Air Development Center (NADC) Contract No. N62269-87-C-0261 and by an equipment grant from the General Electric Foundation.

References and Notes

(1) Wolfe, J. F. In *Encyclopedia of Polymer Science and Engineering*, Vol. 11, 2nd ed.; Wiley: New York, 1988; pp 601–635.

(2) (a) Wolfe, J. F.; Arnold, F. E. *Macromolecules* **1981**, *14*, 909–915. (b) Wolfe, J. F.; Boo, B. H.; Arnold, F. E. *Macromolecules* **1981**, *14*, 915–920.

(3) Wolfe, J. F.; Bitler, S. P. In *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., Ulrich, D. R., Eds.; Plenum: New York, 1988; pp 401–413.

(4) (a) Helminiak, T. E. *Prepr.—Am. Chem. Soc., Div. Org. Coat. Plast.* **1979**, *40*, 475. (b) Helminiak, T. E.; Arnold, F. E.; Benner, C. L. *Polym. Prepr.* **1975**, *16*(2), 659.

(5) Choe, E. W.; Kim, S. N. *Macromolecules* **1981**, *14*, 920–927.

(6) (a) Chu, S.-G.; Venkatraman, S.; Berry, G. C.; Einaga, Y. *Macromolecules* **1981**, *14*, 939. (b) Berry, G. C.; Cotts, P. M.; Chu, S.-G. *Br. Polym. J.* **1981**, *13*, 47.

(7) Chow, A. W.; Sandell, J. F.; Wolfe, J. F. *Polymer* **1988**, *29*, 1307–1312.

(8) Tsai, T.-T.; Arnold, F. E. *Polym. Prepr.* **1988**, *29*(2), 324–325.

(9) DePra, P. A.; Gaudiello, J. G.; Marks, T. J. *Macromolecules* **1988**, *21*, 2295–2297.

(10) Rao, D. N.; Swiatkiewicz, J.; Chopra, P.; Ghoshal, S. K.; Prasad, P. N. *Appl. Phys. Lett.* **1986**, *48*, 1187–1189.

(11) Jenekhe, S. A.; Johnson, P. O.; Agrawal, A. K. *Polym. Mater. Sci. Eng.* **1989**, 60, 404–409 and manuscript in preparation.

(12) Berry, G. C.; Metzger, P. C.; Venkatraman, S.; Cotts, D. B. *Polym. Prepr.* **1979**, *20*(1), 42.

(13) Morgan, P. W. *Macromolecules* **1977**, *10*, 1381–1390.

(14) Planar, M.; Beste, L. F. *Macromolecules* **1977**, *10*, 1401–1406.

Modified Hammett Treatment on Copolymerizations of 7,8-Dibenzoyl- and 7,8-Bis(butoxycarbonyl)-7,8-dicyanoquinodimethane with Para-Substituted Styrenes: Differences between Alternating and Random Copolymerizations

Shouji Iwatsuki,* Takahito Itoh, Tatsuya Higuchi, Miyuki Yamada, and Katsuyuki Enomoto

Department of Chemical Research for Resources, Faculty of Engineering Mie University, Kamihama-cho, Tsu, 514, Japan.

Received May 27, 1988;
Revised Manuscript Received January 25, 1989

ABSTRACT: Copolymerizations of 7,8-dibenzoyl- (BzCQ) and 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ) with five kinds of para-substituted styrenes were carried out under a few different polymerization conditions considering the equilibrium monomer concentration of BzCQ or BCQ. The monomer reactivity ratios obtained were analyzed by the modified Hammett equation of Yamamoto and Otsu to determine the polar and resonance reaction constants of the cross-propagation steps in these copolymerizations. On the basis of these results is discussed the mechanism of the cross propagations in the copolymerizations.

Recently it was found out that some quinodimethane compounds with two different groups at the 7,8 positions such as 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethane (1),[1,2] 7,8-diacyl-7,8-dicyanoquinodimethane (2),[3] and 7,8-bis(alkylthio)-7,8-dicyanoquinodimethane[4] are obtainable as stable crystals at room temperature and also are homopolymerizable with radical and other initiators in spite of being very highly conjugative. In the previous work[5] it was reported that 1 and 2 undergo typical of equilibrium polymerization with characteristic thermodynamic parameters of polymerization. Their values of entropy of polymerization are a third as large as those of conventional vinyl compounds, which generally exhibit values of entropy of polymerization in a given range of 100–130 J/(K·mol), and those of enthalpy of polymerization also lie in a low level from 21.6 to 26.4 kJ/mol, resulting in a negative but small free energy of polymerization. As another interesting feature of their polymerization behaviors it was found in their copolymerizations with styrene (St) that when their monomer concentrations in feed are higher than their respective equilibrium monomer concentrations, their copolymerizations are in a random fashion, whereas when the concentrations are lower than the equilibrium concentration, their copolymerizations change from a random to an alternating fashion. On the basis of this finding, a new mechanism[5] for alternating copolymerization has been proposed that when the more highly conjugative monomer between a pair of monomers loses its homopolymerizability due to participation of its depolymerization, their copolymerizations become alternating, and that the very stable and unreactive polymer radical with the terminal unit of the more conjugative monomer undergoes a bare cross propagation under the favor of a strong charge-transfer interaction with the comonomer such as St, conceivably composing the rate-determining process of an alternating copolymerization.

Moreover, in the previous studies of the terpolymerizations among two donor and a common acceptor monomers[6] and among two acceptor and a common donor monomers,[7] which can be regarded as combination of a pair of alternating copolymerization systems, it was pointed out that an alternating copolymerization is controlled much more with polar effect of component monomers and much less with general reactivity (resonance) effect compared to conventional random copolymerization.

Therefore, it was considered to be interesting and significant that the cross-propagation steps in copolymerizations of 1 and 2 with St would be investigated by the linear free energy principle to attain characteristics of an alternating copolymerization in a quantitative sense.

