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Radiation-Induced Copolymerization of Thiophene with Maleic Anhydride

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ABSTRACT

Radiation-induced copolymerization of thiophene with maleic anhydride has been studied. On the copolymerization in chloroform solution, the effects of dose rate, polymerization temperature, and, monomer composition and concentration on the yield and molecular weight of the copolymer were determined. The copolymerization proceeds via a radical mechanism with bimolecular termination of propagating polymer radicals, and the apparent activation energy is 5.3 kcal/mole. By NMR spectroscopy of copolymer, it was also found that these monomers copolymerize alternately to give a copolymer having structure I. In this copolymerization, the higher initial rates were obtained at an equimolar composition of monomers and by using solvents containing chlorine, such as CCl_4, $CHCl_3$, and C_6H_5Cl.

INTRODUCTION

It is well known that maleic anhydride can copolymerize with monomers such as α-olefins and allylic compounds, which do not

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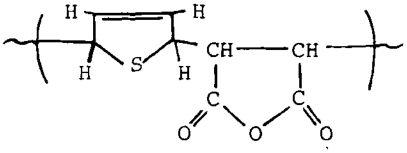
readily homopolymerize by radical initiator, and gives alternating copolymers with relatively high molecular weight. The alternating copolymerizations of maleic anhydride with olefins, vinyl ethers, allylic monomers, and vinyl sulfides, have been extensively studied by several workers [1-4].

On the other hand, it is also known that maleic anhydride can alternately copolymerize with some cyclic compounds such as p-dioxene [1] and furan [2, 3] which form a charge-transfer complex with maleic anhydride. Cardon et al. [4], studying the copolymerization of maleic anhydride with thiophene by radical initiator, found that polymerization occurs via a charge-transfer complex. Yoshida et al. [5] already found that thiophene forms a charge-transfer complex with maleic anhydride.

In the present work, radiation-induced copolymerization of thiophene with maleic anhydride has been studied, and it was found that these monomers give the alternating copolymer I by ionizing radiation,



I

even though neither thiophene nor maleic anhydride polymerizes under action of ionizing radiation.

EXPERIMENTAL

Thiophene was distilled in a stream of nitrogen gas, and the absence of impurity was ascertained by gas chromatography before use. Maleic anhydride obtained commercially was purified by sublimation under 10-15 Torr at 70°C. Solvents were purified according to conventional methods.

The monomer solution in the glass ampoule (12 mm in diameter, 100 mm in length) was degassed thoroughly by repeated (usually more than three times) freezing and thawing under 10^{-6} Torr. Subsequently, the ampoule was sealed off under vacuum, placed in the thermostated bath, and subjected to γ-irradiation from a cobalt-60 source. The reaction mixture was added to a large amount of diethyl ether in order to precipitate the copolymer formed and dried under reduced pressure for 24 hr at room temperature. The copolymer yield was

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determined gravimetrically. The reduced viscosity, η_{sp}/c, of the copolymer was measured at 30°C in 0.5 g/dl acetone solution.

NMR spectra of the copolymer were measured at room temperature in dimethyl sulfoxide (about 3 wt % solution), with a Japan Electron Optics spectrometer, Model JNM-SP-100, working at 100 MHz.

RESULTS AND DISCUSSION

It is well known that in solution polymerization, the rate of polymerization and the molecular weight of polymer are influenced by solvent. In the radiation-induced copolymerization of thiophene with maleic anhydride, it was found that polymerization rate and molecular weight of the copolymer are strongly influenced by the nature and the amount of solvent. As described later, the copolymerization of thiophene with maleic anhydride gave the highest polymerization rate in chloroform solution. So, the effects of dose rate, polymerization temperature, and concentration and composition of monomer on this copolymerization were investigated using chloroform as a solvent.

