Reactivity of an Alternating Copolymerization: Terpolymerization among Two Donor Monomers and a Common Acceptor Monomer

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ABSTRACT: Copolymerizations of the six pairs of donor monomers styrene–*p*-chlorostyrene, 2,3-dimethylbutadiene–*p*-chlorostyrene, styrene–vinyl acetate, styrene–2-chloroethyl vinyl ether, *p*-chlorostyrene–1,3-cyclooctadiene, and 2-chloroethyl vinyl ether–vinyl acetate were examined as well as terpolymerizations of these pairs with maleic anhydride (a weak acceptor monomer) or 7,7,8,8-tetracyanoquinodimethane (a strong acceptor monomer). These terpolymerizations can be regarded as a combination of two alternating copolymerizations. The co- and terpolymerizations were analyzed by both a complex mechanism and a free propagating mechanism for alternating copolymerization. The observed change in the co- and terpolymerization behaviors led to the concept that the alternating copolymerization is more like an ionic copolymerization than a random radical copolymerization, because of (i) the ideal copolymerization behavior in the treatment of the complex mechanism or being able to be analyzed with one ratio of relative reactivities in the treatment of the free propagating mechanism and (ii) the preferential influence of the polarity term of the donor monomers to the relative reactivity of the alternating copolymerization. The relative reactivity was found to be closely related with the polarity of the donor monomers.

Certainly, a terpolymerization is a very effective means for studying a radical alternating copolymerization. Previously, it was reported that it affords not only a quantitative estimation[1,2] of the relative reactivity of an alternating copolymerization monomer pair according to the scheme of the complex or the free propagating mechanism but also a discrimination of the reaction mechanisms in a radical alternating copolymerization; the composition analyses[1,3] and the dilution effect[1,4] in the terpolymerizations containing the third monomer in addition to the alternating copolymerization monomer pair such as vinyl ethers and maleic anhydride (MAnh) favor the complex mechanism over the free propagating mechanism.[1] Moreover, the terpolymerization of *p*-oxathiene, MAnh, and acrylonitrile (AN)[5] has led to the concept that the reactivity of these MAnh complexes is controlled exclusively by an electron-donating property of the donor monomer instead of both its resonance and polarity terms, differing from the case of conventional radical copolymerization. In addition to MAnh, the following quinodimethane compounds with electron-withdrawing substituents were recently found to react as alternatingly copolymerizable acceptor monomers: 7,7,8,8-tetracyanoquinodimethane (TCNQ),[6] 2,3-dichloro-5,6-dicyano-*p*-benzoquinone,[7,8] 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane (TMCQ),[9] and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$).[10] Thus, there are now a number of alternatingly copolymerizable acceptor monomers. Accordingly, comparison of the relative reactivity of the alternating copolymerization monomer pairs can be carried out readily upon replacement of acceptor monomers as well as donor monomers. A terpolymerization among two donor monomers and one acceptor monomer, which can be thought of as a combination of two alternating copolymerization systems with a common acceptor monomer, has to yield a terpolymer containing naturally 0.5 mol fraction of acceptor monomer unit; the remaining 0.5 mol fraction should be shared between the two donor monomer units. The ratio of the two donor monomer unit fractions permits the quantitative estimation of the relative reactivity of the alternating copolymerization monomer pairs or the monomer reactivity ratios of the complexes between donor and acceptor monomers. Moreover, when a common acceptor monomer is replaced under a fixed combination of two donor monomers, the influence of the acceptor monomer on the relative reactivity of the alternating copolymerization monomer pairs can be examined in a quantitative sense, leading to a more detailed understanding of the role of the acceptor monomer in the alternating copolymerization and furthermore giving precise and defined information on the mechanism of the alternating copolymerization.

In this work we studied the terpolymerizations among two donor monomers and an acceptor monomer, that is, the first donor–second donor–common acceptor system, regarded as a combination of two alternating copolymerization systems, viz., the first donor–acceptor and second donor–acceptor systems. The six combinations of the two donor monomers were employed as follows: as both conjugate monomers, the styrene (St)–*p*-chlorostyrene (pClSt) and 2,3-dimethylbutadiene (DBD)–pClSt systems; as conjugate and nonconjugate monomers, the St–vinyl acetate (VAc), St–2-chloroethyl vinyl ether (CEVE), and pClSt–1,3-cyclooctadiene (COD) systems; as both nonconjugate monomers, the CEVE–VAc system. MAnh, TCNQ, and TMCQ were used as acceptor monomers. Composition analyses of these terpolymerizations were carried out to obtain the relative reactivity of the alternating copolymerization monomer pairs or the monomer reactivity ratios of the complexes between donor and acceptor monomers. Some of the factors governing the relative reactivity of the alternating copolymerization monomer pairs and the mechanism of the alternating copolymerization are discussed.

Theoretical Background

1. Complex Mechanism.[11] Two kinds of complexes, C_1 between the first donor monomer (M_1) and the acceptor monomer (M_3) and C_2 between the second donor monomer (M_2) and the acceptor monomer (M_3), exist, because a 1:1 molecular complex is formed between a donor and an acceptor monomer. The equilibria of their formations are

$$M_1 + M_3 \overset{K_1}{\rightleftharpoons} C_1 \quad (1)$$

$$M_2 + M_3 \overset{K_2}{\rightleftharpoons} C_2 \quad (2)$$

where K_1 and K_2 are the respective equilibrium constants of complex formation and their values are much less than unity. Therefore, the concentrations of the complexes can be described by

$$[C_1] = K_1[M_1][M_3] \quad (3)$$

and

$$[C_2] = K_2[M_2][M_3] \quad (4)$$

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Table I
Copolymerization of AN with COD in Benzene[a] at 60 °C

run no.	monomer feed, mmol COD	monomer feed, mmol AN	amt of COD, mol %	time, h	conversn, %	elemental anal. % H	elemental anal. % C	elemental anal. % N	copolymer comp, mol % AN	η_{sp}/C,[b] dL·g^{-1}	$\bar{M}_n$[c]
1	7.99	2.02	79.8	81.5	1.4	8.24	78.10	13.67	68.7		
2	7.00	3.25	68.3	83.8	2.4	8.19	77.92	13.89	69.4		2930
3	6.50	3.51	65.0	53	3.6	7.92	76.98	15.10	73.2		3920
4	6.04	4.02	60.1	38.3	2.7	7.76	77.09	15.21	73.5		3020
5	5.04	5.01	50.1	39.4	3.9	6.63	75.90	17.47	80.0	0.02	2840
6	4.07	6.08	40.1	22.2	4.7	7.23	75.10	17.67	80.5	0.08	3140
7	3.51	6.48	35.1	25	4.5	7.22	74.54	18.24	82.0		5590
8	3.00	7.01	29.9	22.8	7.2	6.01	74.03	19.96	86.4	0.13	
9	2.08	8.09	20.5	23.7	13.0	6.63	71.72	21.65	90.3	0.32	

[a] 10 mL, 2 mg of AIBN. [b] Acetone solvent for run no. 5 and 6 and DMF solvent for run no. 8 and 9. t = 30 °C. [c] Determined by vapor pressure osmometry. Acetone solvent.

Assuming copolymerization between C_1 and C_2, eq 3 and 4 are substituted into the Mayo and Lewis equation of copolymerization to give eq 5, which makes it possible to

$$\frac{d[C_1]}{d[C_2]} = \frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left\{\frac{r_1(K_1/K_2)[M_1] + [M_2]}{[M_1] + r_2(K_2/K_1)[M_2]}\right\} \quad (5)$$

determine the modified monomer reactivity ratios $r_1(K_1/K_2)$ and $r_2(K_2/K_1)$ of the complexes C_1 and C_2.

