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

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ABSTRACT: In the terpolymerization of two acceptor monomers such as 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane (TECQ) and maleic anhydride (MAnh) and a common donor monomer such as 2-chloroethyl vinyl ether (CEVE) or *p*-chlorostyrene (ClSt), which can be regarded as a combination of a pair of alternating copolymerization systems, it was found that in the case of CEVE as a common acceptor monomer TECQ is about 9 times as reactive as MAnh. In the case of ClSt, more electron donating than CEVE, TECQ is about 30 times as reactive as MAnh, indicating that reactivity of the acceptor monomers in alternating copolymerization is actually influenced by an electron-donating character of donor monomers in addition to their electron-accepting character. A reasonable concept for alternating copolymerization was proposed.

A terpolymerization technique has permitted us to find out the unusual characteristics of a radical alternating copolymerization.[1-3] Recently, a so-called alternating terpolymerization was studied in detail of two donor and one common acceptor monomers, conceivably equivalent to a combination of a pair of alternating copolymerization systems with a common acceptor monomer, to obtain some interesting features of an alternating copolymerization.[4] It was pointed out that in an alternating copolymerization the monomer reactivity is controlled much more with the polarity and much less with the general reactivity than in a random radical copolymerization, in which the monomer reactivity is influenced with both the polarity and the general reactivity in a well-known manner.[5] Moreover, it was interestingly discovered in the terpolymerization using various common acceptor monomers that a content ratio of the two donor monomer units incorporated into terpolymers is dependent markedly upon the electron-accepting property of the common acceptor monomer, the stronger electron-accepting property of the common acceptor monomer resulting in a higher content ratio of the strong to weak donor monomer units in the terpolymers, suggesting that the difference in reactivity between the strong and the weak donor monomers becomes greater when the stronger common acceptor monomer is used.

On the other hand, terpolymerization with another monomer combination, i.e., two acceptor and one common donor monomers, has been studied only in two systems, maleic anhydride (MAnh)–sulfur dioxide–1,3-butadiene[6] and MAnh–fumaronitrile–2-chloroethyl vinyl ether (CEVE),[7] but they did not involve detailed experiments using various common donor monomers. The alternating terpolymerization of this monomer combination should also provide us with useful information about the mechanism and reactivity of a radical alternating copolymerization. Alternating copolymerizable acceptor monomers are very few compared to corresponding donor ones if electron-accepting quinodimethane and quinone compounds are included,[8] and it is not easy to find a pair of copolymerizable acceptor monomers with similar reactivities toward a common donor monomer. When two acceptor monomers with slightly different reactivities and a common donor monomer are polymerized together, most polymers obtained are two-component polymers composed of the higher reactive acceptor and the donor monomer instead of a three-component polymer,[3] the less reactive acceptor monomer being unable to be incorporated into the polymer.

7,7,8,8-Tetrakis(ethoxycarbonyl)quinodimethane (TECQ) was found to be alternating copolymerizable with donor monomers such as styrene and vinyl ethers and also to be the weakest in electron-accepting character among the electron-accepting quinodimethane compounds[8] polymerizable as acceptor monomers, being approximately equivalent to MAnh.

In this work was studied the terpolymerization of TECQ, MAnh, and common donor monomers such as CEVE and *p*-chlorostyrene (ClSt), and a reasonable concept about the reactivity of the alternating copolymerization was proposed.

Experimental Section

Materials. TECQ was prepared according to the method described previously.[8] MAnh was purified just before use by subliming the mixture of the commercial product with phosphorus pentoxide. ClSt was prepared from monochlorobenzene and acetyl chloride according to the methods of Nollar et al.,[9] Iwai et al.,[10] and Overberger et al.[11] CEVE was prepared by dehydrochlorination of 2,2′-dichloroethyl ether with sodium hydroxide.[12] Tetracyanoethylene (TCNE) and *N*,*N*-diethylaniline (DEA) was purified from the commercial products by sublimation and by distillation under nitrogen atmosphere, respectively. α,α'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Benzene, cyclohexane, and dichloromethane were purified from the commercial products by the respective conventional methods.

Polymerization Procedure. Given amounts of TECQ, MAnh, a common donor monomer such as CEVE or ClSt, AIBN as free-radical initiator, and benzene as solvent were placed in an ampule, which was degassed completely by the freeze–thaw method (repeated 3 times) and sealed. The ampule was set in a bath thermostated at 60 °C for the time of polymerization and opened. The reaction mixture was poured into excess isopropyl ether to precipitate the terpolymer. For purification, the terpolymer obtained was dissolved in a small amount of chloroform and the resulting solution was poured again into excess isopropyl ether to precipitate the terpolymer, which was dried under reduced pressure.

