3-diphenoxy-6,7-dinitroquinoxaline was dissolved in 350 ml. of benzene, and under magnetic stirring ammonia was bubbled at room temperature through the solution for 24 hr. After a few hours the yellow solution gave a yellow precipitate, which did not dissolve on heating the mixture to the boiling point. The precipitate was washed with petroleum ether, and ammonia was again bubbled through the mother liquid to give a further precipitate. The reaction was complete after a few days. The total yield was 5.3 g (60%). The compound was crystallized from 95% ethyl alcohol and washed with hot benzene; mp 255–256°C.

ANAL. Calcd for $C_{14}H_9N_5O_5$: C, 51.3%; H, 2.75%; N, 21.4%. Found: C, 51.21%; H, 2.80%; N, 21.48%.

2,6,7-Triamino-3-phenoxyquinoxaline

2-Amino-3-phenoxy-6,7-dinitroquinoxaline (8 g, 0.0245 mole) was completely dissolved in 250 ml of THF and shaken in a Parr apparatus with hydrogen and 1 g of 10% palladium on charcoal at room temperature at a pressure of 40 psi. After 2 hr the absorption of gas was complete, and a greenish precipitate was observed. The mixture was diluted with THF until complete solution of precipitate occurred at the reflux temperature. The solution was filtered from the catalyst, and concentrated to dryness. The compound was recrystallized from 95% ethyl alcohol. The yield was 6 g (100%); mp 243–244°C.

ANAL. Calcd for $C_{14}H_{13}N_5O$: C, 63.0%; H, 4.87%; N, 26.2%. Found: C, 62.36%; N, 4.96%; N, 25.82%.

2,3-Diamino-6,7-dinitroquinoxaline

2,3-Diphenoxy-6,7-dinitroquinoxaline (6 g, 0.0149 mole) was dissolved in 150 ml of liquid ammonia in pressure bottles, then heated at 60°C under shaking for 40 hr. The reaction mixture was cooled and filtered. The recovered red-brown product was dried, extracted with 95% ethyl alcohol, and recrystallized from the same solvent. The yield was 3.2 g (80%); mp >350°C.

Anal. Calcd for $C_8H_6O_4N_6$: C, 38.4%; H, 2.4%; N, 33.6%. Found: C, 38.2%; H, 2.76%; N, 33.1%.

Melt Condensation of 2,6,7-Triamino-3-phenoxyquinoxaline and Diphenyl Isophthalate

A mixture of 2,6,7-triamino-3-phenoxyquinoxaline (1.33 g, 0.005 mole) and diphenyl isophthalate (1.59 g; 0.005 mole) was placed in a 100-ml round-bottomed flask. The system was evacuated and filled with dry nitrogen three times. The flask was heated to 280°C for 1.75 hr under nitrogen atmosphere. Reaction began at 200°C, and phenol and water were collected in the Dry Ice condenser and trap. The flask was cooled to room temperature while a positive nitrogen pressure was maintained. The pressure was reduced and the flask was heated to 280°C for 1.5 hr. The flask was cooled to room temperature; the solid black prepolymer was removed from the flask and finely ground in a mortar.

The prepolymer was placed in a rotary evaporator and the system was evacuated and filled with dry nitrogen three times and heated slowly to 350°C over a period of 5 hr. The product was extracted with 95% ethyl alcohol until a colorless mother liquor was obtained, then dried under reduced pressure. The yield was 1.8 g (80%); $\eta_{\text{inh}} = 0.17$ (0.46% concentrated sulfuric acid, 31°C). It was soluble in concentrated sulfuric acid, partly soluble in methanesulfonic acid, and practically insoluble in other solvents like DMSO, DMAc, hexamethylphosphoramide, pyridine, acetic acid, and tetramethylene sulfone.

Anal. Calcd. for $(C_{16}H_7N_5O)_n$: C, 67.4%; H, 2.47%; H. 24.5%. Found: C, 66.42%; H, 3.06%; N, 19.22%; residue 0.24%.

A sample of 0.6 g of polymer was heated at 380°C under a pressure of 0.3 mm Hg for 6 hr. The yield, after heating, was 0.55 g. The compound was only partly soluble in concentrated sulfuric acid and methanesulfonic acid; $\eta_{\text{inh}} = 0.33$ (0.22% concentrated sulfuric acid); $\lambda_{\max} = 251.5$ mμ.

Anal. Found: C, 66.63%; H, 3.33%; N, 24.15%; Res. 0.43%.

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A. Banihashemi*
C. S. Marvel

Department of Chemistry
University of Arizona
Tucson, Arizona 85721

Received March 19, 1969
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* Present address: Department of Chemistry, Pahlavi University, Shiraz, Iran.