2. Free Propagating Mechanism.[11,12] There are three different types of active growing chain ends, $\sim m_1\cdot$, $\sim m_2\cdot$, and $\sim m_3\cdot$. Each of the $\sim m_i\cdot$ can react with a monomer M_j only when the polar character of $\sim m_i\cdot$ and M_j is different (i.e., a donor radical vs. an acceptor monomer and vice versa). Here, M_1 and M_2 are donor monomers, M_3 is an acceptor monomer, and there are four different possible elementary cross-propagating reactions:

$$\sim m_1\cdot + M_3 \xrightarrow{k_{13}} \sim m_1m_3\cdot \quad (6)$$

$$\sim m_2\cdot + M_3 \xrightarrow{k_{23}} \sim m_2m_3\cdot \quad (7)$$

$$\sim m_3\cdot + M_1 \xrightarrow{k_{31}} \sim m_3m_1\cdot \quad (8)$$

$$\sim m_3\cdot + M_2 \xrightarrow{k_{32}} \sim m_3m_2\cdot \quad (9)$$

where k_{ij} is a rate constant of the reaction of an active growing chain end $\sim m_i\cdot$ with monomer M_j. Assuming a steady-state concentration of each active growing chain end, $\sim m_1\cdot$, $\sim m_2\cdot$, and $\sim m_3\cdot$, the compositions of the terpolymers are

$$-\frac{d[M_3]}{dt} = -\left(\frac{d[M_1]}{dt} + \frac{d[M_2]}{dt}\right); \qquad m_3 = m_1 + m_2 \quad (10)$$

$$\left(-\frac{d[M_3]}{dt}\right)\Big/\left(-\frac{d[M_1]}{dt}\right) = \frac{m_3}{m_1} = 1 + \frac{k_{32}}{k_{31}}\frac{[M_2]}{[M_1]} \quad (11)$$

$$\left(-\frac{d[M_3]}{dt}\right)\Big/\left(-\frac{d[M_2]}{dt}\right) = \frac{m_3}{m_2} = 1 + \frac{k_{31}}{k_{32}}\frac{[M_1]}{[M_2]} \quad (12)$$

$$\left(-\frac{d[M_1]}{dt}\right)\Big/\left(-\frac{d[M_2]}{dt}\right) = \frac{m_1}{m_2} = \frac{k_{31}}{k_{32}}\frac{[M_1]}{[M_2]} \quad (13)$$

where m_1, m_2, and m_3 are the mole fractions of M_1, M_2, and M_3 units in the terpolymer, respectively. Equations 11–13 can give the reactivity ratio k_{31}/k_{32} from the experimental results.

Results and Discussion

Experimental results of the copolymerization between AN and COD are summarized in Table I and its composition diagram is shown in Figure 1. Monomer reactivity ratios of AN and COD were calculated to be r_1(AN) = 2.8 ± 0.3 and r_2(COD) = 0.06 ± 0.03 at 60 °C. The Q and e values for COD were estimated to be Q = 0.03 and e = −0.2 on the basis of the monomer reactivity ratios and Q = 0.44 and e = 1.20 for AN. Accordingly, it is obvious that COD is a nonconjugate monomer, unexpectedly since it has two double bonds connected with one single bond.

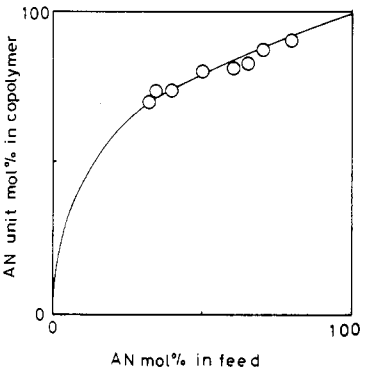

Figure 1. Composition diagram of the copolymerization between AN and COD. The line was calculated by using r_1 = 2.8 and r_2 = 0.06.

MAnh (electron affinity, EA = 1.65 eV[13]), a weak acceptor compound, and TCNQ (EA = 2.88 eV[13]), a strong acceptor compound, were used as acceptor monomers for the intended terpolymerizations. However, the copolymerization of DBD with MAnh was found to give exclusively their 1:1 adduct instead of their alternating copolymer, and thus TMCQ was used instead of MAnh for the terpolymerizations containing DBD. The results of the co- and terpolymerizations for the St–pClSt, St–pClSt–MAnh, and St–pClSt–TCNQ systems, the DBD–pClSt, DBD–pClSt–TMCQ, and DBD–pClSt–TCNQ systems, the St–VAc–MAnh and St–VAc–TCNQ systems, the pClSt–COD, pClSt–COD–MAnh, and pClSt–COD–TCNQ systems, the CEVE–St–MAnh and CEVE–St–TCNQ systems, and the CEVE–VAc, CEVE–VAc–MAnh, and CEVE–VAc–TCNQ systems are summarized in Tables II–VIII, respectively, and their composition diagrams as the binary copolymerization between the two donor monomers are shown in Figures 2–7, respectively.

The relative reactivity ratios k_{31}/k_{32} calculated by using eq 11–13 in the treatment of the free propagating mechanism are shown in the last columns of Tables II–VII, and their best values fitted to all of the experimental data are summarized in Table VIII, which also includes real monomer reactivity ratios of the TCNQ complexes calculated by using equilibrium constants at 60 °C for each charge-transfer complex formation. UV spectrophotometry was

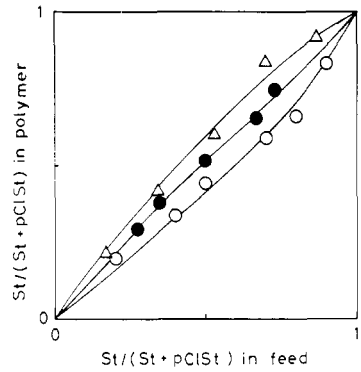

Figure 2. Composition diagram of the copolymerization between St and pClSt and the terpolymerizations of St, pClSt, and acceptor (MAnh and TCNQ) as the binary copolymerization between St and pClSt. The lines were calculated by using $r_1 = 0.42$ and $r_2 = 0.85$ for the St–pClSt system (○), $r_1(K_1/K_2) = 1.10$ and $r_2(K_2/K_1) = 0.81$ for the St–pClSt–MAnh system (●), and $r_1(K_1/K_2) = 1.34$ and $r_2(K_2/K_1) = 0.74$ for the St–pClSt–TCNQ system (△).

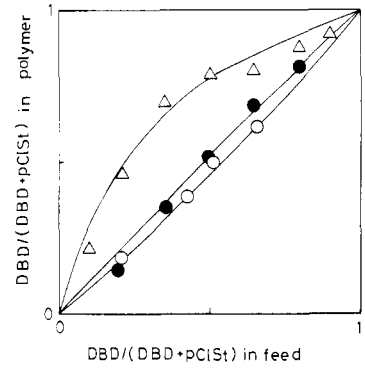

Figure 3. Composition diagram of the copolymerization between DBD and pClSt and the terpolymerizations of DBD, pClSt, and acceptor (TMCQ and TCNQ) as the binary copolymerization between DBD and pClSt. The lines were calculated by using $r_1 = 0.8$ and $r_2 = 1.1$ for the DBD–pClSt system (○), $r_1(K_1/K_2) = 1.1$ and $r_2(K_2/K_1) = 0.9$ for the DBD–pClSt–TMCQ system (●), and $r_1(K_1/K_2) = 2.8$ and $r_2(K_2/K_1) = 0.2$ for the DBD–pClSt–TCNQ system (△).

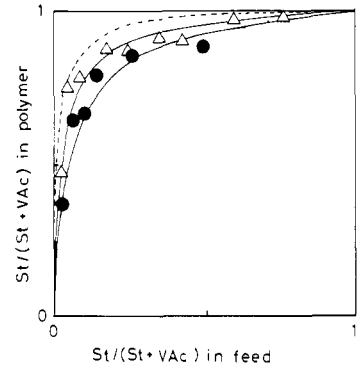

Figure 4. Composition diagram of the copolymerization between St and VAc and the terpolymerizations of St, VAc, and acceptor (MAnh and TCNQ) as the binary copolymerization between St and VAc. The lines were calculated by using $r_1 = 55$ and $r_2 = 0.01$ for the St–VAc system (---), $r_1(K_1/K_2) = 16.08$ and $r_2(K_2/K_1) = 0.03$ for the St–VAc–MAnh system (●), and $r_1(K_1/K_2) = 19.33$ and $r_2(K_2/K_1) = 0.02$ for the St–VAc–TCNQ system (△).

used in an attempt to obtain equilibrium constants for MAnh complex formation, but the MAnh complexes with weak donors such as St, pClSt, and VAc gave no definite constants, probably due to a contact-type charge-transfer complex formation. Therefore, real monomer reactivity ratios for MAnh complexes are not discussed here. Modified monomer reactivity ratios of the complexes between

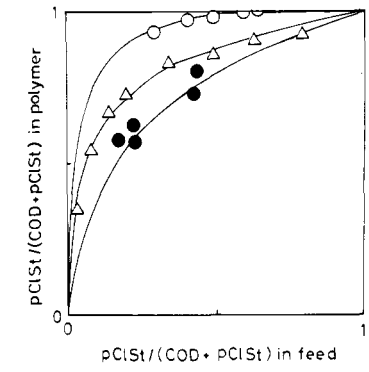

Figure 5. Composition diagram of the copolymerization between pClSt and COD and the terpolymerizations of pClSt, COD, and acceptor (MAnh and TCNQ) as the binary copolymerization between pClSt and COD. The lines were calculated by using $r_1 = 35$ and $r_2 = 0.01$ for the pClSt–COD system (○), $r_1(K_1/K_2) = 4.5$ and $r_2(K_2/K_1) = 0.2$ for the pClSt–COD–MAnh system (●), and $r_1(K_1/K_2) = 6.3$ and $r_2(K_2/K_1) = 0.01$ for the pClSt–COD–TCNQ system (△).