In preliminary experiments, it was found that both thiophene and maleic anhydride give no homopolymer by γ-irradiation, i. e., when 3.3 mole/liter thiophene or maleic anhydride in chloroform was irradiated at a dose rate of 3×10^4 rad/hr, for 96 hr at 50°C, no polymer was obtained. Only the thiophene-chloroform solution changed from colorless to brown. On the other hand, the equimolar solution of thiophene and maleic anhydride in chloroform gave the deposited copolymer under the same experimental conditions.

It was also found that the presence of air in the solution inhibits the formation of copolymer, and that the reproducibility of the data was invariably poor when the samples were degassed incompletely. In order to obtain reproducible data, the sample should be sealed off after thorough degassing by repeated freezing and thawing more than three times under less than 10^{-6} Torr.

Figure 1 shows polymer yield-time curves obtained at various dose rates in the equimolar solution of thiophene and maleic anhydride with chloroform as a solvent. Logarithmic plots of initial polymerization rate (obtained from Fig. 1) against the dose rate were found to give a straight line whose slope was approximately 0.5, as seen in Fig. 2. It was clear that the polymerization rate is proportional to the 0.5 power of dose rate, i. e., the copolymerization of thiophene with maleic anhydride proceeds by radical mechanism with bimoleular termination reaction of propagating radicals.

Figure 3 shows polymer yield-time curves obtained at a constant

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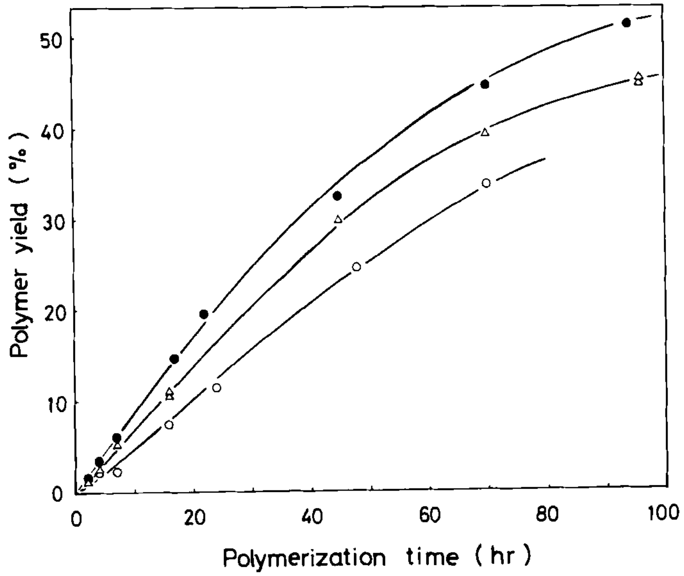

FIG. 1. Effect of dose rate on polymer yield-time curve: (●) 1 × 10^5 rad/hr; (△) 6 × 10^4 rad/hr; (○) 3 × 10^4 rad/hr. Monomer concentration, 3.3 mole/liter; thiophene in monomer, 50 mole %; solvent, $CHCl_3$; polymerization temperature, 50° C.

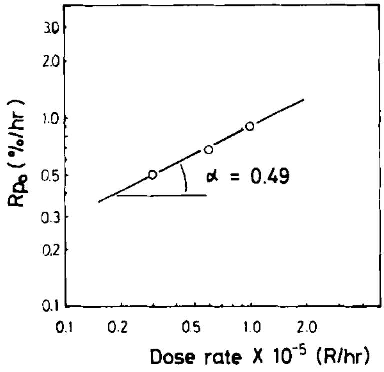

FIG. 2. Logarithmic plots of initial polymerization rate R_{p_0} against dose rate. R_{p_0} values were determined from Fig. 1.