Polycyanurates from 2-Alkoxy-4,6-dichloro-s-triazines and 2,2-Bis(p-hydroxyphenyl)propane

INTRODUCTION

From time to time, attempts to prepare polymers from 2-substituted aryl or arylamino 4,6-dichloro-*s*-triazines and aromatic diols have been reported. Most of these attempts led to materials of low molecular weight with poor solubility characteristics.[1,2] A condensate of higher molecular weight was recently reported[3] as the product of the interfacial polycondensation of monomers in aqueous sodium hydroxide and nitrobenzene.

Some time ago we studied interfacial polycondensations of 2-alkoxy-4,6-dichloro-*s*-triazines with aromatic diols in the presence of *s*-collidine and obtained poly(arylene-*s*-triazinyl ethers) that had high molecular weights and were soluble in nonpolar solvents such as toluene and chloroform. We now wish to report this new series of polymers and some observations on their preparation.

EXPERIMENTAL

Monomers

Carefully redistilled 2-alkoxy-4,6-dichloro-*s*-triazines were used in the experiments: 2-*n*-pentyloxy-4,6-dichloro-*s*-triazine, bp 88°C/0.06 mm, n_D^{20} 1.5055; 2-*n*-2,2,3,3,4,4,5,5-octafluoropentyloxy-4,6-dichloro-*s*-triazine, bp 74°C/0.14 mm, n_D^{20} 1.4302.

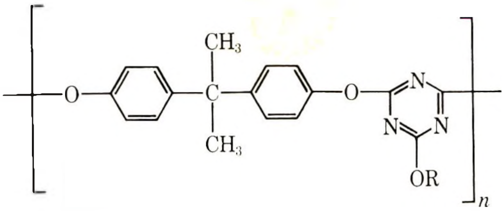
Polymerization

After 2.2841 g (0.0100 mole) of 2,2-bis(*p*-hydroxyphenyl)propane, 2.3611 g (0.0100 mole) of 2,4-dichloro-6-pentyloxy-*s*-triazine, 2.66 g (0.0220 mole) of *s*-collidine (free of infrared bands in the 713 and 815 cm^{-1} regions),[4] 25 ml of water, and 25 ml of chloroform were stirred for 10 min in a Waring Blendor, the organic phase was separated, washed with 100 ml of water, and concentrated on a steam bath. Once the solvent had evaporated, heating was continued for 1 hr. The cooled mass was broken up and washed sequentially with 180 ml of 2% hydrochloric acid and water in the blender. After the product was dried (80°C at 0.1 mm) for 18 hr, 3.9 g (100%) of a light-green polymer (polymer A) with an inherent viscosity of 1.24 dl/g (0.5% in chloroform at 30°C) was obtained.

A similar procedure with 3.80 g (0.010 mole) of 2-*n*-2,2,3,3,4,4,5,5-octafluoropentyloxy-4,6-dichloro-*s*-triazine gave 5.1 g (95%) of a light-orange polymer (polymer B) with an inherent viscosity of 0.89 dl/g.

RESULTS

Characterization data were obtained for the two polymers described in the experimental section.



Polymer A, R = $-(CH_2)_4CH_3$
Polymer B, R = $-CH_2(CF_2)_4H$

TABLE I
Elemental Analyses of Polymers

	Formula	Calculated C, %	Calculated H, %	Calculated N, %	Calculated F, %	Found C, %	Found H, %	Found N, %	Found F, %
Polymer A	$C_{23}H_{25}N_3O_3$	70.56	6.44	10.74		70.44	6.42	10.85	
Polymer B	$C_{23}H_{25}F_8N_3O_3$	51.59	3.20	7.85	28.39	51.75	3.33	7.76	28.38

The results of elemental analyses are reported in Table I.

Thermogravimetric analyses data showed good heat stability (Table II) with surprisingly little difference between the stability in air and nitrogen. Infrared spectra for the two polymers are shown in Figure 1.

TABLE II
Thermogravimetric Analyses of Polymers

	Weight residue, %			
	Polymer A		Polymer B	
Temperature, °C	In air[a]	In nitrogen[b]	In air[a]	In nitrogen[b]
300	101	99	99	99
350	99	95	98	98
400	81	70	97	97
450	47	42	68	77
500	39	37	46	53
550	34	33	38	48
600	24	31	24	44
650	8	29	5	42
700	1	27	0	40

[a] Heating rate, 6°C/min.

[b] Heating rate, 3°C/min.