Polymer Characterization. The terpolymer composition was established by elemental analysis. The molecular weight ($\bar{M}_n$) of the terpolymer was determined by gel permeation chromatography (GPC) using standard polystyrenes as the reference and tetrahydrofuran as the eluent. Solution viscosity of the terpolymer was determined at 30 °C by using the Ostwald viscometer and chloroform as the solvent.

Charge-Transfer Absorption Band. Absorption spectra of the charge-transfer transition for the TECQ–DEA, MAnh–DEA, ClSt–TCNE, and CEVE–TCNE systems were taken at room temperature in benzene for the former two systems and in a mixture of cyclohexane with dichloromethane (9/1 by volume) for the latter two, respectively. The concentrations of solutions employed were as follows: [TECQ] = 1.0×10^{-2} mol/L and [DEA] = 2.12 mol/L for the TECQ–DEA system, [MAnh] = 1.0×10^{-2} mol/L and DEA = 0.30 mol/L for the MAnh–DEA system, and [ClSt] = [CEVE] = 0.1 mol/L and [TCNE] = 1.0×10^{-3} mol/L for the ClSt–TCNE and CEVE–TCNE systems.

Results and Discussion

Electron-Accepting Character of TECQ and MAnh and Electron-Donating Character of ClSt and CEVE.

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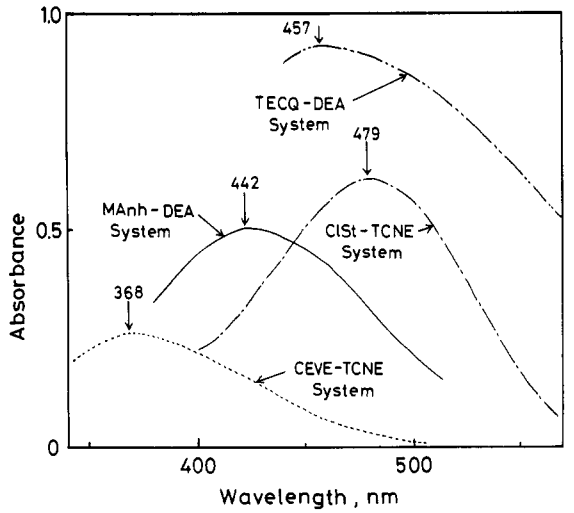

Figure 1. UV–vis difference spectra of the TECQ–DEA and MAnh–DEA systems in a mixture of cyclohexane and dichloromethane (9/1 by volume) at room temperature.

The polar property of TECQ, MAnh, ClSt, and CEVE was evaluated by measurement of the charge-transfer transition absorption band with a standard donor or acceptor compound. Absorption maxima of the charge-transfer transition for the TECQ–DEA, MAnh–DEA, ClSt–TCNE, and CEVE–TCNE systems were observed at 457, 422, 479, and 369 nm, respectively, as shown in Figure 1. The absorption maximum for the TECQ–DEA system appears at a wavelength longer than that for the MAnh–DEA system, implying that TECQ is stronger in electron-accepting character than MAnh. From the well-known relationship,[13] $h\nu_{CT} = IP - EA + C$, where ν_{CT} refers to absorption maximum in wavenumber of the charge-transfer transition band, EA the electron affinity of the acceptor compound, and IP the ionization potential of the donor compound, EA of TECQ could be estimated numerically to be 2.27 eV on the basis of the EA value of 1.33 eV[14] for MAnh.

The charge-transfer transition maximum for the ClSt–TCNE system appears at a wavelength longer than that for the CEVE–TCNE system, implying that ClSt is stronger in electron-donating character than CEVE. From the equation, $IP = h\nu_{CT} + 5.84$, derived by Ledwith and Woods[15] using the IP value of 8.93 eV for methyl vinyl ether as a standard. IP values for ClSt and CEVE could be estimated to be 8.43 and 9.20 eV, respectively.

Terpolymerizations of the TECQ–MAnh–CEVE and TECQ–MAnh–ClSt Systems. TECQ and MAnh are not homopolymerizable by free-readical initiation and also are not copolymerizable with each other at all. When a donor monomer such as St or vinyl ether was added to the acceptor monomer pair, radical polymerization took place readily to yield the terpolymer composed of the two acceptor and the donor monomer units.