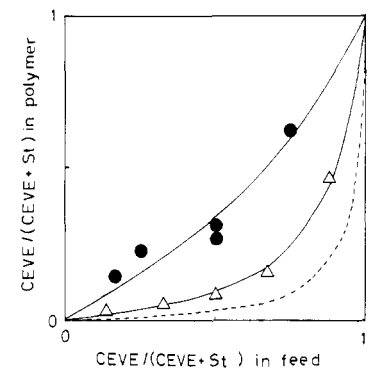

Figure 6. Composition diagram of the copolymerization between CEVE and St and the terpolymerizations of CEVE, St, and acceptor (MAnh and TCNQ) as the binary copolymerization between CEVE and St. The lines were calculated by using $r_1 = 0.03$ and $r_2 = 30.3$ for the CEVE–St system (---), $r_1(K_1/K_2) = 0.45$ and $r_2(K_2/K_1) = 1.83$ for the CEVE–St–MAnh system (●), and $r_1(K_1/K_2) = 0.1$ and $r_2(K_2/K_1) = 9.5$ for the CEVE–St–TCNQ system (△).

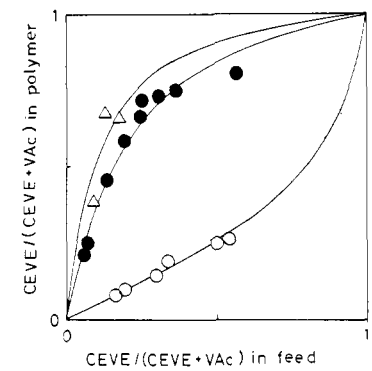

Figure 7. Composition diagram of the copolymerization between CEVE and VAc and the terpolymerizations of CEVE, VAc, and acceptor (MAnh and TCNQ) as the binary copolymerization between CEVE and VAc. The lines were calculated by using $r_1 = 0.15$ and $r_2 = 2.30$ for the CEVE–VAc system (○), $r_1(K_1/K_2) = 5.50$ and $r_2(K_2/K_1) = 0.18$ for the CEVE–VAc–MAnh system (●), and $r_1(K_1/K_2) = 10.0$ and $r_2(K_2/K_1) = 0.1$ for the CEVE–VAc–TCNQ system (△).

donor and acceptor monomers obtained in the treatment of the complex mechanism are also summarized in Table VIII. It is noteworthy in all those terpolymerizations that all the products of the modified monomer reactivity ratios of the complexes, $r_1(K_1/K_2)r_2(K_2/K_1)$, obtained in the treatment of the complex mechanism are approximately

Table II
Polymerization for the St-pClSt-Acceptor System at 60 °C[a]

run no.	monomer feed, mol % St	pClSt	acceptor	time, min	conversn, %	elemental anal. % H	% C	% Cl	% N	polymer comp, mol % St	pClSt	acceptor	η_{sp}/C,[b] dL·g^{-1}	k_{31}/k_{32} (11)	(12)	(13)
							No Acceptor									
1	79.7	20.3		55	1.2	6.98	82.73	10.29		66.4	33.6		0.24			
2	70.0	30.0		55	1.8	6.89	80.90	12.21		59.3	40.7					
3	20.1	79.9		55	1.9	5.92	72.60	21.48		20.3	79.7					
4	49.8	50.2		195	6.5	6.31	77.75	15.94		44.6	55.4		0.20			
5	39.7	60.3		195	6.6	6.13	75.59	18.28		34.7	65.3					
6	89.8	10.2		195	5.9	7.40	87.18	5.42		83.2	16.8					
							Manh Acceptor									
7	55.7	21.0	23.3	28	9.1	4.65	68.76	4.46		38.6	13.3	48.0	1.40	1.55	0.98	1.09
8	39.7	40.2	20.1	53	7.8	4.57	65.98	7.88		26.1	24.3	49.6	0.73	1.12	1.05	1.09
9	21.4	57.7	20.8	65	9.5	4.21	63.61	11.04		14.7	35.2	50.1	0.71	1.12	1.14	1.13
10	41.3	21.0	37.7	37	18.5	4.21	66.67	5.48		31.3	16.5	52.1	1.67	0.76	1.10	0.96
11	19.9	39.2	40.9	45	15.9	3.95	62.65	9.17		17.5	28.6	53.9	1.45	0.94	1.74	1.21
														av 1.10	1.20	1.10
							TCNQ Acceptor									
12	80.1	12.0	7.9	19	10.3	3.75	77.72	1.03	17.49	47.7	4.4	47.9	0.32	37.5	1.48	1.62
13	64.1	27.9	8.0	19	10.5	3.50	77.02	1.98	17.49	43.0	8.7	48.3	0.47	3.54	1.98	2.15
14	49.1	42.8	8.1	19	8.5	3.39	75.10	4.72	16.78	31.6	21.1	47.3	0.31	1.76	1.08	1.31
15	32.1	59.9	8.0	18	5.3	3.28	73.47	6.76	16.49	21.5	30.9	47.7	0.43	1.53	1.02	1.30
16	16.1	76.2	7.7	19	6.7	3.16	71.84	8.90	16.10	10.8	41.6	47.6	0.32	1.39	0.68	1.23
														av 9.14	1.25	1.52

[a] 10 mg of AIBN and 11 mL of benzene for the St-pClSt and St-pClSt-MAnh systems and 5 mg of AIBN and 11 mL of acetonitrile for the St-pClSt-TCNQ system. Total moles of monomers were 10 mmol for the St-pClSt and St-pClSt-MAnh systems and 5 mmol for the St-pClSt-TCNQ system. [b] Chloroform solvent for the St-pClSt system. DMF containing 0.1 wt % of LiCl solvent for the St-pClSt-MAnh and St-pClSt-TCNQ systems. t = 30 °C.

Table III
Polymerization for the DBD-pClSt-Acceptor System at 60 °C[a]

run no.	monomer feed, mol % DBD	pClSt	acceptor	time, min	conversn, %	elemental anal. % H	% C	% Cl	% N	polymer comp, mol % DBD	pClSt	acceptor	η_{sp}/C,[b] dL·g^{-1}	k_{31}/k_{32} (11)	(12)	(13)
							No Acceptor									
1	20.5	79.5		2820	8.8	5.34	72.14	22.52		18.7	81.3		0.10			
2	42.7	57.3		2820	9.3	6.60	74.76	18.64		38.6	61.4					
3	51.0	49.0		2820	7.3	7.15	76.76	16.08		49.9	50.1		0.07			
4	65.3	34.7		4380	6.3	7.95	79.22	12.84		61.7	38.3		0.07			
							TMCQ Acceptor									
5	32.4	58.9	8.7	35	9.8		62.83	4.96		17.3	32.1	50.6	0.37	0.94	1.05	0.98
6	17.4	71.5	11.1	31	8.6		62.23	6.08		6.8	40.9	52.3	0.39	0.61	1.15	0.68
7	44.0	44.9	11.1	29	7.2		61.78	3.81		25.5	24.0	50.5	0.39	1.04	1.13	1.08
8	57.7	31.3	11.0	25	6.6		60.75	2.51		34.0	15.5	50.5	0.29	1.12	1.23	1.19
9	71.2	17.8	11.0	34	9.2		61.40	1.60		41.6	9.5	48.9	0.35	1.43	1.04	1.10
														av 1.03	1.12	1.01

								TCNQ Acceptor								
10	9.3	83.7	7.0	30	11.5	3.91	71.03	8.55	16.51	11.0	40.0	49.0	0.38		2.61	2.03	2.48
11	19.9	73.8	6.4	30	10.8	4.07	72.47	6.07	17.38	23.3	27.2	49.5	0.34		3.30	3.04	3.17
12	32.5	60.6	6.9	20	10.1	4.17	74.19	3.62	18.01	35.4	15.5	49.0	0.31		4.86	4.03	4.26
13	46.8	46.2	7.0	20	8.6	4.23	74.55	2.63	18.33	39.9	11.1	49.0	0.22		4.33	3.37	3.55
14	60.2	32.9	7.0	20	6.5	4.46	76.39	2.47	18.23	40.8	10.3	48.9	0.27		2.75	2.05	2.16
15	74.2	18.9	6.9	20	9.5	4.63	75.34	1.57	18.48	45.2	6.5	48.3	0.25		3.72	1.64	1.77
16	83.6	9.4	6.9	20	9.0	4.77	75.60	1.01	18.73	47.2	4.2	48.7			3.50	1.19	1.26
														av	3.58	2.48	2.67

[a] 6 mg of AIBN for the DBD-pClSt system and 1 mg of AIBN for the DBD-pClSt-TMCQ and DBD-pClSt-TCNQ systems. 10 mL of benzene for the DBD-pClSt and DBD-pClSt-TMCQ systems and 10 mL of acetonitrile for the DBD-pClSt-TCNQ system. Total moles of monomers were 4 mmol for the DBD-pClSt system, 4.5 mmol for the DBD-pClSt-TMCQ system, and 4.3 mmol for the DBD-pClSt-TCNQ system. [b] Tetrahydrofuran solvent for the DBD-pClSt system, chloroform solvent for the DBD-pClSt-TMCQ system, and DMF containing 0.1 wt % of LiCl solvent for the DBD-pClSt-TCNQ system. t = 30 °C.