In addition to their good heat stability, these polymers were soluble in nonpolar solvents such as chloroform and toluene and could be cast as tough films from these solvents. Films (2.3 mils) cast from chloroform had tensile strengths greater than 7000 psi. Glass-cloth laminates (4-ply) prepared at 350°F and 5000 psi and containing 47 wt-% of the polymer had a tensile strength of 50300 psi.

The polymers softened visibly at 170–180°C. No glass transition temperatures could be detected by differential thermal analyses.

DISCUSSION

Although most of the experiments were carried out by techniques used for interfacial polycondensation, the mechanism of the polymerization was proved not to be interfacial. The fact became evident in the importance of the manner in which the polymers were heated after the chloroform phase was taken from the blender and solvents were removed. Unless the heating step was carefully reproduced, high molecular weight polymers were not obtained consistently.

Studies on the system showed that collidine and 2,2-bis(p-hydroxyphenyl)propane formed a complex that in a water–chloroform mixture was partitioned nearly entirely into the chloroform phase. The presence of a water phase in the interfacial step simply served to remove the collidine hydrochloride as it was formed. When the quantity of collidine hydrochloride in the water phase was determined, it was found that only about 50% of the expected amount had formed. Therefore, only a prepolymer was formed in the interfacial step, and the second polymerization step was required.

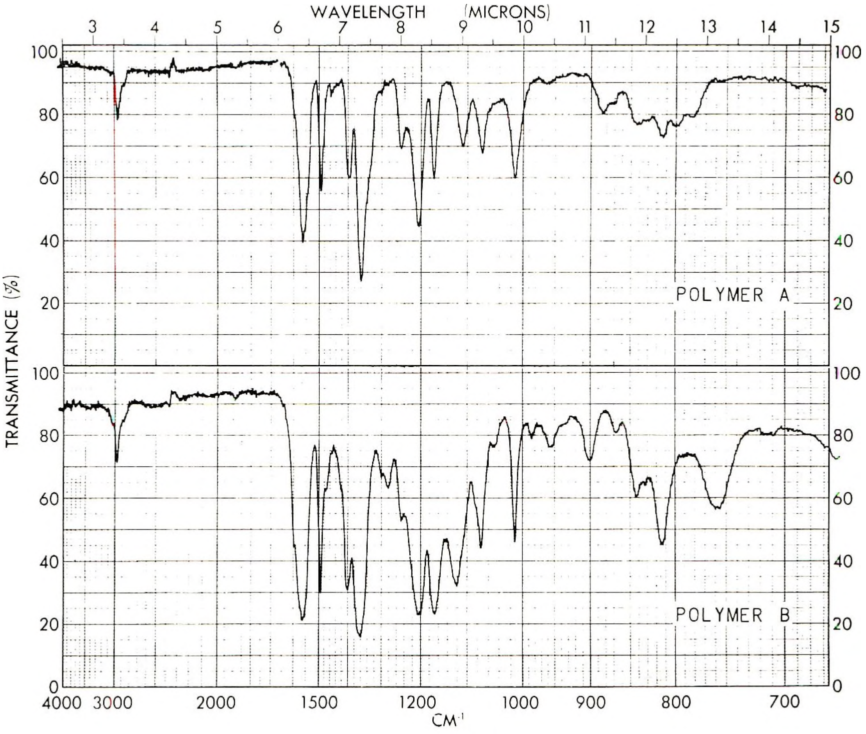


Fig. 1. Infrared spectra of polymer films.

The polycondensation was essentially completed in the second step in which the prepolymer was heated on the steam bath. The hot liquid residue obtained after the chloroform distilled gradually hardened to a tough mass. The final step, in which the powdered polymer was heated at 80°C under vacuum simply served to remove traces of solvents and water and did not advance the polymerization. The inherent viscosity of one polymer that was not heated at 80°C under vacuum was 1.07 dl/g; in a parallel experiment, a polymer with an inherent viscosity of 1.10 dl/g was obtained after the 80°C vacuum.

In a number of polymerizations following the method described here, polymers with inherent viscosities as great as 1.61 dl/g were obtained, but alternate procedures were satisfactory. A polymer with an inherent viscosity of 1.20 dl/g (94% yield) could be obtained whe nthe same quantities of triazine, diol, and collidine were first mixed in chloroform with no water present. Also, refluxing the reactants for 16 hr in 75 ml of chloroform gave 92% of a polymer with an inherent viscosity of 0.67 dl/g.