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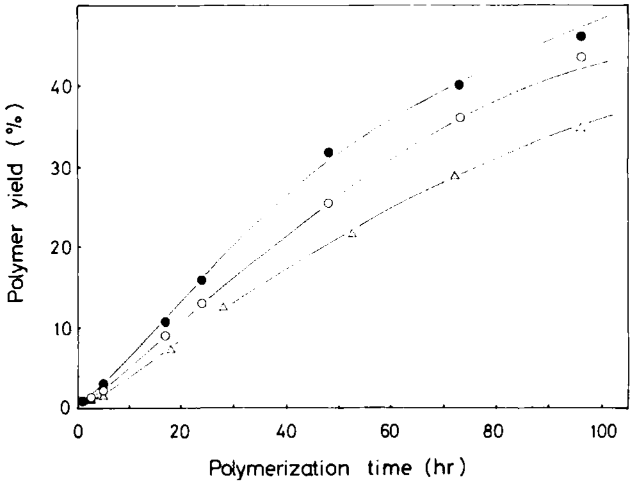

FIG. 3. Effect of polymerization temperature on polymer yield-time curve: (●) 60°C; (○) 50°C; (△) 40°C. Dose rate, 3×10^4 rad/hr; monomer concentration, 3.3 mole/liter; thiophene in monomer, 50 mole %; solvent, $CHCl_3$.

dose rate and at various temperatures from 40°C to 60°C. Arrhenius plots of the polymerization rates are shown in Fig. 4. The overall activation energy in this system is estimated approximately 5.3 kcal/mole. This activation energy is very small compared with that (17 kcal/mole) found in the AIBN-catalyzed copolymerization reported by Cardon et al. [4]. These values seem, however, to be reasonable. The overall activation energy E_a of radical polymerization is given by Eq. (1).

$$E_a = (E_i/2) + (E_p - E_t/2) \tag{1}$$

where, E_i, E_p, and E_t are activation energies of the initiation, propagation, and termination reactions, respectively. E_p and E_t in the radiation-induced polymerization are considered to be equal to those in the AIBN-catalyzed reaction. In the former polymerization, E_i is considered to be approximately zero, but in the latter, it is 30.8 kcal/mole [6]. So, the apparent activation energy of the radiation-induced copolymerization is smaller than that obtained AIBN system.

Figure 5 shows the relationship between monomer composition

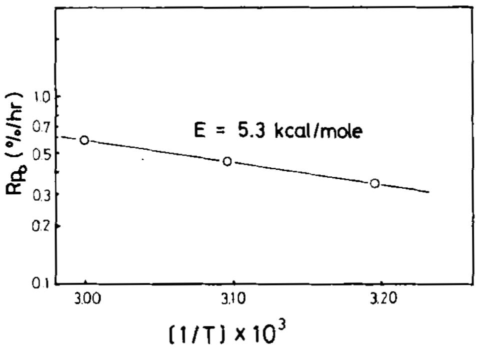

FIG. 4. Arrhenius plots for copolymerization of thiophene with maleic anhydride. R_{p_0} values were determined from Fig. 2.

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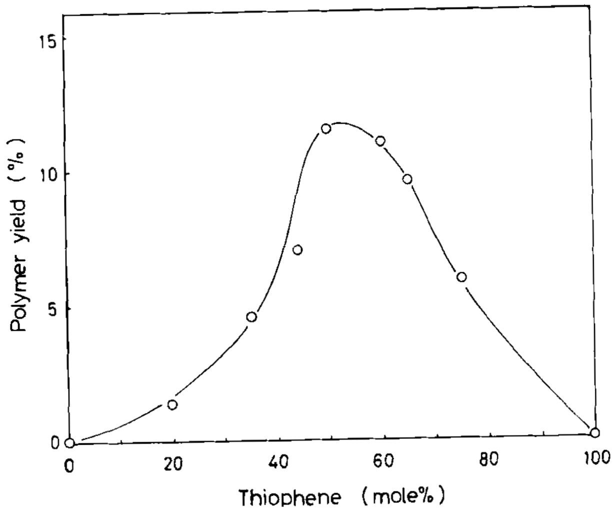

FIG. 5. Effect of monomer composition on polymer yield. Monomer concentration, 3.3 mole/liter; solvent, $CHCl_3$; dose rate, 3×10^4 rad/hr; polymerization, 24 hr at 50°C.