Tables I and II summarize the results of terpolymerizations of the TECQ–MAnh–CEVE and TECQ–MAnh–ClSt systems, respectively. The terpolymers of both systems were always composed of about 50 mol % of the common donor monomer unit such as CEVE and ClSt, regardless of the monomer feed ratio, the sum of TECQ and MAnh unit contents being about 50 mol %. The terpolymerization composition of these systems can be illustrated completely as a binary copolymerization composition diagram between TECQ and MAnh, shown in Figure 2. According to the treatment of complex mechanism,[7] the apparent monomer reactivity ratios of the complexes were calculated to be $r_1(K_1/K_2)$(TECQ–CEVE complex) = 9.0 ± 0.8 and $r_2(K_2/K_1)$(MAnh–CEVE com-

Table I
Terpolymerization[a] of the TECQ–MAnh–CEVE System in Benzene at 60 °C

run no.	monomer feed, mg			monomer feed, mol %			polym time, h	conv, %	anal			polym. compn. mol %			$M_n^b/10^3$	k_{31}/k_{32}^c		
	TECQ	MAnh	CEVE	TECQ	MAnh	CEVE			% H	% C	% Cl	TECQ	MAnh	CEVE		(1)	(2)	(3)
1	76.8	178.2	223.2	4.8	44.2	51.0	28.5	12.2	5.20	53.22	11.19	19.0	31.0	50.0		5.65	5.62	5.62
2	99.4	145.1	110.6	9.1	53.4	37.5	28.1	11.3	5.75	55.66	9.11	31.5	18.5	50.0		10.00	10.02	10.02
3	130.1	134.6	78.1	13.6	56.3	30.1	27.4	7.1	5.91	56.51	8.30	37.9	12.0	50.1	7.3	12.82	13.12	13.06
4	134.5	111.7	154.0	11.7	38.9	49.4	27.7	7.2	5.49	56.03	8.71	34.1	16.3	49.7	8.2	7.30	6.81	6.95
5	134.5	109.5	150.0	12.0	39.0	49.0	37.8	9.0	5.72	56.30	8.49	36.2	13.8	50.0		8.55	8.51	8.51
6	149.9	117.2	71.5	17.0	53.2	29.8	25.3	8.3	6.28	56.65	8.19	39.1	10.6	50.3	8.5	10.99	11.70	11.53
7	133.1	80.1	134.3	14.0	33.8	52.2	20.5	11.5	5.94	56.52	8.30	38.0	11.9	50.1		7.58	7.75	7.71
8	130.5	76.5	130.8	14.2	33.3	52.5	37.8	9.8	5.79	56.46	8.34	37.5	12.5	50.0	18.0	7.04	7.04	7.04
9	149.8	71.6	117.7	17.2	33.0	49.8	46.5	10.3	5.73	57.01	7.82	42.3	7.7	50.0		10.53	10.55	10.54
10	151.2	68.0	120.2	17.5	31.4	51.1	20.0	11.3	5.86	56.99	7.83	42.0	8.3	49.7		9.80	8.96	9.08
11	199.1	69.6	82.0	25.6	35.7	38.7	20.3	13.0	5.84	57.30	7.52	45.0	5.4	49.6		13.70	11.42	11.62
av[d]																9.45	9.23	9.24

[a] AIBN, 3 mg. Solvent, 2 mL. [b] Determined by GPC. [c] Calculated by using the following equations in the free propagating mechanism treatment:[7,16] $m_3/m_1 = 1 + (k_{32}/k_{31})([M_2]/[M_1])$ (1), $m_3/m_2 = 1 + (k_{31}/k_{32})([M_1]/[M_2])$ (2), and $m_1/m_2 = (k_{31}/k_{32})([M_1]/[M_2])$ (3), where the m_1, m_2, and m_3 are the mole fractions of M_1, M_2, and M_3 units in the terpolymer, respectively, and $[M_1]$ and $[M_2]$ are the initial concentrations of acceptor monomers M_1 and M_2, and $[M_3]$ that of a common donor monomer, M_3. k_{ij} is a rate constant of the reaction of an active growing chain end $\sim m_i^*$ with monomer M_j. [d] Grand average is 9.31.