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L. W. BREED
R. L. ELLIOTT

Midwest Research Institute
Kansas City, Missouri 64110

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Copolymerization of Octamethylcyclotetrasiloxane with Vinyl Compounds. II. Synthesis of Block Copolymers of Dimethylsiloxane and Vinyl Compounds

INTRODUCTION

Octamethylcyclotetrasiloxane (D_4) is known to be polymerized by anionic catalysts[1-3] including alkali metal–naphthalene complexes. The polymerization mechanism with such catalysts is an equilibrium polymerization involving a silanolate intermediate and is thought to be sort of a "living" polymerization.

We carried out block copolymerization of styrene, methyl methacrylate, and acrylonitrile with D_4 using various alkali metal–naphthalene complexes. The catalysts used were potassium naphthalene (K-Naph), sodium naphthalene (Na-Naph), lithium naphthalene (Li-Naph), and *n*-butyllithium (BuLi).

EXPERIMENTAL

Reagents

D_4, supplied by the Shin-Etsu Chemical Co., was distilled under reduced pressure and stored over sodium wire. It was redistilled over calcium hydride just before use.

Styrene (St), methyl methacrylate (MMA), acrylonitrile (AN), and tetrahydrofuran (THF) were purified by the usual methods and distilled over calcium hydride just before use.

Preparation of Catalysts

The calculated amounts of the alkali metal and naphthalene in THF were reacted in an Erlenmeyer flask at room temperature under N_2, under stirring with a magnetic stirrer. The complexes formed had the dark green color characteristic of such radical anions. A known amount of the THF solution was drawn out by means of a syringe and decomposed by methanol; deionized water was added and the solution titrated with standard HCl solution. The concentration of *n*-butyllithium (BuLi) in *n*-hexane solution was determined by the usual method.

Copolymerization Procedure

The copolymerization was carried out in polymerization tubes equipped with breakseals. Living poly-D_4 was prepared and then the vinyl monomers were added to it, and alternatively living poly-St, poly-MMA, and poly-AN were prepared and D_4 was added.

RESULTS AND DISCUSSION

Block Copolymerization of Vinyl Monomers with Living Poly-D_4

The block copolymerization was attempted by adding St, MMA, and AN to living poly-D_4. The D_4 concentration was 1.3 mole/l. (3.8 g/10 ml), and the catalysts used were K-Naph, Na-Naph, Li-Naph, and BuLi. The polymer obtained was treated with *n*-hexane in order to remove poly-D_4 originally presented. The *n*-hexane-soluble part was identified as poly-D_4. In case of copolymerizations with St and MMA, the yield of *n*-hexane-insoluble materials was small, and such materials were identified as homopolymers of St and MMA.

In the copolymerization with AN, considerable amounts of *n*-hexane-insoluble material was formed. The infrared spectrum of the *n*-hexane-insoluble material showed the presence of Si-O-Si (1024 cm^{-1}) and Si-C (801 cm^{-1}) linkages, though their intensities

TABLE I
Block Copolymerization of AN with Living Poly-D_4 with K-Naph[a]

K-Naph $\times 10^2$, mole/l.	Conversion, %	n-Hexane-soluble, %	n-Hexane-insoluble, %	Properties of block copolymer		
				Softening point, °C	dl/g[b]	AN/D[c]
1.3	66	81.0	19.0	98.7	0.077	12.62
0.8	74	78.9	21.1	68.5	0.108	10.57

[a] Initial [D_4] = 1.3 mole/l., [AN] = 1.5 mole/l., at 0°C in THF, prepolymerization time, 120 hr; block copolymerization time, 126 hr.

[b] Measured at 30°C in DMF.

[c] Ratio of AN units to siloxane units (—SiO—) calculated from analysis (C, H).

were small. The results obtained with AN are shown in Table I. K-Naph was the most active catalyst, and sodum or lithium compounds were inactive.

AN is thought to be initiated by weak bases such as silanolate. However, the content of D_4 units in the copolymer was very low, and furthermore, the molecular weight was thought to be very low. Therefore, in this procedure, the polymerization mechanism is thought not to accord with the usual "living" mechanism.

Block Copolymerization of D_4 with Living Vinyl Polymer

The block copolymerization was carried out adding D_4 to living polystyrene (PSt), poly(methyl methacrylate) (PMMA), and polyacrylonitrile (PAN) prepared by using K-Naph, Na-Naph, Li-Naph, and BuLi in THF. The apparatus used was the same as described previously. When living PSt was used, the characteristic red color disappeared as soon as D_4 was added, and the color of the copolymerization system changed to a pale yellow. The other systems showed no significant change on addition of D_4. The concentrations of St, MMA, AN, and D_4 were 0.87, 0.94, 1.50, and 1.30 mole/l., respectively. The catalyst concentration was nearly 0.1 mole/l., and the copolymerization was carried out at 0°C in THF. In these cases, the formation of a liquid polymer was observed. The formation of free poly-D_4 having been considered, the polymer obtained was extracted with n-hexane as previously described. A significant amount of n-hexane-soluble part was formed even when the block copolymerization was initiated with living vinyl polymers. The soluble part was identified as poly-D_4 by means of infrared spectroscopy. The formation of poly-D_4 in this case is impossible to explain if the polymerization proceeds according to the usual living propagation mechanism. Mitoh et al.[4] showed that high molecular weight poly-D_4 underwent degradation to oligopolymer of D_4 when K-Naph was used as a catalyst.