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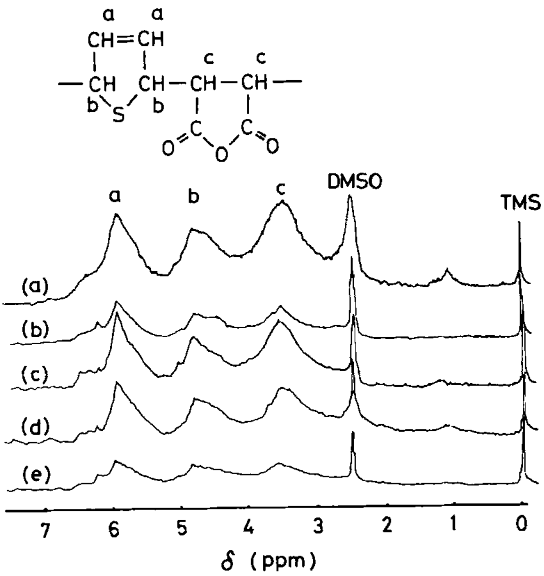

FIG. 6. NMR spectra of thiophene-maleic anhydride copolymer obtained (a) in bulk; (b) in 1,4-dioxane; (c) in methyl ethyl ketone; (d) in CH_2Cl_2; (e) in C_6H_5Cl.

and polymer yield. Figure 5 indicates polymer yield based on the monomer weight in the feed. As mentioned above, neither thiophene nor maleic anhydride homopolymerizes by γ-irradiation under the experimental conditions adopted in this study. On the other hand, thiophene copolymerizes with maleic anhydride to give the copolymer in the highest yield when monomer composition is equimolar.

Figures 6 and 7 show high-resolution NMR spectra of the copolymers obtained by γ-irradiation. These spectra suggest that all of the copolymers have approximately equimolar composition of thiophene and maleic anhydride irrespective of polymerization conditions such as composition of monomer in the feed and the nature of solvent. These spectra are also in accord with that of the copolymer obtained in the AIBN-catalyzed copolymerization [4]. These facts indicate that in this system, thiophene copolymerizes alternately with maleic anhydride.

Figure 8 shows the polymer yield-time curves at thiophene concentrations of 35, 50, and 65 mole %, respectively. The highest initial rate of copolymerization was obtained at an equimolar composition of monomers and the initial rate decreases in the order of 50, 65, and

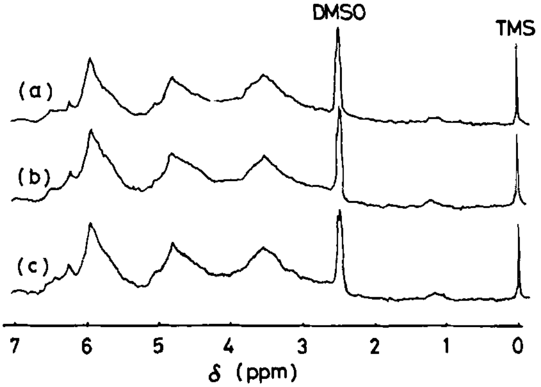

FIG. 7. NMR spectra of thiophene-maleic anhydride copolymer obtained at various thiophene concentrations: (a) 65 mole %; (b) 50 mole %; (c) 35 mole %.

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35 mole % of thiophene. In the earlier stage of this copolymerization, the polymer yield at 65 mole % was higher than that at 35 mole %. In the later stage (after ca. 35 hr), however, the relationship reversed. As discussed later (on the measurement of the solution viscosity of copolymer), it was found that acetone-insoluble copolymer was obtained at a polymerization time of more than 48 hr, although at 65 mole % only acetone-soluble copolymer was obtained over the entire range of polymerization time. The acetone-insoluble copolymer swells in acetone, methyl ethyl ketone, and N,N-dimethylformamide and seems to be crosslinked. Maleic anhydride seems to contribute to the crosslinking reaction and to increase the copolymer yield, since the polymerization time at which the polymer conversion curves at thiophene concentration of 35 and 65 mole % intersect each other is roughly consistent with the time at which the acetone-insoluble copolymer begins to be formed. The solubility of the copolymer depends not only on the concentration of monomer but also on the nature of solvent. From the fact that the yield of the insoluble copolymer (crosslinked copolymer) increases with increasing monomer concentration, unreacted monomer might contribute to crosslinking reaction.

