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Polymerization Behavior of Peri-Substituted Anthraquinodimethanes. 1-Methyl- and 1,4-Dimethyl-9,10-anthraquinodimethanes

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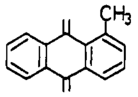
ABSTRACT: Polymerization behaviors of 1-methyl-9,10-anthraquinodimethane (1) and 1,4-dimethyl-9,10-anthraquinodimethane (2) were studied. It was found that 1 is homopolymerizable only with boron trifluoride etherate, while 2 is not homopolymerizable with any initiator, that 1 is copolymerizable in an alternating fashion with maleic anhydride, while 2 is not, and that both 1 and 2 are copolymerizable in a random fashion with highly conjugative substituted quinodimethanes such as 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ), 7,8-dibenzoyl-7,8-dicyanoquinodimethane (BzCQ), and 7,8-bis(ethylthio)-7,8-dicyanoquinodimethane (ESCQ). From the monomer reactivity ratios, 1 is much more reactive toward any polymer radicals with either terminal BCQ, BzCQ, or ESCQ monomer unit than 2. It was concluded that polymerizability of methyl-substituted 9,10-anthraquinodimethanes primarily depends upon the steric hindrance effect of methyl groups at the peri position with respect to the reactive methylene groups of the 9,10-positions.

Introduction

Unsubstituted quinodimethane (*p*-xylylene) is so reactive that when it is prepared, it polymerizes spontaneously to give the polymer and the dimers.[1] When resonance-stabilizing substituents are introduced at its 7 and 8 positions, it becomes less reactive and obtainable as stable crystals at room temperature like the following compounds: 7,7,8,8-tetracyanoquinodimethane (TCNQ),[2] 7,7,8,8-tetrakis(alkoxycarbonyl)quinodimethane,[3] 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethane,[4,5] 7,8-diacyl-7,8-dicyanoquinodimethane,[6] and 7,8-bis(ethylthio)-7,8-dicyanoquinodimethane.[7] The former two exhibit no homopolymerizability but copolymerizability, while the latter two exhibit homopolymerizability and copolymerizability.

Although 9,10-anthraquinodimethane is expected[8] to be less reactive than quinodimethane because the carbons at the 9 and 10 positions of anthracene exhibit high carbon–carbon double bond character and less aromatic resonance,[9] it remains still reactive and it cannot be obtained as a pure compound except for its highly dilute solution at low temperature.[10,11] Bowden et al.[12] and Lancaster et al.[13] reported independently that 1-methyl-9,10-anthraquinodimethane (1) and 1,4-dimethyl-9,10-anthraquinodimethane (2), carrying methyl groups at the peri position with respect to the reactive methylene groups, are obtainable as stable crystals at room temperature. These peri-substituted 9,10-anthraquinodimethanes are expected to react as quinodimethane monomers with high electron-donating character because they may be taken as quinodimethanes with two fused benzene rings and electron-donating methyl groups.



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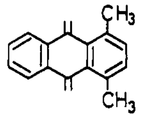

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In this paper homopolymerizations of 1 and 2 and their copolymerizations with vinyl compounds and 7,8-tetrakis-substituted quinodimethanes were studied to determine the features of their polymerization behavior.

Experimental Section

1-Methyl-9,10-anthraquinodimethane (1). Compound 1 was prepared from 1-methylanthrone[14] according to the method of Bowden et al.:[12] yield 84%; mp 90 °C dec; IR (KBr) $\nu_{C=C}$ 1620, 1645 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.7–7.1 (m, 7 H), 5.84 (s, 1 H), 5.71 (s, 1 H), 5.66 (s, 1 H), 5.52 (s, 1 H), 2.59 (s, 3 H).

1,4-Dimethyl-9,10-anthraquinodimethane (2). Compound 2 was prepared from 1,4-dimethylanthrone[15] according to the method of Bowden et al.:[12] yield 59%; mp 99–100 °C (lit. 105 °C,[11] 100–101 °C[12]); IR (KBr) $\nu_{C=C}$ 1620 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.7–7.0 (m, 6 H), 5.79 (s, 2 H), 5.51 (s, 2 H), 2.55 (s, 6 H).

Table I
First Oxidation Potentials[a]

compd	E_1/V
1	−1.50
2	−1.64
anthracene	−1.15

[a] Solvent, dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L); reference electrode, Ag/AgCl; scan rate, 100 mV/s.