Therefore, it is necessary to consider the chain transfer reaction in order to explain the formation of free poly-D_4 in the course of the block copolymerization.

The infrared spectra of the n-hexane-insoluble materials showed absorptions at 1024 and 801 cm^{-1} due to Si-O-Si and Si-C, respectively, as well as absorption bands due to the homopolymers of the vinyl monomer used. The some properties of the copolymers are shown in Table II.

In the case of the block copolymerization with a living polycarbanion, a significant amount of n-hexane-insoluble material formed, regardless of the monomer used (St, MMA, or AN). However, the ratios of vinyl monomers to siloxane units (V/D) were fairly large and the degradation of block-copolymerized poly-D_4 or termination of the living end is considered to play an important role in the block copolymerization.

When living PSt was used, the V/D value was fairly small, though a significant amount of free poly-D_4 (n-hexane soluble) formed. Therefore the reaction of the styryl carbanion with D_4 is thought to take place to a considerable extent. However, the

TABLE II
Properties of Copolymers Obtained with Living PSt, PMMA, and PAN[a]

Vinyl monomer	Catalyst	Conversion, %	Softening point, °C	[η],(dl/g)[b]	V/D[c]
St	K-Naph	70	71	0.011[d]	5.02
St	Na-Naph	31	—	0.132[d]	1.47
St	Li-Naph	38	70	0.121[d]	4.31
MMA	K-Naph	19	100	0.304	40.2
MMA	Na-Naph	22	84	0.195	18.0
MMA	Li-Naph	23	140	—	13.8
AN	K-Naph	19	100	0.272	8.9
AN	Na-Naph	17	no	0.168	12.8
AN	Li-Naph	26	no	0.198	9.4

[a] Initial [St] = 0.87 mole/l.; [D_4] = 1.30 mole/l.; [cat] = 0.1 mole/l. at 0°C in THF; prepolymerization time, 140 hr; block copolymerization time, 140 hr (with Li-Naph 336 hr).

[b] Measured at 30°C in DMF unless otherwise noted.

[c] Ratio of vinyl monomer units to siloxane units.

[d] Measured at 30°C in benzene.

transfer reaction took place to a significant extent. On the other hand, in the case of living PMMA, the formation of free poly-D_4 was negligible, except in the case where Li compounds were used as catalysts. Furthermore, the V/D values were large. This suggests that the polymer obtained contains free PMMA. Considering that MMA is apt to undergo pseudo-termination and that PAN precipitates in the system, the polymers obtained with PMMA and PAN contain a significant amount of homopolymers, but isolation of the homopolymers was impossible.

Effect of Living End Concentration

The block copolymerization of the living PSt–D_4 system was carried out at quite high K-Naph concentrations to investigate the existence of the transfer reaction.

The St and D_4 concentrations were 0.87 and 1.30 mole/l., respectively, and the copolymerization was carried out at 0°C in THF. The effect of varying the concentration of living ends is shown in Table III. When the copolymerization was carried out with living PSt, the higher the living end concentration, the greater the formation of free poly-D_4. As described previously, the formation of poly-D_4 cannot be explained as-

TABLE III
Effect of Living End Concentration on Copolymerization[a]

K-Naph × 10^2, mole/l.	Conversion %	n-Hexane soluble material, %	n-Hexane insoluble material			
			%	Softening point, °C	[η], dl/g[b]	V/D
6.7	87	74.4	25.6	100	0.149	6.54
3.4	79	70.7	29.3	87	0.183	4.13
1.7	89	54.6	45.4	82	—	8.20

[a] Initial [St] = 0.87 mole/l.; [D_4] = 1.30 mole/l.; at 0°C in THF; prepolymerization time, 72 hr; block copolymerization time, 96 hr.

[b] Measured at 0°C in benzene.

suming a "living" polymerization mechanism. Therefore, the formation of poly-D_4 is considered to be the result of a transfer reaction.

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YUJI MINOURA
MOTONORI MITOH
AKIRA TABUSE
YOICHIRO YAMADA

Research Institute for Atomic Energy
Osaka City University
Osaka, Japan.

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