In the radiation-induced solution polymerization, the effect of solvent on polymerization reaction is usually considered to reduce polymerization rate due to dilution of monomer concentration and to accelerate it due to formation of some initiating species from solvent. If it is assumed that the charge-transfer complex (CT complex) formed between monomers contributes to the alternating copolymerization, the effect of solvent on the formation of CT complex should be

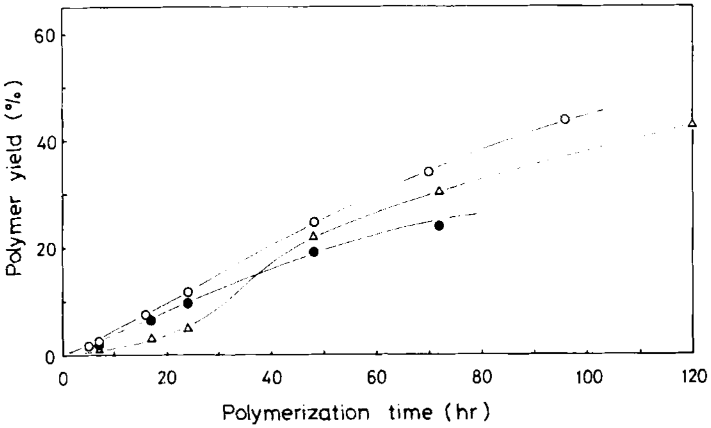

FIG. 8. Effect of monomer composition on polymer yield-time curve: (●) 65 mole % thiophene; (○) 50 mole % thiophene; (△) 35 mole % thiophene. Dose rate, 3×10^4 rad/hr; polymerization temperature, 50°C; monomer concentration, 3.3 mole/liter; solvent, $CHCl_3$.

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also considered. Because Yoshida et al. [5] measured the absorption spectra of thiophene, maleic anhydride and their mixture in the visible and near-UV regions, and found that thiophene forms a 1:1 CT complex having an absorption maximum (λ_{max}) of 270 nm, with maleic anhydride.

Figure 9 shows the relationship between polymer yield and monomer concentration at various copolymerization times. The concentration of the equimolar mixture of thiophene and maleic anhydride is estimated to be 13.25 mole/liter. As seen in Fig. 9, in this copolymerization system, the polymer yield increased with increasing monomer concentration and reached a maximum at a monomer concentration of 3-4 mole/liter and then decreased with increasing monomer concentration. Although this result can be elucidated by the contribution of solvent to initiation reaction, and the dilution effect of solvent, these phenomena cannot be well elucidated only by the initiation and the dilution effects of solvent. The monomer-solvent composition (monomer concentration, ca. 4 mole/liter), giving the maximum polymer yield, is composed of ca. 1 ml monomer and ca. 3 ml solvent, that is, if the increase in the copolymer yield depends only on the increase in initiation reaction, the maximum copolymer yield shown in Fig. 9 should be located at the higher monomer concentration side. As mentioned above, this copolymerization proceeds by a radical mechanism, and chloroform is a solvent which easily forms radical