Table IV
Polymerization for the St-VAc-Acceptor System at 60 °C[a]

run	monomer feed, mol %			time,	conversn,	elemental anal.			polymer comp, mol %			η_{sp}/C,[b]		k_{31}/k_{32}	
no.	St	VAc	acceptor	min	%	% H	% C	% N	St	VAc	acceptor	dL·g^{-1}		(11)	(12)	(13)
								MAnh Acceptor								
1	39.6	40.4	20.0	23	10.4	4.96	68.97		43.5	6.1	50.4	1.20		6.43	7.41	7.28
2	20.3	59.9	19.8	23	10.2	5.03	70.04		45.6	7.7	46.7	1.09		122.33	14.94	17.47
3	11.0	66.9	22.1	25	9.8	4.97	67.59		39.5	11.0	49.5	0.81		24.02	21.34	21.90
4	5.1	75.0	19.9	30	8.3	4.90	65.42		33.3	18.6	48.1	0.43		33.09	23.32	26.32
5	2.6	77.5	19.9	35	11.5	4.75	59.77		18.6	32.3	49.1	0.48		18.18	15.53	17.19
6	5.9	54.3	39.8	20	10.3	4.75	65.39		33.3	17.8	48.9	0.65		19.65	16.03	17.17
													av	37.28	16.43	17.89
								TCNQ Acceptor								
7	23.9	70.1	6.0	70	13.1	4.51	76.96	17.50	46.3	7.0	46.7	0.57		339.50	16.63	19.40
8	40.3	53.7	6.0	47	10.2	4.67	77.35	17.56	47.9	5.0	47.1	0.67		−79.81	11.23	12.77
9	56.2	37.7	6.1	37	19.0	3.74	77.96	17.76	50.4	1.4	48.2	0.42		−15.37	22.42	24.15
10	72.4	21.7	5.9	34	20.0	4.52	78.22	17.66	52.1	0.5	47.5	0.43		−3.40	28.18	31.24
11	16.6	75.4	8.0	70	5.3	4.58	77.14	17.39	47.1	6.6	46.3	0.52		−267.40	27.34	32.44
12	32.6	59.3	8.1	60	12.5	4.67	77.49	17.49	48.6	4.5	46.9	0.54		−52.00	17.13	19.64
13	7.9	85.9	6.2	135	7.7	3.93	76.07	17.38	42.5	11.6	45.9	0.28		135.91	32.14	39.83
14	4.1	89.9	6.0	223	5.8	3.92	75.67	17.39	40.9	13.4	45.7	0.28		186.84	52.86	66.93
15	2.2	91.7	6.1	1320	7.5	3.74	72.14	16.94	26.9	30.3	42.8	0.11		70.52	17.19	37.00
													av	183.19[c]	25.01	31.49

[a] 10 mg of AIBN and 11 mL of benzene for the St-VAc-MAnh system and 5 mg of AIBN and 11 mL of acetonitrile for the St-VAc-TCNQ system. Total moles of monomer were 10 mmol for the St-VAc-MAnh system and 5 mmol for the St-VAc-TCNQ system. [b] DMF containing 0.1 wt % of LiCl solvent. t = 30 °C. [c] Calculated from run no. 7, 13, 14, and 15.

Table V
Polymerization for the pClSt–COD–Acceptor System at 60 °C[a]

run no.	monomer feed, mol % pClSt	COD	acceptor	time, h	conversn, %	elemental anal. % H	% C	% Cl	% N	polymer comp, mol % pClSt	COD	acceptor	η_{sp}/C,[b] dL·g^{-1}		k_{31}/k_{32} (11)	(12)	(13)
								No Acceptor									
1	64.8	35.8		17	11.9	5.03	69.72	25.25		99.2	0.8		0.10				
2	59.8	40.2		98	12.1	4.56	68.03	25.23		99.2	0.8						
3	50.0	50.0		98	12.3	4.72	69.25	25.14		99.6	0.4		0.11				
4	40.9	59.1		98	11.2	4.86	68.30	24.81		97.6	2.4		0.10				
5	30.1	69.9		98	5.1	5.22	69.11	23.82		93.7	6.3						
								MAnh Acceptor									
6	60.9	10.1	29.1	4	8.9	4.33	60.90	15.11		51.0	0	49.0	1.10		−4.23	∞	∞
7	20.0	25.1	54.9	2.2	6.9	4.02	61.75	12.50		41.1	9.6	49.3	0.69		6.29	5.19	5.37
8	19.9	25.8	54.4	4	11.8	4.26	62.84	11.39		36.6	13.4	50.0			3.54	3.54	3.54
9	15.4	49.7	34.9	4	9.4	4.71	63.40	9.55		28.6	21.4	50.1			4.29	4.33	4.31
10	15.0	49.9	35.1	4	5.1	5.04	63.48	9.99		32.0	18.5	49.5			6.08	5.57	5.75
11	15.7	74.3	10.0	6	3.2	5.22	63.51	9.28		29.0	21.0	49.6			6.66	6.46	6.55
														av	5.37[c]	5.02	5.10
								TCNQ Acceptor									
12	4.7	88.4	7.0	2.6	10.8	4.69	73.64	3.81	17.57	17.6	30.7	50.9	0.34		9.94	12.37	10.77
13	9.5	83.5	7.0	2.6	9.8	4.64	72.46	5.66	17.13	26.6	22.3	51.1	0.46		9.54	11.33	10.47
14	14.2	78.9	7.0	2.6	11.5	4.46	71.64	6.74	17.28	32.2	15.3	52.5	0.46		8.81	13.51	11.69
15	18.3	74.8	6.9	1.2	4.4	3.96	71.91	7.97	16.16	37.7	14.0	48.3	0.58		14.54	10.00	10.99
16	32.5	60.5	7.0	1.2	6.7	3.56	71.53	8.85	16.21	42.3	8.6	49.2	0.74		11.42	8.79	9.16
17	46.6	46.4	7.0	1.5	13.4	3.62	70.97	9.18	16.09	44.0	7.2	48.8	0.95		9.17	6.78	6.11
18	59.7	33.3	7.0	0.7	7.6	3.39	70.99	9.99	15.64	47.7	4.9	47.4	1.01		−88.72	4.84	5.43
19	74.6	18.4	7.0	0.7	8.6	3.41	70.50	10.01	15.72	47.9	4.2	47.9	1.00		0	2.57	2.81
														av	10.57[d]	8.77	8.43

[a] 2.2 mg of AIBN and 10 mL of acetonitrile for the pClSt–COD system, 1.3 mg of AIBN and 10 mL of benzene for the pClSt–COD–MAnh system, and 3.7 mg of AIBN and 10 mL of acetonitrile for the pClSt–COD–TCNQ system. Total moles of monomers were 4 mmol for the pClSt–COD system, 8 mmol for the pClSt–COD–MAnh system, and 4.3 mmol for the pClSt–COD–TCNQ system. [b] Chloroform solvent for the pClSt–COD system, tetrahydrofuran solvent for the pClSt–MAnh system, and DMF containing 0.1 wt % of LiCl solvent for the pClSt–COD–TCNQ system. t = 30 °C. [c] Calculated except for run no. 6. [d] Calculated except for run no. 18 and 19.