In this work were studied the copolymerizations of 7,8-dibenzoyl-7,8-dicyanoquinodimethane (BzCQ) and 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ) with five kinds of para-substituted styrenes under some polymerization conditions considering the equilibrium monomer concentrations of BzCQ and BCQ, to obtain the monomer reactivity ratios, which were treated by the modified Hammett equation of Yamamoto and Otsu[8] to determine the polar and resonance reaction constants of their cross propagations.

Experimental Section

Monomers. BzCQ[3] and BCQ[2] were prepared according to the methods reported previously. As para-substituted styrenes, styrene (St), *p*-chlorostyrene (ClSt), *p*-methylstyrene (MeSt), *p*-methoxystyrene (MeOSt), and methyl *p*-vinylbenzoate (MeO_2CSt) were employed. MeO_2CSt was prepared according to the method of Emerson et al.[9] Other para-substituted styrenes commercially available were purified by each conventional method.[10]

Other Materials. 2,2′-Azobis(isobutyronitrile) (AIBN) as free-radical initiator was recrystallized from ethanol. Chloroform as solvent was refluxed over calcium hydride for 24 h and distilled.

Polymerization Procedure. In an ampule were placed given amounts of BzCQ or BCQ, para-substituted styrene, AIBN, and chloroform, and two drops of acetic acid was added to inhibit an anionic polymerization of BzCQ or BCQ. Amounts of chloroform as solvent were determined by taking into consideration of weight and density of BzCQ or BCQ and para-substituted styrenes to attain fixed concentrations of BzCQ or BCQ. The ampule was degassed by the freeze–thaw method (repeatedly three times) and sealed. It was set in a bath thermostated at 50 or 60 °C for the time of polymerization and unsealed. Its contents were poured into an excess of hexane to deposit the product, which was dissolved in small amount of dichloroethane. Its solution was poured again into an excess of hexane to deposit the product. The dissolution–precipitation process was carried out more than three times for purification. The purified product was dried under reduced pressure until a constant weight was achieved. The composition of the copolymer obtained was established by elemental analysis. The number-average molecular weight of the copolymer was determined by gel permeation chromatography using tetrahydrofuran (THF) as eluent, standard polystyrenes as reference, and a series of four columns, TOSOH G6000H, G4000H, G3000H, and G2500H.

Results and Discussion

Copolymerizations of BzCQ with five kinds of para-substituted styrenes were carried out at 60 °C in chloroform with two BzCQ monomer concentrations, 42 and 21 mmol/L, which were determined by taking into accounts the equilibrium monomer concentration of BzCQ of 36.6 mmol/L at 60 °C.[5] This difference in monomer concentration corresponds to the difference of 1.9 kJ/mol in free energy of polymerization for BzCQ. Their results are summarized in Table I. The results of the same copolymerizations at 50 °C with 21 mmol/L BzCQ monomer concentration are summarized in Table II. The difference between 50 and 60 °C under the monomer concentration corresponds to 0.4 kJ/mol of free energy of polymerization for BzCQ, almost one-fifth as large as that of the above-mentioned difference in monomer concentration.

Copolymerizations of BCQ with five kinds of para-substituted styrenes were carried out at 60 °C in chloroform with two BCQ monomer concentrations, 33 and 5 mmol/L, which were fixed as above and below the BCQ equilibrium monomer concentration of 6.5 mmol/L at 60 °C, respectively.[3] Their results are compiled in Table III. It is obvious from the shapes of these copolymerization curves that all of these copolymerizations are in a random fashion. Their results were analyzed according to cross section,[11] integral equation,[11] and Kelen–Tüdös methods[12] to obtain the monomer reactivity ratios as summarized in Table IV. It is obvious in the case of the decrease of the monomer concentration of BzCQ or BCQ from above the equilibrium monomer concentration to below one that the r_1 values decrease definitely while the r_2 values remain almost unchanged. It is conceivable as one of the main reasons that BzCQ or BCQ remarkably loses the homopolymerizability due to the serious participation of depolymerization to result in the decrease of r_1 values. On the other hand, in the case of the increase of polymerization from 50 to 60 °C both values of r_1 and r_2 were found to come close to unity as observed often in conventional radical copolymerization. Because the change of polymerization energy for BzCQ due to this polymerization-temperature change is only about 3 times smaller than that due to the above-mentioned monomer concentration change, thermodynamic change of the conventional radical copolymerization was considered to predominate over an influence of depolymerization.

The best known and most widely studied linear free energy relationship is the Hammett equation[13]

$$\log (k/k_0) = \rho\sigma \qquad (1)$$

where k is the rate constant of the reaction of a substituted compound, k_0 is the value for the unsubstituted substance, σ is a constant characteristic of the substituent, generally referred to as the Hammett substituent constant, and ρ is a constant for the particular reaction and is a measure of the sensitivity of the reaction to substituent change, informing us of the nature of transition state of the reaction. The equation originally was based on the ionization of substituted benzoic acids in water at 25 °C, for which $\rho = 1.00$, and k_0 is the equilibrium dissociation constant for the unsubstituted acid.

To apply the linear free energy relationship to a radical addition reaction, Yamamoto and Otsu[8,14] proposed the modified Hammett equation

$$\log (k/k_0) = \rho\sigma + \gamma E_R \qquad (2)$$

where E_R is a resonance substituent constant and γ is a resonance reaction constant for the particular radical addition reaction, whereas ρ is referred to a polar reaction constant. E_R values were estimated from the chain-transfer reaction of para-substituted cumenes in styrene radical polymerization in which appropriate E_R values were fixed to allow the plot of [log (k/k_0) − E_R] versus Hammett σ constants of substituents to be a straight line from the slope of which the ρ value was given to be −0.70, whereas the Hammett plot of log (k/k_0) versus the σ values gave not a straight line but a concave curve. In copolymerizations between para-substituted styrenes and St, the cross-propagation steps of the polymer radical with terminal St unit toward para-substituted styrenes were successfully analyzed with eq 2 to give $\rho = 0.60$ and $\gamma = 1.4$,[8] while the other cross-propagation steps of the polymer radicals with terminal para-substituted styrene unit toward St gave a straight line in the treatment of the original Hammett equation (1),[15] suggesting that rate-determining transition states of these cross propagations should be very close to the product radical structure.