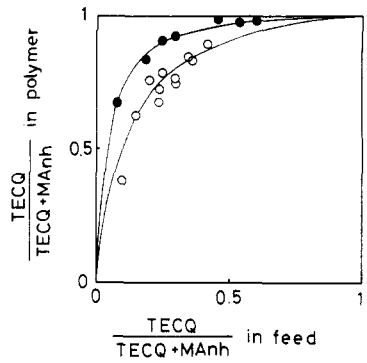

Figure 2. Composition diagrams of the terpolymerizations of the TECQ–MAnh–CEVE (○) and TECQ–MAnh–ClSt (●) systems as a binary copolymerization between TECQ and MAnh. The lines were calculated by using $r_1(K_1/K_2) = 9.0$ and $r_2(K_2/K_1) = 0.09$ for the TECQ–MAnh–CEVE system and $r_1(K_1/K_2) = 26$ and $r_2(K_2/K_1) = 0.034$ for the TECQ–MAnh–ClSt system.

plex) = 0.09 ± 0.08 for the TECQ–MAnh–CEVE system and to be $r_1(K_1/K_2)$(TECQ–ClSt complex) = 26 ± 3 and $r_2(K_2/K_1)$(MAnh–ClSt complex) = 0.034 ± 0.010 for the TECQ–MAnh–ClSt system. The products of the modified monomer reactivity ratios, $r_1(K_1/K_2)r_2(K_2/K_1)$, are 0.81 for the TECQ–MAnh–CEVE system and 0.88 for the TECQ–MAnh–ClSt system, being close to unity, indicating that the copolymerizations of two complexes for both systems take place approximately in an ideal manner and consequently that the alternating copolymerizations can be regarded to occur in a manner similar to an ionic copolymerization rather than a radical copolymerization, as discussed previously in the terpolymerizations of two donor and one common acceptor monomers.[4] The treatment of free propagating mechanism[7,16] can be successfully applied to both terpolymerizations due to their ideal behavior.

The relative reactivities in the alternating copolymerization could be quantitatively compared on the basis of the reciprocals of the monomer reactivity ratios of the same complex to other complexes in the case of the complex mechanism or the relative reactivity ratio, k_{31}/k_{32}, of the acceptor monomers in the case of free propagating mechanism.

For the TECQ–MAnh–CEVE system, relative reactivities ($1/r_1$) in the treatment of the complex mechanism of 1 for the TECQ–CEVE complex and 1/9 for the MAnh–CEVE complex toward the polymer radical with a terminal TECQ-CEVE unit and 1/0.09 for the TECQ–CEVE complex and 1 for the MAhn–CEVE complex toward the polymer radical with a terminal MAnh-CEVE unit were obtained, suggesting that the TECQ–CEVE complex is about 10 times as reactive as the MAnh–CEVE complex toward both polymer radicals with terminal complex units, TECQ–CEVE and MAnh–CEVE. An average value of the relative reactivity ratios, k_{31}/k_{32}, of 9.31 was obtained in the treatment of the free propagating mechanism as shown in Table I, indicating that TECQ reacts with the polymer radical with a CEVE terminal unit about 9.31 times as fast as MAnh does. Anyway, TECQ is more reactive than MAnh by a factor of about 10 as an acceptor monomer in the alternating copolymerization with CEVE.

For the TECQ–MAnh–ClSt system, in the treatment of the complex mechanism, relative reactivities of 1 for the TECQ–ClSt complex and 1/26 for the MAnh–ClSt complex toward the polymer radical with a terminal TECQ–ClSt unit and 1/0.034 for the TECQ–ClSt complex and 1 for the MAhn–ClSt complex toward the polymer radical with a terminal MAnh–ClSt unit were obtained, and in the treatment of the free propagating mechanism, an average value of the relative reactivity ratio, k_{31}/k_{32}, was found to

Table II
Terpolymerization[a] of the TECQ–MAnh–ClSt System in Benzene at 60 °C

run no.	monomer feed, mg			monomer feed, mol %			polym time, h	conv, %	anal.			polym. compn, mol %			η_{sp}/c,[b] dL·g^{-1}	k_{31}/k_{32}[c]		
	TECQ	MAnh	CEVE	TECQ	MAnh	CEVE			% H	% C	% Cl	TECQ	MAnh	ClSt		(1)	(2)	(3)
1	70.3	209.7	299.1	4.0	47.8	48.2	4.0	9.2	4.12	62.88	8.17	33.5	16.6	49.9		24.39	23.88	24.02
2	100.9	113.3	160.2	10.0	45.0	45.0	2.1	7.6	5.61	63.21	7.62	40.6	8.2	51.2	0.56	17.24	23.62	22.30
3	133.3	99.8	141.6	14.3	42.8	42.9	4.0	13.0	4.74	63.26	7.16	44.8	4.6	50.6		23.20	29.94	29.16
4	152.6	90.8	124.7	17.6	41.8	40.6	2.8	11.0	5.66	63.29	7.15	45.3	3.9	50.8	0.45	19.63	28.56	27.59
5	169.4	50.3	62.3	31.0	36.8	32.2	7.0	10.6	6.43	63.13	6.14	52.4	0.6	47.0	0.28	−11.52	91.84	103.72
6	202.2	43.7	76.5	34.0	29.5	36.5	4.3	9.5	5.89	63.31	6.80	48.5	1.4	50.1		26.30	30.17	30.05
7	278.5	44.6	96.7	37.2	24.8	38.0	4.5	11.0	5.73	63.70	8.00	43.1	1.0	55.9		2.25	36.60	28.73
av[e]																18.84[d]	37.80	37.94