Table VI
Polymerization for the CEVE–St–Acceptor System at 60 °C[a]

run no.	monomer feed, mol % CEVE	St	acceptor	time, min	conversn, %	elemental anal. % H	% C	% Cl	% N	polymer comp, mol % CEVE	St	acceptor	η_{sp}/C,[b] dL·g^{-1}		k_{31}/k_{32} (11)	(12)	(13)
								MAnh Acceptor									
1	20.1	60.0	19.9	20	9.3	5.20	67.46	4.04		11.5	39.2	49.2	0.94		0.91	0.76	0.88
2	60.1	20.2	19.7	20	9.3	4.81	59.91	10.21		29.3	17.6	53.7			0.41	0.68	0.56
3	18.3	18.3	63.5	10	8.4	4.83	63.34	5.41		15.5	33.8	50.5			0.44	0.50	0.46
4	40.1	39.8	20.1	20	9.4	5.31	65.32	4.75		13.6	38.8	47.6	0.65		0.40	0.23	0.35
5	12.5	62.3	25.2	20	8.9	5.24	68.48	2.49		7.1	42.7	50.2			0.82	0.88	0.83
														av	0.60	0.61	0.61

								TCNQ Acceptor								
6	30.6	63.5	5.9	40	15.7	4.30	77.02	0.74	17.47	3.2	49.6	47.2	0.39		0.15	−1.00	0.13
7	63.0	30.8	6.2	80	8.9	4.27	75.84	1.93	17.43	8.3	44.6	47.1	0.23		0.11	0.03	0.09
8	12.2	81.9	5.9	38	16.4	4.45	78.29	0.50	17.45	2.1	50.7	47.2			0.31	−0.46	0.28
9	81.7	12.2	6.1	104	11.2	4.37	70.95	5.73	17.59	24.7	27.4	47.9	0.11		0.16	0.11	0.15
10	46.6	47.3	6.1	40	12.0	4.37	75.61	1.04	17.47	4.4	48.3	47.3			0.10	−0.02	0.09
														av	0.17	0.07[c]	0.15

[a] 10 mg of AIBN and 11 mL of benzene for the CEVE-St-MAnh system and 5.5 mg of AIBN and 11 mL of acetonitrile for the CEVE-St-TCNQ system. Total moles of monomers were 10 mmol for the CEVE-St-MAnh system and 16.5 mmol for the CEVE-St-TCNQ system. [b] DMF containing 0.1 wt % LiCl solvent. t = 30 °C. [c] Calculated from run no. 7 and 9.

Table VII
Polymerization for the CEVE-VAc-Acceptor System at 60 °C[a]

run	monomer feed, mol %			time,	conversn,	elemental anal.				polymer comp, mol %			η_{sp}/C,[b]	k_{31}/k_{32}		
no.	CEVE	VAc	acceptor	h	%	% H	% C	% Cl	% N	CEVE	VAc	acceptor	dL·g^{-1}	(11)	(12)	(13)
								No Acceptor								
1	16.6	83.4		24	12.3	6.83	55.20	2.95		7.3	92.7		0.07			
2	18.3	81.7		66	13.2	6.81	57.54	3.77		9.4	90.6					
3	33.3	66.7		47	10.5	6.75	55.27	7.69		19.5	80.5		0.05			
4	54.7	45.3		45	9.9	6.64	52.92	10.24		26.4	73.6					
5	49.9	50.1		51	6.7	6.93	53.15	9.60		24.7	75.3					
6	29.9	70.1		43	11.1	6.94	53.29	5.81		14.6	85.4					
								MAnh Acceptor								
7	19.3	60.3	20.4	0.73	13.0	4.37	48.51	11.51		32.2	15.4	52.4	0.24	4.98	7.51	6.53
8	4.4	55.0	40.6	0.67	18.0	4.30	49.66	4.25		11.4	35.0	53.6	0.50	3.30	6.50	3.99
9	22.2	38.0	39.8	0.35	11.2	4.40	47.14	12.77		35.9	12.5	51.6	0.44	3.92	5.36	4.92
10	14.9	44.8	40.3	0.4	9.7	4.38	48.11	11.52		33.3	12.8	53.9	0.37	4.86	9.64	7.81
11	23.9	11.3	64.8	0.3	11.4	4.24	46.89	13.38		37.8	9.6	52.6	0.38	1.21	2.12	1.86
12	24.9	56.5	18.6	0.4	15.9	4.66	48.92	12.01		33.7	12.3	54.0	0.44	3.77	7.69	6.21
13	4.8	77.5	17.7	0.4	13.3	4.55	51.04	4.08		10.8	38.6	50.6	0.32	4.38	5.02	4.52
14	11.3	59.2	19.5	0.4	17.4	4.68	49.25	7.99		21.8	25.0	53.2	0.44	4.25	6.92	5.35
15	14.1	59.3	26.6	0.34	15.5	4.67	49.31	10.15		28.0	20.0	52.0	0.39	4.91	6.73	5.89
														av 3.95	6.39	5.23
								TCNQ Acceptor								
16	12.1	80.1	7.8	163	9.0	3.78	61.73	8.51	17.64	35.7	17.5	46.0	0.22	21.29	11.09	13.51
17	17.5	75.3	7.2	308	8.6	3.87	63.88	8.67	17.27	35.8	18.9	45.0	0.22	16.22	6.02	8.16
18	9.0	84.0	7.0	425	8.5	3.74	63.17	5.00	17.77	20.4	33.9	45.7	0.26	7.53	3.25	5.63
														av 15.01	6.79	9.10

[a] 10 mg AIBN and 11 mL of benzene for the CEVE-VAc and CEVE-VAc-MAnh system and 10 mg of AIBN and 11 mL of acetonitrile for the CEVE-VAc-TCNQ system. Total moles of monomers were 10 mmol for the CEVE-VAc and CEVE-VAc-MAnh systems and 5.3 mmol for the CEVE-VAc-TCNQ system. [b] Chloroform solvent for the CEVE-VAc system. DMF containing 0.1 wt % of LiCl solvent for the CEVE-VAc-MAnh and CEVE-VAc-TCNQ systems. t = 30 °C.

Table VIII
Relative Reactivity Calculated from the Free Propagating Mechanism (FPM) and the Complex Mechanism (CM)

system	k_{31}/k_{32}	monomer reactivity ratio: calcd, FPM	monomer reactivity ratio: modified, CM	real, CM[b]	r_1r_2
St-pClSt			$r_1 = 0.42 \pm 0.08$ $r_2 = 0.85 \pm 0.08$		0.36
St-pClSt-MAnh	1.10	$r_1 = 1.10$ $r_2 = 0.91$	$r_1(K_1/K_2) = 1.10 \pm 0.13$ $r_2(K_2/K_1) = 0.81 \pm 0.13$		0.89
St-pClSt-TCNQ	1.25	$r_1 = 1.25$ $r_2 = 0.8$	$r_1(K_1/K_2) = 1.34 \pm 0.24$ $r_2(K_2/K_1) = 0.74 \pm 0.24$	$r_1 = 1.06 \pm 0.18$ $r_2 = 0.94 \pm 0.30$	0.99
DBD-pClSt			$r_1 = 0.80 \pm 0.20$ $r_2 = 1.12 \pm 0.10$		0.90
DBD-pClSt-TMCQ	1.12	$r_1 = 1.12$ $r_2 = 0.89$	$r_1(K_1/K_2) = 1.1 \pm 0.5$ $r_2(K_2/K_1) = 0.9 \pm 0.3$		0.99
DBD-pClSt-TCNQ	2.67	$r_1 = 2.67$ $r_2 = 0.37$	$r_1(K_1/K_2) = 2.80 \pm 1.4$ $r_2(K_2/K_1) = 0.2 \pm 0.4$	$r_1 = 14.74 \pm 7.37$ $r_2 = 0.04 \pm 0.08$	0.56
St-VAc[16]			$r_1 = 55 \pm 10$ $r_2 = 0.01 \pm 0.01$		0.55
St-VAc-MAnh	17.89	$r_1 = 17.89$ $r_2 = 0.056$	$r_1(K_1/K_2) = 16.08 \pm 0.4$ $r_2(K_2/K_1) = 0.03 \pm 0.01$		0.48
St-VAc-TCNQ	25.0	$r_1 = 25.0$ $r_2 = 0.04$	$r_1(K_1/K_2) = 19.33 \pm 2.0$ $r_2(K_2/K_1) = 0.02 \pm 0.02$	$r_1 = 1.69 \pm 0.17$ $r_2 = 0.23 \pm 0.23$	0.39
pClSt-COD			$r_1 = 35 \pm 20$ $r_2 = 0.01 \pm 0.02$		0.35
pClSt-COD-MAnh	5.1	$r_1 = 5.1$ $r_2 = 0.196$	$r_1(K_1/K_2) = 4.5 \pm 2.4$ $r_2(K_2/K_1) = 0.2 \pm 0.2$		0.90
pClSt-COD-TCNQ	8.5	$r_1 = 8.5$ $r_2 = 0.12$	$r_1(K_1/K_2) = 6.30 \pm 1.2$ $r_2(K_2/K_1) = 0.01 \pm 0.02$	$r_1 = 3.56 \pm 0.68$ $r_2 = 0.02 \pm 0.04$	0.06
CEVE-St[a]			$r_1 = 0.03$ $r_2 = 30.3$		0.91
CEVE-St-MAnh	0.61	$r_1 = 0.61$ $r_2 = 1.64$	$r_1(K_1/K_2) = 0.45 \pm 0.3$ $r_2(K_2/K_1) = 1.83 \pm 0.8$		0.82
CEVE-St-TCNQ	0.16	$r_1 = 0.16$ $r_2 = 6.25$	$r_1(K_1/K_2) = 0.1 \pm 0.3$ $r_2(K_2/K_1) = 9.5 \pm 3.5$	$r_1 = 0.93 \pm 2.78$ $r_2 = 1.03 \pm 0.38$	0.95
CEVE-VAc			$r_1 = 0.15 \pm 0.1$ $r_2 = 2.30 \pm 0.3$		0.35
CEVE-VAc-MAnh	5.23	$r_1 = 5.23$ $r_2 = 0.19$	$r_1(K_1/K_2) = 5.50 \pm 2.0$ $r_2(K_2/K_1) = 0.18 \pm 0.1$		0.99
CEVE-VAc-TCNQ	9.09	$r_1 = 9.09$ $r_2 = 0.11$	$r_1(K_1/K_2) = 10.0 \pm 5$ $r_2(K_2/K_1) = 0.1 \pm 0.1$	$r_1 = 8.06 \pm 4.03$ $r_2 = 0.12 \pm 0.12$	1.00