In copolymerizations between BzCQ(M_1) and para-substituted styrenes, the reactivity, k_{12}, of para-substituted styrenes toward the polymer radical with a terminal BzCQ unit is evaluated as values of $1/r_1$, which are plotted against Hammett σ values of para substituents as shown in Figure 1a. The corresponding plots in copolymerizations between BCQ(M_1) and para-substituted styrenes are shown in Figure 2a. Both plots apparently do not give straight lines but compose concave curves, indicating that the cross propagations under consideration are quite beyond eq 1. The reactivities were treated by eq 2 using E_R values of Yamamoto and Otsu[16] and σ values[17] for para substituents. Appropriate γ_1 values were fixed for the plots of [log $(1/r_1)$ − $\gamma_1 E_R$] versus σ to provide good straight lines as shown in Figure 3a and 4a, where slopes of these straight lines

Table I
Copolymerizations[a] of BzCQ with Para-Substituted Styrenes in $CHCl_3$ at 60 °C

run no.	monomer feed, mmol BzCQ	monomer feed, mmol *p*-subst styr	BzCQ, mol %	solvt, mL	time, h	conv, %	copolym comp (BzCQ), mol %	$10^{-3}\bar{M}_n$[b]
				MeOSt				
1	0.0944	1.6325	5.5	2.0	0.3	8.4	29.9	11.0
2	0.1323	1.0861	10.9	3.0	0.3	9.5	34.1	10.0
3	0.1939	0.7126	21.4	4.5	0.5	11.6	44.0	10.0
4	0.2961	0.3958	42.5	7.0	0.5	8.5	62.7	8.6
5	0.3202	0.3263	49.5	7.5	0.5	9.6	65.2	10.0
6	0.4017	0.2168	65.0	9.5	0.5	9.3	65.3	11.0
				MeSt				
7	0.0919	1.9290	4.6	2.0	1.0	9.0	42.8	12.8
8	0.1239	1.3290	8.5	3.0	1.5	8.0	49.4	12.5
9	0.1959	0.9421	17.2	4.5	1.5	6.8	66.2	13.0
10	0.2575	0.6951	27.0	6.0	1.5	6.7	81.0	13.0
11	0.3362	0.4017	45.6	8.0	1.8	7.2	86.0	13.0
12	0.4110	0.3859	51.6	10.0	2.0	7.2	91.8	5.8
				Styrene				
13	0.1025	1.5908	6.1	2.5	2.5	8.5	71.3	11.0
14	0.1340	1.0446	11.4	3.0	2.5	6.1	76.7	12.0
15	0.1917	0.7048	21.4	4.5	2.8	5.9	88.2	12.0
16	0.2334	0.6445	26.6	5.5	2.8	6.0	92.3	12.5
17	0.3161	0.5251	37.6	7.5	2.8	7.8	94.8	12.0
				ClSt				
18	0.0893	1.6122	5.3	2.0	4.0	9.5	50.2	26.0
19	0.1272	1.1096	10.3	3.0	4.0	6.6	57.4	13.0
20	0.1907	0.7983	19.3	4.5	4.5	8.3	68.6	10.0
21	0.2491	0.5421	31.5	6.0	4.5	7.0	80.6	12.0
22	0.3083	0.4831	39.0	7.5	4.5	8.6	85.0	12.5
23	0.4247	0.2026	67.7	10.0	4.5	7.0	94.4	13.0
				MeO_2CSt				
24	0.0847	1.3232	6.0	1.6	3.5	4.4	50.3	10.0
25	0.1942	0.7136	21.4	4.3	5.0	6.0	66.6	9.2
26	0.2375	0.6929	27.9	5.6	5.0	3.7	68.5	8.8
27	0.3031	0.4570	39.9	6.9	5.5	5.3	78.6	9.4
28	0.3941	0.2868	57.9	8.9	6.0	5.1	82.7	9.6
				MeOSt				
29	0.1358	1.1305	10.7	6.3	0.5	12.5	33.3	4.3
30	0.1969	0.8111	19.5	9.2	0.8	10.1	38.7	4.3
31	0.2509	0.7343	25.5	11.7	1.0	6.0	40.4	4.3
32	0.3054	0.4344	41.3	14.4	1.4	3.5	46.6	5.4
33	0.3197	0.2875	52.7	15.1	2.0	3.4	60.0	4.1
				MeSt				
34	0.1084	1.6385	6.2	4.9	4.5	12.9	45.8	12.5
35	0.1300	1.1447	10.2	6.0	5.0	13.3	45.2	11.0
36	0.1930	0.7646	18.2	9.0	6.0	12.6	48.1	9.1
37	0.2476	0.6040	29.1	11.6	6.0	6.3	59.0	9.1
38	0.3082	0.5246	37.0	14.5	8.5	5.1	65.3	11.0
39	0.3212	0.3615	47.1	15.1	9.5	6.3	65.6	12.5
				Styrene				
40	0.0869	1.5710	5.2	4.2	6.0	9.1	46.2	7.4
41	0.1354	1.0740	11.2	6.2	6.0	8.3	47.9	8.0
42	0.1911	0.7338	20.7	8.9	9.0	14.9	53.4	8.4
43	0.2518	0.6494	27.9	11.8	9.0	11.0	61.5	10.5
44	0.3069	0.4457	40.8	14.7	7.0	2.4	64.7	10.5
45	0.3076	0.4147	42.6	14.5	9.5	11.2	71.6	10.0
				ClSt				
46	0.0805	1.6141	4.8	3.6	6.0	12.2	41.8	14.0
47	0.1473	1.1622	11.3	6.8	7.0	10.6	49.6	10.0
48	0.2073	0.8371	19.8	9.7	10.5	13.1	60.0	10.0
49	0.2506	0.6188	28.8	11.7	10.5	9.1	62.8	12.0
50	0.3142	0.5216	37.6	14.8	11.0	7.9	68.0	10.0
51	0.3285	0.3654	47.3	15.5	11.0	11.6	71.6	8.4
				MeO_2CSt				
52	0.0735	1.3401	5.2	3.3	7.5	4.8	45.6	7.5
53	0.0965	0.9052	9.6	4.6	9.0	6.1	49.5	6.6
54	0.1862	0.7415	20.1	8.5	14.0	10.5	56.3	8.0
55	0.2522	0.5378	31.9	11.2	14.0	13.8	62.5	7.8
56	0.3033	0.5273	36.5	13.8	14.5	20.7	57.1	8.3
57	0.3374	0.3744	47.4	15.8	14.5	16.7	61.2	7.2