[a] AIBN; 1 mg. Solvent, 5 mL. [b] Solvent, chloroform. Temperature, 30 °C. [c] Calculated by using the equations described in footnote *c* of Table I. [d] Calculated except for run no. 5. [e] Grand average is 31.53.

be 31.5 as shown in Table II, implying that TECQ reacts with the polymer radical with a ClSt terminal unit about 31.5 times as fast as MAnh does. Anyhow, TECQ is much more reactive than MAnh by a factor of about 30 as the acceptor monomer in the alternating copolymerization with ClSt. It can be pointed out, therefore, in comparing both these terpolymerizations that when a donor monomer is replaced from CEVE (IP = 9.20 eV) to ClSt(IP = 8.80 eV)), the reactivity ratio of TECQ to MAnh changes significantly from about 10 to about 30, indicating that a reactivity of acceptor monomers in the alternating copolymerization is actually influence by an electron-donating character of the donor monomer.

Consequently, it is concluded that the reactivity of the acceptor monomers in the alternating copolymerization is determined not only by their own electron-accepting character but also by the electron-donating character of donor comonomers.

Already it has been mentioned as a feature of alternating copolymerization on the basis of the alternating copolymerizations of TCNQ with comonomers such as methyl methacrylate,[17] methyl acrylate,[17] and even TECQ[18] that the polarity of these monomers is able to be switched with the nature of the counter monomers, i.e., St and and TCNQ and the polar effect of the monomers is determined on a relative scale with the difference in electron density (polarity) between a pair of alternating copolymerizable monomers, substantially different from that in the Alfrey–Price Q,e scheme, where the polarity of monomer is determined on an absolute scale.

First an impromptu idea occurred to us on the manner that the reactivity of an alternating copolymerization is correlated to the electron density of the monomers; i.e., the reactivity would be related linearly to the difference in the electron density between donor and acceptor monomers. This idea may reasonably hold for all experimental results in alternating copolymerization but does not for the results of alternating terpolymerization experiments using various common donor or acceptor monomers. This idea says that when a common donor or acceptor monomer is replaced with one of stronger polar character, the differences in electron density between a common donor or acceptor monmer and a pair of residual acceptor or donor monomers should be larger, while the ratio of these two differences in electron density (i.e., the ratio of the difference between the common polar monomer and the more counterpolar comonomer to the difference between the common polar monomer and the less counterpolar comonomer) has to be smaller to approach unity, implying that reactivities of the two alternating copolymerizations are predicted to become alike, which is apparently contrary to the experimental results.

A better idea, which meets all of the experimental results, is that a charge-transfer type interaction takes place between the donor and acceptor monomers and its intensity relates to an amount and a degree of the dative bond structure in which a Coulomb force type of an interaction should take place between the cation radical and anion radical species. The greater difference in electron density (polar character) between the donor and acceptor monomers may allow them to be subject to the stronger charge-transfer type interaction arising from the greater contribution of the dative bond structure in which the stronger Coulomb force exerts. Presumedly, the Coulomb force type of interaction contributes to the reactivity in the alternating copolymerization in a manner similar to the polar term in the Alfrey–Price Q,e scheme. Here in place of the e value in the Alfrey–Price Q,e scheme, a value should be taken in connection with the difference in electron density, and the polar effect between donor and acceptor monomers should be expressed in terms of the product of the values. This idea could not yet be constructed in a quantitative expression. However, this idea might be successfully applied to all of the alternating copolymerization and terpolymerization results even if in a qualitative sense.

In summary, it can be mentioned that an alternating copolymerization is controlled much more with a polar effect of component monomers and much less with their general reactivity (resonance) effect compared to a conventional random copolymerization and further that its polar effect is reasonably related to an interaction somewhat similar to a Coulomb force type of interaction taking place within the dative bond structure of the charge-transfer complex between the donor and acceptor monomers.

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