[a] Monomer reactivity ratios calculated by using Q and e values of CEVE ($Q = 0.036$, $e = -0.91$)[19] and St ($Q = 1.0$, $e = -0.8$). [b] Equilibrium constants, K_{CT}, of the change-transfer TCNQ complex formations were measured in acetonitrile at 10, 20, and 30 °C by using the Benesi-Hildebrand and Scott equations. K_{CT} values at 60 °C were calculated from the observed values of 10, 20, and 30 °C to be 0.24 for the St-TCNQ system, 0.189 for the pClSt-TCNQ system, 0.036 for the DBD-TCNQ system, 0.026 for the CEVE-TCNQ system, 0.021 for the VAc-TCNQ system, and 0.107 for the COD-TCNQ system, respectively.

equal to unity, indicating that the copolymerizations between the two complexes behave as an ideal copolymerization in which the addition of a monomer to an active growing chain end is not influenced by the nature of the monomer unit previously incorporated. It was pointed out previously in the solvent chain-transfer reaction study[14] in the alternating copolymerization between *p*-dioxene and MAnh and also in the terpolymerization study[15] of MAnh–vinyl ether systems that the active growing chain end should have an electron-accepting character rather than an electron-donating one, indicating an acceptor monomer unit. Then, since active growing chain ends in these terpolymerizations are of a common acceptor monomer unit, the copolymerizations between two complexes behave naturally as ideal copolymerizations. Morton[16] pointed out as features of ionic copolymerizations differing from radical ones that, first, the relative reactivities of the two monomers depend largely on the tendency of the substituents to donate or withdraw electrons to or from the double bond and, second, both types of growing chain ions exhibit similar reactivities toward the two monomers, corresponding exactly to an ideal copolymerization. Moreover, as described later, it can be pointed out as a feature of the alternating copolymerization that the reactivity of the alternating copolymerization monomer pairs depends largely on the polarity term of the component monomers and hardly on their resonance term. Therefore, it can be concluded that the alternating copolymerization behaves like an ionic copolymerization rather than a radical copolymerization. The treatment of the free propagating mechanism, of course, can be applied successfully to those terpolymerizations, and the ideal copolymerization behavior can be observed in the treatment of the complex mechanism. It is noteworthy that those terpolymerizations can be analyzed by only one parameter of the relative reactivity ratio, k_{31}/k_{32}, implying evidence for the free propagating mechanism in place of the complex mechanism. However, those terpolymerizations can also be well explained in terms of the complex mechanism. Therefore, it would be a rash conclusion to discriminate against the alternating copolymerization mechanism only from the standpoint of the ideal copolymerization behavior of those terpolymerizations.

As shown in Figures 2–7, an apparent copolymerization behavior between two donor monomers changes interestingly in a somewhat regular fashion, when no acceptor monomer, the weak acceptor monomer such as MAnh, and the strong acceptor monomer such as TCNQ in turn are added. In the complex mechanism, the changes in the copolymerization behavior should correspond to the change in reactivity of the complexes formed between the donor

Table IX
Relative Reactivity of the MAnh, TCNQ, and TMCQ Complexes toward Various Polymer Radicals and That of the Donor Monomers toward MAnh, TCNQ, and TMCQ Terminal Radicals

end-group complex unit	MAnh and TMCQ complexes					
	VAc-MAnh	COD-MAnh	CEVE-MAnh	pClSt-MAnh (pClSt-TMCQ)	St-MAnh	DBD-MAnh (DBD-TMCQ)
(a) Based on Modified Monomer Reactivity Ratios						
pClSt-MAnh		0.22		1	1.23	
St-MAnh	0.06 (0.07)		0.55 (0.6)	0.91 (1)	1 (1.10)	
CEVE-MAnh	0.18 (0.1)		1 (0.55)		2.22 (1.23)	
VAc-MAnh	1 (0.037)		5.56 (0.21)		33.3 (1.23)	
COD-MAnh		1 (0.2)		5.0 (1)		
DBD-TMCQ				0.91 (1)		1 (1.10)
pClSt-TMCQ				1		1.11
order of reactivity of these complexes: VAc-MAnh < COD-MAnh < CEVE-MAnh < pClSt-MAnh < St-MAnh (pClSt-TMCQ < DBD-TMCQ)						

end-group complex unit	TCNQ complexes					
	VAc-TCNQ	COD-TCNQ	CEVE-TCNQ	pClSt-TCNQ	St-TCNQ	DBD-TCNQ
(a) Based on Modified Monomer Reactivity Ratios						
pClSt-TCNQ		0.16		1	1.35	5.0
St-TCNQ	0.052 (0.07)		0.11 (0.15)	0.75 (1)	1 (1.33)	
CEVE-TCNQ	0.1 (0.0135)		1 (0.135)		10 (1.35)	
DBD-TCNQ				0.36 (1)		1 (2.78)
VAc-TCNQ	1 (0.027)		10 (0.27)		50 (1.35)	
COD-TCNQ		1 (0.01)		100 (1)		
order of reactivity of these complexes: VAc-TCNQ < COD-TCNQ ≃ CEVE-TCNQ < pClSt-TCNQ < St-TCNQ < DBD-TCNQ						
(b) Based on Real Monomer Reactivity Ratios						
pClSt-TCNQ		0.28		1	1.06	26.32
St-TCNQ	0.59 (0.63)		0.97 (1.03)	0.94 (1)	1 (1.06)	
CEVE-TCNQ	0.12 (0.12)		1 (0.98)		1.08 (1.06)	
DBD-TCNQ				0.068 (1)		1 (14.7)
VAc-TCNQ	1 (0.24)		8.33 (2.03)		4.35 (1.06)	
COD-TCNQ		1 (0.018)		55.56 (1)		
order of reactivity of these complexes: VAc-TCNQ < COD-TCNQ < CEVE-TCNQ ≃ pClSt-TCNQ ≃ St-TCNQ < DBD-TCNQ						

end-group radical	VAc (0.026, −0.22)[a]	COD (0.03, −0.2)	CEVE (0.03, −0.91)	pClSt (1.03, −0.33)	St (1.0, −0.8)	DBD (5.6, −1.82)
Based on the Ratio k_{31}/k_{32} from the Free Propagating Mechanism						
MAnh radical	0.06	0.20	0.67	1	1.10	
TMCQ radical				1		1.12
TCNQ radical	0.05	0.12	0.2	1	1.25	2.67
order of reactivity of donor monomers: VAc < COD < CEVE < pClSt < St < DBD						

[a] Q,e values in parentheses.

monomers and an acceptor monomer. On the other hand, in the free propagating mechanism it should correspond to the change in the ratio of the rate constants of radical addition reactions of the two donor monomers toward various polymer radicals such as ones with terminal units of the donor, the weak and the strong acceptor monomers. At least, the latter case can be treated theoretically with the Alfrey–Price Q–e scheme,[17] in which the ratio of the rate constants k_{ij} and k_{ik} of the radical addition reactions of monomers j and k to the polymer radical i is expressed as follows:

$$k_{ij}/k_{ik} = (Q_j/Q_k) \exp[-e_i(e_j - e_k)] \quad (14)$$

then

$$r_1 = k_{11}/k_{12} = (Q_1/Q_2) \exp[-e_1(e_1 - e_2)] \quad (15)$$

$$k_{31}/k_{32} = (Q_1/Q_2) \exp[-e_3(e_1 - e_2)] \quad (16)$$

where Q is the general reactivity of monomer and e is the polarity term of the polymer radical and monomer.

In the given pairs of the donor monomers employed in this work, the stronger electron-donating monomer was made to be the first donor monomer and the weaker one the second, meaning that the value of $e_1 - e_2$ is not larger than zero.

Q and e values for the donor monomers, summarized in Table IX, were quoted from Young's Table[18] except for the ones for COD, which were calculated from the copolymerization results between AN and COD.