[a] Run nos. 1–28, [BzCQ] = 41 mmol/L; run nos. 29–57, [BzCQ] = 21 mmol/L; AIBN, 1 mg; AcOH, 2 drops. [b] Determined by GPC using THF as eluent.

give ρ_1 values of the reactions under consideration. The other reactivity of BzCQ or BCQ toward the polymer radical with a terminal para-substituted styrene unit should be estimated as k_{21} values. Since para-substituted

Table II
Copolymerizations[a] of BzCQ with Para-Substituted Styrenes in $CHCl_3$ at 50 °C

run no.	monomer feed, mmol BzCQ	monomer feed, mmol *p*-subst styr	BzCQ, mol %	solvt, mL	time, h	conv, %	copolym comp (BzCQ), mol %	$10^{-3}\bar{M}_n$[b]
				MeOSt				
1	0.1893	0.7531	20.1	9.0	2.0	8.6	43.2	2.0
2	0.2339	0.5042	31.7	11.0	4.0	9.6	46.3	1.9
3	0.2924	0.3995	42.3	14.0	4.5	7.2	44.1	2.0
4	0.3144	0.2822	52.7	15.0	5.0	3.7	53.2	1.9
				Styrene				
5	0.0838	1.5868	5.0	4.0	7.0	2.6	40.1	1.9
6	0.1283	1.1110	10.4	6.0	8.0	4.1	43.8	1.8
7	0.1899	0.7517	20.2	9.0	13.5	2.9	48.1	1.5
8	0.2534	0.5740	30.6	12.0	13.0	4.2	51.2	8.6
9	0.2928	0.4162	41.3	14.0	14.3	4.2	64.6	14.0
10	0.3169	0.2880	52.4	15.0	16.0	4.0	65.1	14.0
				ClSt				
11	0.0847	1.5941	5.0	4.0	7.8	6.1	42.3	2.8
12	0.1484	1.3351	10.0	7.0	9.5	4.5	53.5	10.0
13	0.2109	0.8350	20.2	10.0	13.0	6.2	58.3	14.0
14	0.2943	0.4499	39.5	14.0	18.0	2.6	63.2	4.8
15	0.3152	0.2987	51.3	15.0	21.0	5.7	70.2	13.0

[a] [BzCQ] = 21 mmol/L; AIBN, 1 mg; AcOH, 2 drops. [b] Determined by GPC using THF as eluent.

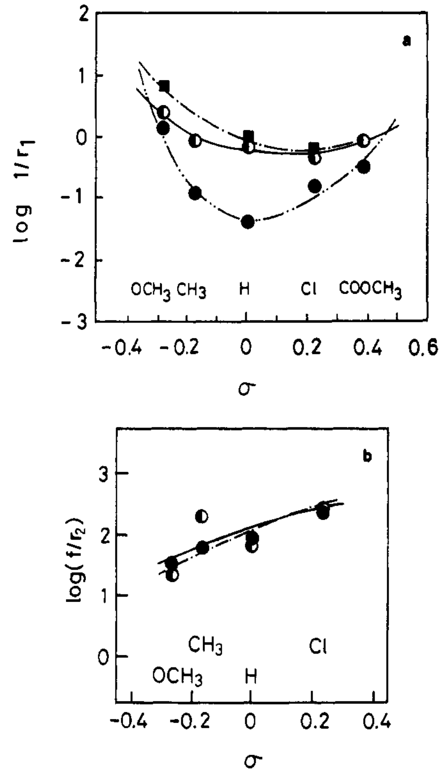

Figure 1. (a) Hammett plot of log $(1/r_1)$ vs σ in the copolymerizations of BzCQ(M_1) with para-substituted styrenes: (●··–) [BzCQ] = 42 mmol/L at 60 °C; (◐—) [BzCQ] = 21 mmol/L at 60 °C; (■–·–) [BzCQ] = 21 mmol/L at 50 °C. (b) Hammett plot of log (f/r_2) vs σ in the copolymerization of BzCQ(M_1) with para-substituted styrenes: f refers to (k(para-substituted St)/k_{St}), and other symbols are indicated in Figure 1a.