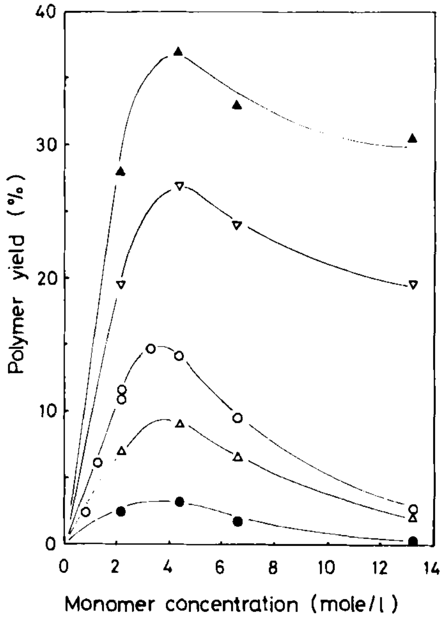

FIG. 9. Effect of monomer concentration on polymer yield at various polymerization times: (▲) 72 hr; (▽) 48 hr; (○) 24 hr; (△) 16 hr; (●) 7 hr. Thiophene concentration, 50 mole %; solvent, $CHCl_3$; dose rate, 3×10^4 rad/hr; polymerization temperature, 50°C.

species by γ-irradiation. Therefore, the contribution of radical species formed from solvent to initiation reaction might be large. If the radical species contribute greatly to this copolymerization reaction, the solvent easily forming radical species by γ-irradiation, might give a higher copolymer yield as compared with that forming less radical species. The results obtained by using various solvents in this copolymerization are, however, not always in agreement with this speculation. Further investigation is required.

Figure 10 shows the effect of aromatic solvent on the polymer yield-time curves. The initial rate of copolymerization, the solubility of the copolymer, dielectric constants, and dissociation energies of the solvents are shown in Table 1. It can be seen that in the copolymerization, the initial rate of copolymerization depends largely on the solvent, and that solvents containing a chlorine atom give a relatively large initial rate. For example, copolymerization in the solvent containing no chlorine atoms, such as benzene and toluene,

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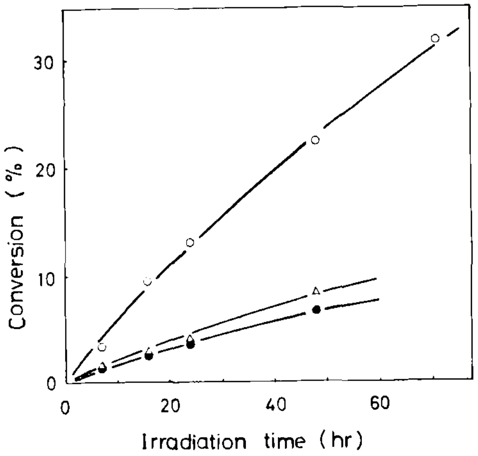

FIG. 10. Effect of solvent on the polymer yield-time curve: (○) C_6H_5Cl; (△) $C_6H_5CH_3$; (●) C_6H_6. Thiophene concentration, 50 mole %; dose rate, 3×10^4 rad/hr; polymerization temperature, 50°C.

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has a lower initial rate of copolymerization compared with that found in such chlorine-containing solvents as chlorobenzene. Consequently, it might be concluded that radical species formed from solvent by γ-irradiation contribute to the initial rate of copolymerization. The difference in the initial rate listed in Table 1, however, is not always attributed to the radical-forming ability of solvent; all the initial rate of copolymerization could not be relative to the dielectric constant and dissociation energy of solvent. The relationships between the copolymerization rate and the nature of solvent are very complex.

Table 1 also indicates the solubilities of copolymer. Most of the solution copolymerizations examined proceed heterogeneously, i. e., the copolymer precipitates during polymerization. The copolymers obtained in homogeneous system are soluble in acetone, but most of those obtained in heterogeneous polymerization are acetone-insoluble and are considered to be crosslinked copolymers.