When the polymerization systems contain, in turn, no acceptor monomer, the weak and the strong ones in addition to a given pair of donor monomers, exponential terms in eq 15 and 16 are predicted to change as follows: (i) for the real copolymerization of two donor monomers without acceptor monomer, values of $-e_1(e_1 - e_2)$ or $-e_2(e_1 - e_2)$ should be negative; (ii) for the terpolymerization with the weak acceptor monomer, values of $-e_3(e_1 - e_2)$ should become positive and, furthermore, when a strong acceptor monomer is used, the positive values become larger. Since the ratio of Q values is constant, the reactivity ratios could be predicted to increase in the order of no acceptor, weak acceptor, and strong acceptor, implying that a relative reactivity of the first (stronger) donor monomer against

the second (weaker) one increases when an acceptor monomer or the stronger acceptor one is added. This predicted tendency of change in relative reactivity can be seen in Figures 2, 3, and 7, but not in Figures 4–6. It can be pointed out in the latter figures that the change in relative reactivity in the time of the addition of an acceptor monomer to two donor monomers does not agree with the theoretically predicted tendency, but the change upon the replacement of the weak acceptor monomer with the strong one agrees well. Besides, the systems of the latter three figures were found out to be composed of conjugate and nonconjugate donor monomers such as the St–VAc, pClSt–COD, and St–CEVE systems. It is well-known that the copolymerization for those systems behaves as a so-called unbalanced copolymerization in which the conjugate monomer with the much larger Q value is incorporated preferentially into the copolymer almost regardless of its e value except for the copolymerization with a strong alternating tendency. When an acceptor monomer is added to those unbalanced copolymerization systems, it is obvious that the reactivities of both donor monomers become so close as to be incorporated into the terpolymer in a more balanced fashion, implying that the reactivity of the donor monomer in the alternating copolymerization is no longer influenced by the general reactivity of the donor monomer itself.

In addition, it was found that the St–CEVE system shows an exceptional change in the copolymerization behavior when the e values of CEVE and St are taken as –0.91[19] and –0.8, respectively. When the strong acceptor monomer was used instead of the weak one, in all other systems of this work the strong donor monomers were found to become more reactive toward the weak ones, this change in reactivity being in agreement with the theoretically predicted tendency mentioned above. The St–CEVE system behaved in an opposite manner. The exception conceivably arises from the polarities, as measured by e values, of St and CEVE. The e values for CEVE and St were reported to be –0.91[19] and –0.8, and their ionization potentials were reported as 8.98[20] and 8.45[21] eV, respectively. The order of these polarity parameters is not consistent. The e value of CEVE was determined from its almost alternating copolymerization with MAnh,[19] resulting in very small values of the two monomer reactivity ratios. Thus, the validity of the e value is questionable. It is better to regard St as a stronger donor monomer than CEVE because of their ionization values and the observed change in the terpolymerization behavior upon replacement of the weak acceptor monomer with the strong one.

It is noteworthy that the change in the copolymerization behaviors of conjugate and nonconjugate donor monomers in copolymerizations with and without the acceptor monomer cannot be explained well by the application of the Alfrey–Price Q–e scheme in the free propagating mechanism for the alternating copolymerization. If the free propagating mechanism were the case, the general reactivity (resonance term) of the individual donor monomers should be effective in the alternating propagating step as well as in the cross-propagating step in the conventional copolymerizations.

It can be pointed out, therefore, that in alternating copolymerization the relative reactivity of the donor monomer is controlled almost exclusively by the polarity term of the donor monomer, whereas in conventional radical copolymerization the monomer reactivity ratios are controlled by both the polarity and the resonance terms of the monomers, indicating one of the characteristic differences between alternating and conventional copolymerizations.

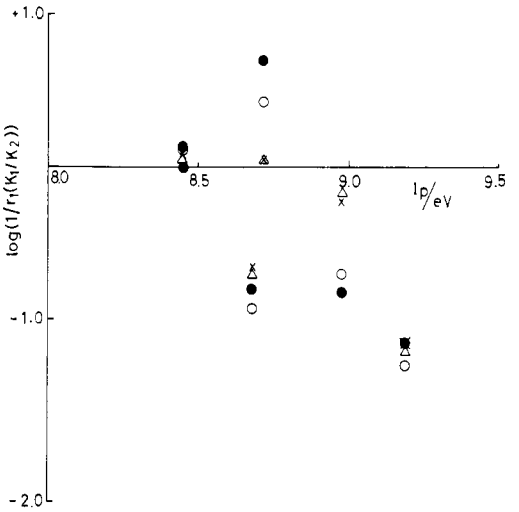

Figure 8. Plot of logarithmic values for the relative reactivity of the complexes or the donor monomers against the ionization potential of the donor monomers. The reactivities are for the MAnh complexes (×) and TCNQ complexes (●) toward the polymer radical with a given terminal complex and those of the donor monomers toward MAnh (△) and TCNQ (○) terminal radicals.

Next, the nature of the relative reactivity of the monomers in alternating copolymerization will be discussed; that is, the monomer reactivity ratios of the complexes in the complex mechanism or the relative reactivity ratios of the donor monomers, k_{31}/k_{32}, in the free porpagating mechanism will be compared with the polarity of the donor monomers.

In the treatment of the complex mechanism the relative reactivity of the second complex toward the polymer radical with a given terminal complex i unit can be obtained as the reciprocal of the monomer reactivity ratio, $1/r_1$, while in the treatment of the free propagating mechanism the relative reactivity of the the donor monomer can be compared with the reactivity ratios, k_{31}/k_{32}, when an acceptor monomer and one donor monomer are common. The relative reactivities of MAnh, TCNQ, and TMCQ complexes toward various polymer radicals and the relative reactivities of the donor monomers toward the polymer radicals with MAnh, TCNQ, and TMCQ terminal units are summarized in Table IX, where the complexes or the donor monomers are arranged in order of the magnitude of the relative reactivities. It is obvious that the found orders of the complexes, represented as their component donor monomers, and also the ones of the donor monomers are similar: VAc < COD < CEVE < pClSt < St < DBD, conceivably being intimately related to the polar characters of the donor monomers. The ionization potentials were reported to be 9.19,[22] 8.98,[20] 8.72,[23] 8.68,[24] 8.45,[21] and 8.45[21] eV for VAc, CEVE, DBD, COD, pClSt, and St, respectively, and e values of –0.20, –0.22,[18] –0.33,[18] –0.8,[18] –0.91,[19] and –1.82[18] were reported for COD, VAc, pClSt, St, CEVE, and DBD, respectively.

Logarithmic values for each relative reactivity of the complexes or the donor monomers are plotted against the ionization potential and e value of the donor monomers in Figures 8 and 9, respectively. It can be concluded, therefore, that the relative reactivities of the complexes or the donor monomers in their alternating copolymerizations are dependent roughly but primarily upon the polar character of the component donor monomers of the complexes or the donor monomers, and the dependence is quite different from that for conventional radical polymerization, where both resonance and polarity terms of

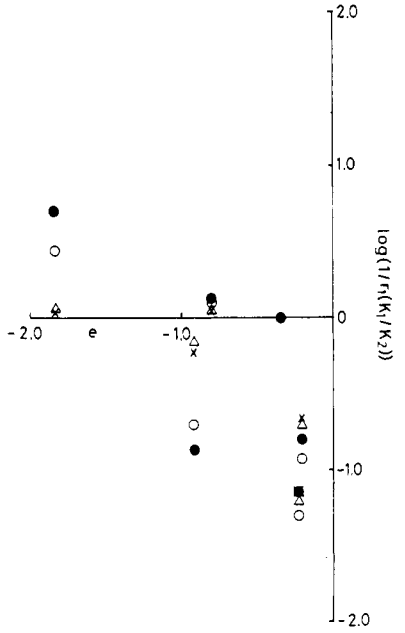

Figure 9. Plot of logarithmic values for relative reactivity of the complexes or the donor monomers against e value. The reactivities are for the MAnh complexes (×) and TCNQ complexes (●) toward the polymer radical with a given terminal complex and those of the donor monomers toward MAnh (△) and TCNQ (○) terminal radicals.

the monomers affect their reactivity. Moreover, in previous works on the alternating copolymerizations containing very powerful acceptor monomers such as TCNQ and $TCNQF_4$, it was found that the rates of their alternating copolymerizations with St are closely related with the electron-accepting character of the acceptor monomers[10] and that so-called acceptor monomers with positive e values such as methyl methacrylate and methyl acrylate are alternatingly copolymerizable with these strong acceptor monomers,[10] leading to the concept that the relative difference in the polar character between donor and acceptor monomers is very important in determining their alternating copolymerization behavior. Combining those findings on the alternating copolymerization, we point out that the alternating copolymerization is exclusively influenced by the polar character of the monomers on its reactivity and is more like an ionic copolymerization than a random radical copolymerization.