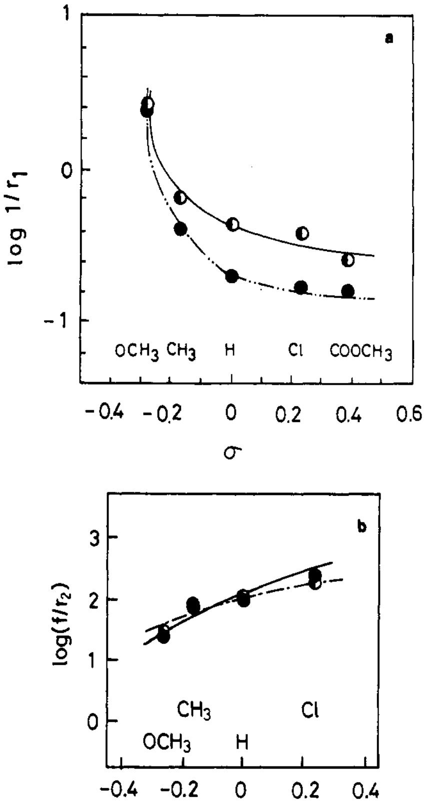

Figure 2. (a) Hammett plot of log $(1/r_1)$ vs σ in the copolymerization of BCQ(M_1) with para-substituted styrenes: (●··–) [BCQ] = 33 mmol/L at 60 °C; (◐—) [BCQ] = 5 mmol/L at 60 °C. (b) Hammett plot of log (f/r_2) vs σ in the copolymerization of BCQ(M_1) with para-substituted styrene: f refers to (k(para-substituted St)/k_{St}), and other symbols are indicated in Figure 2a.

styrenes polymerize at different polymerization rates, multiplication of the $1/r_2$ values by the ratios f of the homopropagation rate constants, k (para-substituted St) of the para-substituted styrenes (M_2) to that, k_{St}, of unsubstituted styrene allows us to determine the normalized k_{12} values with respect to the propagation rate constant of unsubstituted styrene. However, there was a problem in selecting an appropriate value of an absolute propagation rate constant of styrene among many scattering values[18] measured in different types of measurement apparatus by many researchers. Here, on the basis of the same type of the apparatus (the rotating sector method) and the same temperature of measurement, we selected the k_{22} values of 150, 84, 71, and 55 L/(mol s) at 30 °C for *p*-Cl-, *p*-Me-, *p*-MeO-, unsubstituted styrenes, respectively.

The activation energy of propagation of para-substituted styrenes was reported to fall into a narrow range of values,[19] and thus the ratio f is regarded as remaining constant in a wide range of polymerization temperatures if both

Table III
Copolymerizations[a] of BCQ with Para-Substituted Styrenes in $CHCl_3$ at 60 °C

	monomer feed, mmol						copolym comp	
run no.	BCQ	*p*-subst styr	BCQ, mol %	solvt, mL	time, min	conv, %	(BCQ), mol %	$10^{-5}\bar{M}_n$[b]
				MeOSt				
1	0.1405	1.2222	10.3	4.2	15	7.8	43.7	3.0
2	0.2265	0.8369	21.3	6.7	17	6.9	47.4	4.7
3	0.2819	0.6362	30.7	8.3	20	8.0	47.4	6.4
4	0.3384	0.5238	39.3	10.0	23	8.2	55.3	7.0
5	0.4236	0.3017	58.4	12.5	25	7.6	60.2	7.0
6	0.4526	0.2269	66.6	13.3	27	6.5	65.0	7.0
				MeSt				
7	0.0706	1.3182	5.1	2.1	15	3.8	43.3	3.3
8	0.1403	1.2734	9.9	4.2	34	14.2	53.6	5.4
9	0.2269	0.9191	19.8	6.7	39	16.8	61.2	5.4
10	0.3375	0.4460	43.1	10.0	49	20.8	73.3	5.9
11	0.3932	0.3821	50.7	11.7	54	18.5	77.7	5.9
12	0.4521	0.1802	71.5	13.3	70	19.3	86.8	7.3
				Styrene				
13	0.0704	1.3413	5.0	2.1	35	4.3	53.1	3.0
14	0.1407	1.4215	9.0	4.2	40	6.0	61.7	2.1
15	0.3382	0.5129	39.7	10.0	52	8.2	82.1	3.3
16	0.3949	0.4233	48.3	11.7	57	7.9	83.3	2.5
17	0.4232	0.2809	60.1	12.5	62	9.0	89.6	3.3
				ClSt				
18	0.0724	1.3370	5.1	2.1	45	11.3	52.6	1.3
19	0.1418	1.2716	10.0	4.2	47	11.1	63.3	1.7
20	0.2271	0.8999	20.2	6.7	50	12.3	70.7	2.8
21	0.2833	0.6526	30.3	8.3	54	13.1	77.7	2.5
22	0.3937	0.4238	48.2	11.7	61	14.4	84.9	4.6
23	0.4526	0.1948	69.9	13.3	69	15.2	93.2	5.4
				MeO_2CSt				
24	0.0706	1.3547	5.0	1.9	78	2.1	42.5	2.1
25	0.1213	1.0725	10.2	3.2	82	5.0	68.0	2.1
26	0.1973	0.7785	20.2	5.8	86	6.2	79.6	2.5
27	0.2828	0.6143	31.5	8.3	91	5.9	81.6	2.1
28	0.3379	0.4908	40.8	10.0	98	7.1	84.8	2.5
29	0.4233	0.2721	60.9	12.6	108	8.4	94.1	2.8
30	0.4525	0.2300	66.3	13.5	113	9.2	96.5	2.5
				MeOSt				
31	0.0692	1.1962	5.5	13.8	43	6.2	37.2	3.0
32	0.2259	0.8717	20.6	41.5	50	5.4	50.8	1.3
33	0.2825	0.6940	38.9	51.0	55	8.9	53.3	2.0
34	0.3394	0.6713	33.6	61.2	58	7.2	54.5	2.0
35	0.3107	0.3497	47.1	62.3	61	5.7	56.6	2.6
36	0.3127	0.2995	51.1	62.3	64	6.2	56.2	2.0
				MeSt				
37	0.1426	1.1510	11.0	28.0	60	10.3	52.5	1.0
38	0.2272	0.9384	19.5	44.9	63	9.8	58.5	1.1
39	0.2815	0.5628	33.4	56.2	67	11.0	65.5	1.3
40	0.3395	0.4452	43.3	67.5	65	11.1	67.8	1.2
41	0.3088	0.3056	50.3	62.0	72	10.9	70.2	2.6
42	0.3130	0.1881	62.5	61.9	80	7.5	79.7	1.2
				Styrene				
43	0.0703	1.3244	5.0	13.7	115	15.0	36.7	1.0
44	0.1433	1.2119	10.6	28.0	100	8.6	49.9	1.1
45	0.2260	0.8721	20.6	45.0	104	8.1	59.7	1.3
46	0.2820	0.6519	30.2	56.2	107	8.4	68.8	1.2
47	0.3107	0.4607	40.3	61.9	115	9.7	70.1	1.3
48	0.3150	0.2997	51.3	61.9	118	7.3	78.2	1.3
49	0.3044	0.1774	63.2	61.9	130	7.0	77.5	1.2
				ClSt				
50	0.1438	1.3190	9.8	28.0	160	12.8	43.5	2.3
51	0.2269	0.8827	20.5	44.9	163	14.2	57.0	2.6
52	0.2826	0.6616	29.9	56.2	170	12.7	67.5	4.0
53	0.2822	0.4460	38.8	56.3	185	12.4	73.9	3.3
54	0.2813	0.3144	47.2	56.3	189	9.0	74.1	2.8
55	0.2858	0.1798	61.4	56.3	209	11.0	80.4	3.2
				MeO_2CSt				
56	0.0711	1.3256	5.1	13.9	225	2.9	40.7	1.3
57	0.1149	1.0388	10.0	22.4	255	3.5	53.0	1.3
58	0.2824	0.7217	28.1	56.2	290	4.7	66.9	1.2
59	0.3102	0.4500	40.8	61.9	245	4.9	76.2	1.6
60	0.3075	0.3256	48.6	61.9	295	7.8	78.5	2.3
61	0.3113	0.2003	60.9	61.9	340	9.2	83.9	2.6