The reduced viscosities of copolymers are listed in Tables 2 and 3. The molecular weight of copolymer depends on the monomer composition, monomer concentration, and the nature of solvent, but only very slightly on the polymerization time. On the other hand, the solubility of copolymer in acetone depends on the polymerization time (see Table 2). In the copolymerization in chloroform, the reduced viscosity of copolymer decreases as the monomer composition

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TABLE 1. Effects of Solvent on Copolymerization of Thiophene with Maleic Anhydride

Solvent	Initial polymerization rate (%/hr)	Solubility of polymer[a]		Dielectric constant[b]	Dissociation energy (kcal/mole)
		In solvent	In acetone		
CCl_4	0.536	0	0	2.219	D(–Cl) 68.3
$CHCl_3$	0.500	0	0	4.462	D(–Cl) 73.5
CH_2Cl_2	0.177	0	+ (48 hr) 0 (72 hr)	9.08[c]	D(–Cl) 78.5
CH_2ClCH_2Cl	0.320	0	+ (24 hr) 0 (48 hr)	10.36	D(–CH_2Cl) 85.5
C_6H_6	0.102	0	0	2.284[c]	D(–H) 107
$C_6H_5CH_3$	0.112	0	0	2.379	D(–H) 77.5, D(–CH_3) 87
C_6H_5Cl	0.497	0	0	5.61	D(–Cl) 88
1,4-Dioxane	0.251	+	+	2.209	-
$CH_3COC_2H_5$	0.286	+	+	18.51[c]	-
CH_3COCH_3	0.180	+	+	20.70	D(–CH_3) 72

[a] Code: +, soluble; 0, insoluble

[b] At 25°C unless otherwise noted.

[c] At 20°C.

TABLE 2. Effect of Monomer Composition on Viscosity of Copolymer[a]

Thiophene in monomer (mole %)	η_{sp}/c (dl/g)[b]
35.0	0.12
44.4	0.13
50.0	-[c]
60.0	0.18
65.0	0.13
75.0	0.10

[a] Polymerization conditions: dose rate, 3×10^4 rad/hr; 50°C; time, 24 hr; monomer concentration, 3.3 mole/liter; solvent, $CHCl_3$.

[b] Measured in acetone at 30°C, c = 0.50 g/dl.

[c] Insoluble in acetone.

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of thiophene and maleic anhydride deviates from the equimolar composition. Acetone-insoluble copolymers are obtained in the equimolar mixture of monomers (see Tables 2 and 3). Even if the monomer composition is equimolar, acetone-insoluble copolymers are obtained only at the lower monomer concentrations (Tables 2 and 3). Acetone-insoluble copolymers are also obtained after long polymerization times, even if the thiophene composition is 35 mole %. As seen in Table 3, the reduced viscosity of copolymer was found to be constant irrespective of copolymerization time at lower monomer concentration in chloroform solution, e. g., at a thiophene composition of 65 mole %, at which the copolymerization proceeds homogeneously using solvents other than chloroform. The reduced viscosities of the copolymers formed on this radiation-induced copolymerization of thiophene with maleic anhydride are low or almost the same as those obtained by using AIBN as an initiator [4].

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TABLE 3. Effects of Solvent on Viscosity of Copolymer[a]

	Viscosity in various solvents (dl/g)								
	$CHCl_3$				CH_2Cl_2	CH_2ClCH_2Cl	1,4-Dioxane	CH_3COCH_3	$CH_3COC_2H_5$
Polymn. time (hr)	50 mole % thiophene[b]	50 mole % thiophene	35 mole % thiophene	65 mole % thiophene	(50 mole % thiophene)	(50 mole-% thiophene)	(50 mole % thiophene)	(50 mole % thiophene)	(50 mole % thiophene)
7	c	c	c	c	-	-	-	-	0.11
16	0.10	d	c	0.14	-	0.16	0.08	0.11	0.11
24	0.10	d	0.12	0.13	0.05	0.15	0.09	0.14	0.16
48	0.10	d	d	0.14	0.07	d	0.09	0.12	0.12
72	0.10	d	d	0.14	d	d	0.10	-	0.12
96	-	-	-	-	-	-	-	0.13	-
120	-	-	d	-	-	-	-	-	-

[a] Polymerization conditions: dose rate, 3 × 10^4 rad/hr; 50° C; monomer concentration, 3.3 mole/liter unless otherwise noted.

[b] Monomer concentration, 2.2 mole/liter.

[c] Soluble.

[d] Insoluble.

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