The change in the copolymerization behavior of conjugate and nonconjugate donor monomers with and without acceptor monomer should be dramatic. For those so-called unbalanced copolymerizations, the reactivity of the monomers is well-known to be determined exclusively by the general reactivity of the monomers, as reflected in the Q value. On the other hand, for the alternating copolymerization, the copolymerization reactivity is influenced significantly by the polar character of the monomers. Accordingly, when an acceptor monomer is added to the system of the conjugate–nonconjugate donor monomer pair, the great difference in the above-mentioned copolymerization behaviors was considered to be emphasized, compared to systems of conjugate–conjugate or nonconjugate–nonconjugate donor monomer pairs. This difference could not be explained well in terms of the free propagating mechanism, as discussed before, probably favoring the complex mechanism for alternating copolymerization over the free propagating mechanism.

Experimental Section

Materials. TCNQ was prepared according to the method of Acker and Hertler[25] and purified by reacrystallization from ethyl acetate (twice) and sublimation (twice) (mp 294–296 °C). TMCQ was prepared according to the method of Acker and Hertler[25] and Hall and Bentley[26] and purified by recrystallization from a mixture of benzene and hexane (1:2 (v/v)) (mp 154 °C). MAnh was purified by sublimation over phosphorus pentoxide (mp 52.1 °C) and sublimed again just before use. St (bp 53 °C (30 mmHg)), VAc (bp 72 °C), and AN (bp 77 °C) were purified from commercial products by conventional methods. α,α'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. COD was refluxed over calcium hydride for several hours and then distilled (bp 41.0 °C (23 mmHg)). DBD was prepared by the dehydration reaction of pinacol with hydrogen bromide (bp 69.0–71.0 °C).[27,28] CEVE was prepared from the dehydrochlorination reaction of β,β'-dichlorodiethyl ether with sodium hydroxide,[29] refluxed over calcium hydride for several hours, and distilled (bp 108 °C). pClSt was prepared according to the methods of Noller et al.,[30] Iwai et al.,[31] and Overberger et al.[32] (bp 45 °C (25 mmHg)). Acetonitrile was refluxed over phosphorus pentoxide and then distilled at 82.0 °C. Benzene was washed with concentrated sulfuric acid, refluxed over metal sodium, and distilled at 80.0 °C.

Polymerization Procedure. For copolymerizations of donor–donor and AN–COD systems, given amounts of two kinds of monomers, benzene as solvent, and AIBN were placed in an ampule, which was degassed completely by the freeze–thaw method (repeatedly three times) and sealed. The ampule was set in a bath thermostated at 60 °C for the time of polymerization. Then it was opened and the reaction mixture was poured into excess methanol to precipitate the product. For purification, the product obtained was dissolved in chloroform, and the resulting solution was poured into methanol to precipitate the product, which was dried under reduced pressure. For the CEVE–VAc system, benzene and n-hexane were used instead of chloroform and methanol, respectively.

For terpolymerization of donor (1)–donor (2)–acceptor monomer systems, given amounts of the two kinds of donor monomers, the acceptor monomer, solvent such as acetonitrile for TCNQ as an acceptor monomer and benzene for TMCQ and MAnh, and AIBN were placed in an ampule. The subsequent procedure is similar to that of the copolymerization. In the case of MAnh as an acceptor monomer, isopropyl ether instead of methanol was used as precipitant. For purification, the product was dissolved in N,N-dimethylformamide (DMF), and the resulting solution was poured into excess precipitant to precipitate the product. Isopropyl ether was used as precipitant for the product containing the MAnh unit, and methanol was used as precipitant for the product containing the TCNQ unit.

Polymer Characterization. Polymer composition was established by elemental analysis. For the terpolymer containing the MAnh unit, the MAnh unit content was determined by conductometic titration of the hydrolyzed products obtained in alkaline treatment of the terpolymer.[2] The solution viscosity of the copolymers and the terpolymers was determined in chloroform and DMF containing 0.1 wt % lithium chloride, respectively, at 30 °C using an Ostwald viscometer, but tetrahydrofuran was used for the copolymer of the DBD–pClSt system and for the terpolymer of the pClSt–COD–MAnh system and acetone (or DMF) was used for the copolymer of the AN–COD system.

Registry No. AN–COD copolymer, 65759-07-1; St–pClSt copolymer, 62742-92-1; St–pClSt–MAnh copolymer, 86584-21-6; St–pClSt–TCNQ copolymer, 86584-22-7; DBD–pClSt copolymer, 86584-23-8; DBD–pClSt–TMCQ copolymer, 86584-24-9; DBD–pClSt–TNCQ copolymer, 86584-25-0; St–VAc–MAnh copolymer, 26811-58-5; St–VAc–TCNQ copolymer, 86584-26-1; pClSt–COD copolymer, 31938-68-8; pClSt–COD–MAnh copolymer, 86584-27-2; pClSt–COD–TCNQ copolymer, 86584-28-3; CEVE–St–MAnh copolymer, 30111-98-9; CEVE–St–TCNQ copolymer, 86584-29-4; CEVE–VAc copolymer, 86584-30-7; CEVE–VAc–MAnh copolymer, 86584-31-8; CEVE–VAc–TCNQ copolymer, 86584-32-9; St, 100-42-5; pClSt, 1073-67-2; MAnh, 108-31-6; TCNQ, 1518-16-7; DBD, 513-81-5; TMCQ, 65649-20-9; VAc, 108-05-4; COD, 1700-10-3; CEVE, 110-75-8; AN, 107-13-1.

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Structure of *p*-Hydroxybenzoate/Ethylene Terephthalate Copolyester Fibers

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ABSTRACT: X-ray methods are used to investigate the structure of melt-spun fibers of *p*-hydroxybenzoate/ethylene terephthalate copolymers, by analogy with the electron diffraction patterns obtained from single crystals of homopoly(*p*-hydroxybenzoate) [systematic name: poly(1,4-oxybenzoyl)]. The fiber diagrams of copolymers containing 60–80% *p*-hydroxybenzoate are very similar to the electron diffraction patterns of homopolymer single crystals that have been heat treated at 360 °C. These observations indicate that the fibers contain oriented, ordered regions with the same basic structure as the high-temperature form of the homopolymer. These regions probably consist of copolymer sequences rich in hydroxybenzoate, in which some ethylene terephthalate units are present as defects. The data also define the orientation of the chains with respect to the homopolymer crystal morphology. Both the X-ray and electron diffraction data show that the poly(*p*-hydroxybenzoate) chain has a stiff, extended 2_1 helical conformation, with two monomer units repeating in $\sim 12.4 \pm 0.2$ Å, for which a stereochemically acceptable model is presented.

Introduction

Copolymers of *p*-hydroxybenzoate with one or more of a number of aromatic esters are known to form liquid crystalline structures in the melt, and this property can be utilized, e.g., to form high-strength fibers (see, for example, ref 1–8). The homopolymer, poly(*p*-hydroxybenzoate) [systematic name: poly(1,4-oxybenzoyl)], is a crystalline, infusible, intractable polymer,[6,9] and it is necessary to introduce a second component, which is thought to lead to defects in the solid-state structure, thereby lowering the melting point and resulting in a processable material. The present paper describes work by X-ray methods to investigate the structure of copolymers of *p*-hydroxybenzoate and ethylene terephthalate, in which our interpretations are based on electron diffraction studies of poly(*p*-hydroxybenzoate) single crystals. We seek to determine the three-dimensional structure of the copolymer fibers, i.e., how the chains are packed together, and hence to understand why the use of certain copolymerized components leads to better properties.

The *p*-hydroxybenzoate/ethylene terephthalate copolymers are prepared from *p*-acetoxybenzoic acid and poly(ethylene terephthalate) as described by Jackson and Kuhfuss.[5] NMR evidence was presented by these authors in favor of totally random sequences for these copolymers. However, Lenz and Feichtinger[10] have reported the development of blockiness as a result of transesterification in the melt, and Wunderlich and co-workers[11,12] presented optical microscopy and DSC data demonstrating a biphasic structure. We have studied the structure of copolymers containing 60 and 80% *p*-hydroxybenzoate. Jackson and Kuhfuss[5] report an X-ray diffraction maximum at $d = 4.6$ Å for these monomer ratios, which they assign to an ordered poly(*p*-hydroxybenzoate) phase, but no detailed analyses of the structure were made. The structure of the homopolymer, poly(*p*-hydroxybenzoate), is not known at present, although a threefold double-helical conformation has been proposed by Economy et al.,[9] based on limited powder X-ray data for the unoriented polymer. More recently, Hay[13] has performed X-ray and electron diffraction studies for poly(*p*-hydroxybenzoate) and its oriented copolymers and has proposed an orthorhombic unit

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