[a] Run nos. 1–30, [BCQ] = 33 mmol/L; run nos. 31–61, [BCQ] = 5 mmol/L; AIBN, 0.5 mg; AcOH, 2 drops. [b] Determined by GPC using THF as eluent.

Table IV
Monomer Reactivity Ratios of the Copolymerizations between BzCQ or BCQ and Para-Substituted Styrenes under Various Polymerization Conditions

M_1 monomer	polymn temp, °C		M_2 monomer; *p*-subst styr MeO-	Me-	H-	Cl-	MeO_2C-
		Hammett const σ_p[a]	−0.268	−0.170	0.00	0.227	0.39
		reson const E_R[b]	0.11	0.03	0.00	0.10	0.13
		abs rate const of prop/L mol^{-1} s^{-1}	71	84	55	150	
[BzCQ] = 42 mmol/L	60	r_1	0.82 ± 0.30	9.20 ± 3.0	28.0 ± 2.5	6.9 ± 1.3	3.54 ± 0.40
		r_2	0.12 ± 0.04	0.07 ± 0.04	0.033 ± 0.030	0.034 ± 0.020	0.016 ± 0.002
[BzCQ] = 21 mmol/L	60	r_1	0.42 ± 0.40	1.39 ± 0.35	1.67 ± 0.80	2.33 ± 1.40	1.21 ± 0.50
		r_2	0.21 ± 0.09	0.025 ± 0.015	0.035 ± 0.020	0.03 ± 0.02	0.016 ± 0.002
	50	r_1	0.083 ± 0.050		0.91 ± 0.030	1.38 ± 0.45	
		r_2	0.093 ± 0.030		0.049 ± 0.025	0.009 ± 0.010	
[BCQ] = 33 mmol/L	60	r_1	0.42 ± 0.50	2.46 ± 0.70	5.03 ± 1.80	5.64 ± 1.40	7.8 ± 2.0
		r_2	0.06 ± 0.02	0.02 ± 0.01	0.01 ± 0.01	0.013 ± 0.010	0.021 ± 0.015
[BCQ] = 5 mmol/L	60	r_1	0.40 ± 0.20	1.59 ± 0.80	2.3 ± 1.0	2.6 ± 1.0	3.5 ± 1.5
		r_2	0.04 ± 0.02	0.02 ± 0.01	0.01 ± 0.01	0.015 ± 0.010	0.025 ± 0.015

[a] Cited from ref 14. [b] Cited from ref 13. [c] Cited from ref 18.

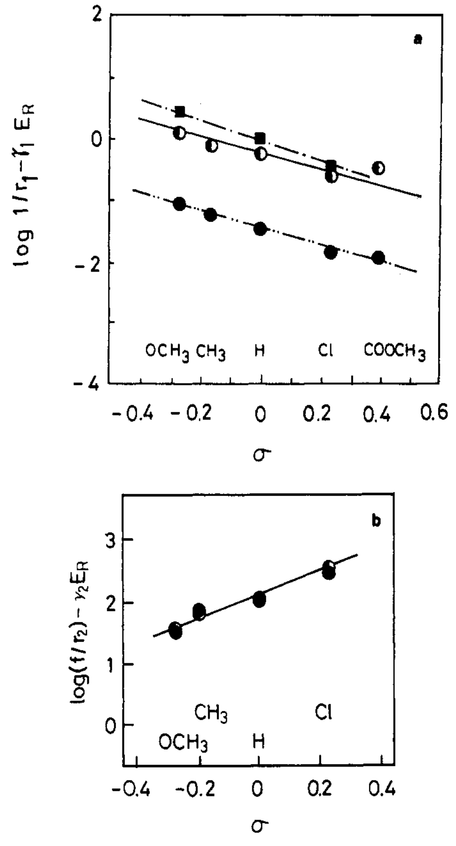

Figure 3. (a) Modified Hammett plot of [log $(1/r_1) - \gamma_1 E_R$] vs σ in the copolymerization of BzCQ(M_1) with para-substituted styrenes: (●··–) [BzCQ] = 42 mmol/L at 60 °C; (◐—) [BzCQ] = 21 mmol/L at 60 °C; (■–·–) [BzCQ] = 21 mmol/L at 50 °C. (b) Modified Hammett plot of [log $(f/r_2) - \gamma_2 E_R$] vs σ in the copolymerization of BzCQ(M_1) with para-substituted styrenes: f refers to (k(para-substituted St)/k_{St}), and other symbols are indicated in Figure 3a.

propagations take place via the same reaction mechanism. Hammett's treatment for the reactivity of k_{12} was carried out with the five kinds of styrenes, whereas that for the reactivity of k_{21} was with four styrenes. Therefore, the latter had to be carried out in a less objective sense.

The reactivity, k_{21}, obtained as f/r_2 was treated in Hammett's and Yamoto-Otsu's treatments as shown in corresponding Figures 1b, 2b, 3b, and 4b.

In Table V are summarized the polar and resonance reaction constants ρ_1, ρ_2, γ_1, and γ_2 of the two cross propagations in copolymerizations between BzCQ or BCQ and para-substituted styrenes.

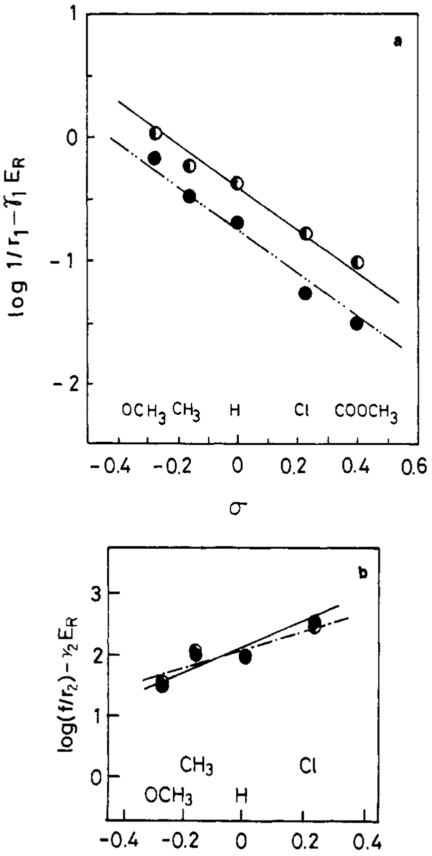

Figure 4. Modified Hammett plot of [log $(1/r_1) - \gamma_1 E_R$] vs σ in the copolymerization of BCQ(M_1) with para-substituted styrenes: (●··–) [BCQ] = 33 mmol/L at 60 °C and (◐—) [BCQ] = 5 mmol/L at 60 °C. (b) Modified Hammett plot of [log $(f/r_2) - \gamma_2 E_R$] vs σ in the copolymerization of BCQ(M_1) with para-substituted styrenes: f refers to (k(para-substituted St)/k_{St}) and other symbols are indicated in Figure 4a.

First, the polar reaction constants, ρ_1, of the cross propagations of the polymer radical with terminal BzCQ or BCQ unit toward para-substituted styrenes are given as negative values ranging from −1.3 to −1.9, reasonably corresponding to the reaction that the strongly electron-accepting polymer radical with terminal BzCQ or BCQ unit attacks the electron-donating para-substituted styrene. On

Table V
Polar and Resonance Reaction Constants, ρ and γ, of Cross Propagations in the Copolymerizations of BzCQ or BCQ (M_1) with Para-Substituted Styrenes (M_2)

		$1/r_1$		$1/r_2$	
M_1 monomer	temp, °C	ρ_1	γ_1	ρ_2	γ_2
[BzCQ] = 42 mmol/L	60	-1.3 ± 0.5	10 ± 0.5	1.6	-1
[BzCQ] = 21 nmol/L	60	-1.3 ± 0.2	2 ± 0.5	1.6	-1
	50	-1.8 ± 0.2	4 ± 0.5		
[BCQ] = 33 mmol/L	60	-1.9 ± 0.1	5 ± 0.5	2.1	-1
[BCQ] = 5 mmol/L	60	-1.8 ± 0.1	3.5 ± 0.5	1.8	-1

the other hand, the other cross propagations of electron-donating polymer radicals with terminal para-substituted styrenes toward electron-accepting BzCQ or BCQ monomers reasonably exhibit positive ρ_2 values from +0.8 to +1.8.

Second, the resonance reaction constants γ_1 of the cross propagations of the polymer radical with terminal BzCQ or BCQ unit toward para-substituted styrenes are given as a wide range of positive values, suggesting that more stabilization of the product radicals by the substituents leads to a greater increase in the rate of the cross propagation because the resulting polymer radicals with terminal para-substituted styrene unit are sufficiently subjected to resonance stabilization with para substituent to result in a decrease of the activation energy of this cross propagation. In contrast, the resonance constants γ_2 of the other cross propagations of the polymer radicals with a terminal para-substituted styrene unit toward BzCQ or BCQ monomer are obtained as negative values of about 1, corresponding to the following: the more stabilization of the attacking radicals by the substituents leads to a greater decrease in the rate of the cross propagation because the attacking polymer radicals are subjected to resonance stabilization with para substituents to result in an increase of the activation energy. Yamamoto and Otsu found out that the radical reactions of polymer radicals with a terminal para-substituted styrene unit toward a given cumene compound[20] or vinyl compound[15] were successfully treated with the original Hammett equation (1), the para-substituents effect operating exclusively in a polar way but not in both polar and resonance ways, suggesting that the transition states of the radical reactions should be very close to the resulting product structure, which is not susceptible to the substituent effect directly because the resulting product radical is remote from the substituents of the attacking radical. This probably first observation of the negative γ_2 values allowed us to assume the stabilization of the attacking radical with terminal para-substituted styrene unit by the para substituents to make the radical less reactive. However, more experimental results are required to obtain the certain mechanism.

Finally, it is worth noting among all polar and resonance reaction constants of the cross propagations in the copolymerizations of the BzCQ and BCQ with para-substituted St that only the resonance reaction constants, γ_1, of the cross propagation of the polymer radical with terminal BzCQ and BCQ unit toward para-substituted styrenes are definitely dependent upon the polymerization conditions concerning an equilibrium polymerization of BzCQ or BCQ. For instance, when the monomer concentration of BzCQ were fixed as 42 and 21 mmol/L, which are above and below the equilibrium monomer concentration of BzCQ of 36.6 mmol/L at 60 °C,[5] values of γ_1 were obtained to be 10 and 2, respectively. Moreover, when the polymerization temperatures of the copolymerizations of BzCQ with para-substituted styrenes were set at 50 and 60 °C, the values of γ_1 were found to be 4 and 2, respectively.

The decrease in γ_1 and unchanged in ρ_1 should be equivalent to the change of the nature of the cross propagation under consideration from the nature balanced with both resonance (general reactivity) and polar effects as expected in the conventional radical copolymerizations to one unbalanced with less resonance and much more polar effects, in other words, to one more exclusively with a polar effect. Since this cross propagation should be regarded to be rate determining in the copolymerization, the less balanced nature of this step can be said to be characteristic of an alternating copolymerization which was reported in the previous papers of alternating terpolymerization.[6,7]

In this work it can be interestingly pointed out in copolymerizations of BzCQ or BCQ with para-substituted styrenes that the cross-propagation steps of polymer radicals with a terminal BzCQ or BCQ unit toward para-substituted styrenes change from the nature balanced with resonance and polar effects to one unbalanced with the less resonance and more polar effect, when the more conjugative monomer, BzCQ or BCQ, is more highly subjected to depolymerization, being fully compatible with the concept of the mechanism of an alternating copolymerization as proposed in the previous paper.[5]

Registry No. BzCQ, 110458-74-7; BCQ, 99214-01-4; St, 100-42-5; ClSt, 1073-67-2; MeSt, 622-97-9; MeOSt, 637-69-4; MeO_2CSt, 1076-96-6; (BzCQ)(MeOSt) (copolymer), 120360-62-5; (BzCQ)(MeSt) (copolymer), 120360-63-6; (BzCQ)(St) (copolymer), 110458-78-1; (BzCQ)(ClSt) (copolymer), 120360-64-7; (BzCQ)(MeO_2CSt) (copolymer), 120410-32-4; (BCQ)(MeOSt) (copolymer), 120360-65-8; (BCQ)(MeSt) (copolymer), 120360-66-9; (BCQ)(St) (copolymer), 99214-28-5; (BCQ)(ClSt) (copolymer), 120360-67-0; (BCQ)(MeO_2CSt) (copolymer), 120360-68-1.

References and Notes

(1) Iwatsuki, S.; Itoh, T.; Nishihara, K.; Furuhashi, H. *Chem. Lett.* **1982**, 517.
(2) Iwatsuki, S.; Itoh, T.; Iwai, T.; Sawada, H. *Macromolecules* **1985**, *18*, 2726.
(3) Iwatsuki, S.; Itoh, T.; Higuchi, T. *Macromolecules* **1987**, *20*, 2651.
(4) Iwatsuki, S.; Itoh, T.; Miyashita, I. *Macromolecules* **1988**, *21*, 557.
(5) Iwatsuki, S.; Itoh, T.; Higuchi, T.; Enomoto, K. *Macromolecules* **1988**, *21*, 1571.
(6) Iwatsuki, S.; Itoh, T.; Shimizu, M.; Ishikawa, S. *Macromolecules* **1983**, *16*, 1407.
(7) Iwatsuki, S.; Itoh, T.; Sato, T. *Macromolecules* **1986**, *19*, 1800.
(8) Yamamoto, T.; Otsu, T. *Chem. Ind. (London)* **1967**, 787.
(9) Emerson, W. S.; Heyd, J. W.; Lucas, V. E.; Chapin, E. C.; Owens, G. R.; Shortridge, R. W. *J. Am. Chem. Soc.* **1946**, *68*, 674.
(10) Otsu, T.; Kinoshita, M. *Experimental Methods of Polymer Synthesis*; Kagakudojin: Kyoto, 1972; p 72 (in Japanese).
(11) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1694.
(12) Kelen, T.; Tüdös, F. *J. Macromol. Sci., Chem.* **1975**, *A9*, 1.
(13) Hammett, L. P. *J. Am. Chem. Soc.* **1937**, *59*, 96.
(14) Otsu, T.; Yamamoto, A. *Yuki Gosei Kagaku Kyokaishi* **1965**, *23*, 643.
(15) Otsu, T.; *Radical Polymerization*, Kagakudojin: Kyoto, 1971; Vol. I, p 104 (in Japanese).
(16) Otsu, T. *Progress in Polymer Science, Japan*; Imoto, T., Onogi, S., Eds.; Kodansha: Tokyo 1971; Vol. 1, p 1.
(17) Gordon, A. T.; Ford, R. A. *The Chemist's Companion: A Handbook of Practical Data, Techniques and References*; Wiley: New York, 1972; pp 145–146.
(18) Korus, R.; O'Driscoll, K. F. *Polymer Handbook*, Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1975; p II-50.
(19) Reference 18, p II-451.
(20) Yamamoto, T.; Otsu, T.; *J. Polym. Sci, Polym. Chem. Ed.* **1969**, *7*, 1279.