Other Materials. BCQ,[4] BzCQ,[6] and ESCQ[7] were prepared according to the methods described previously. TCNQ was recrystallized from acetonitrile. Styrene (St) was washed with 2% aqueous sodium hydroxide solution and water, dried over barium oxide and then over calcium hydride, and then distilled under reduced pressure. Acrylonitrile (AN) and methyl methacrylate (MMA) were distilled under reduced pressure prior to use. Maleic anhydride (Manh) was sublimated. Acetonitrile was refluxed with phosphorus pentoxide and distilled. Chloroform was washed with sulfuric acid and then aqueous sodium bicarbonate solution, dried over calcium chloride, and distilled over calcium hydride. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Boron trifluoride etherate was distilled under reduced pressure. Butyllithium was used without further purification.

Cyclic Voltammetry. The electron-donating character of 1 and 2 was measured by cyclic voltammetry using dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L) as a solvent and Ag/AgCl, a glassy carbon, and a platinum wire as reference, working, and third electrodes, respectively.

Procedure of Homopolymerization. Ionic polymerizations using butyllithium as an anionic initiator and boron trifluoride etherate as a cationic initiator were carried out under nitrogen according to a procedure similar to that for the polymerization of 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ).[5] After polymerization, an aliquot of the reaction mixture was dissolved in tetrahydrofuran (THF). The resulting solution was subjected to gel permeation chromatography (GPC). Only when the polymerization was carried out with boron trifluoride etherate was the reaction mixture poured into excess hexane to deposit polymeric material, which was then repeatedly washed with dichloromethane and dried under reduced pressure. In the case of free-radical polymerization, given amounts of monomer, AIBN,

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Table II
Homopolymerizations of 1 and 2 with Various Initiators

run	monomer, mg	initiator	[M]/[I]	solvent (mL)	temp, °C	time, h	yield, %
				1			
1	53.3	AIBN	32.0	$CHCl_3$ (2)	60	24	no polym
2	53.3	BF_3OEt_2	32.5	CH_2Cl_2 (5)	0	5	80.9
3	53.3	BuLi	31.3	toluene (2)	0	24	no polym
				2			
4	51.0	AIBN	33.6	benzene (2)	60	24	no polym
5	41.3	BF_3OEt_2	28.0	CH_2Cl_2 (2)	0	17	no polym
6	50.2	BuLi	30.4	toluene (2)	0	24	no polym

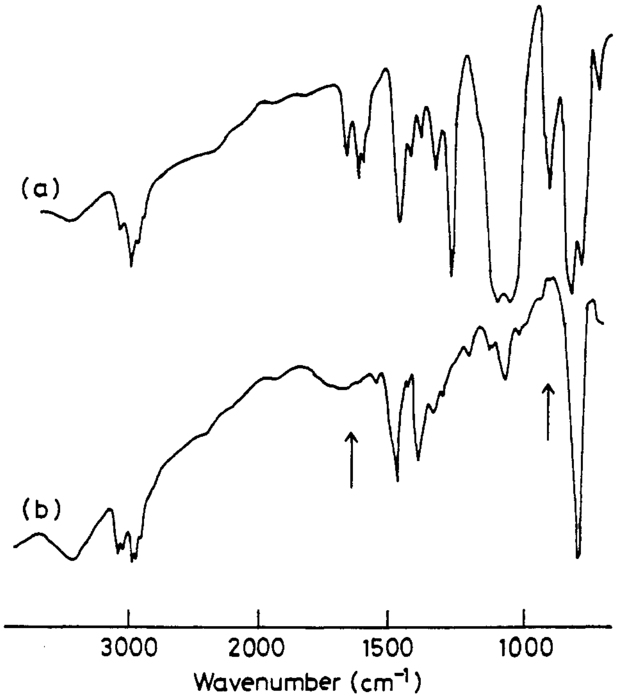

Figure 1. IR spectra of (a) 1 and (b) polymer of 1.

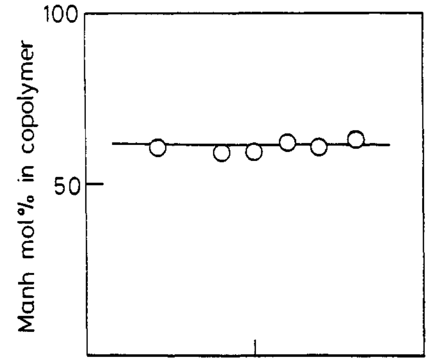

Figure 2. Composition diagram for the copolymerization of 1 with Manh.

and chloroform were placed in an ampule, which was degassed three times by the freeze–thaw method and sealed. It was set in a bath held at 60 °C during polymerization and then opened. An aliquot of the reaction mixture was dissolved in THF, and the resulting solution was subjected to GPC.

Copolymerization Procedure. Given amounts of monomers, chloroform or acetonitrile as solvent, and AIBN as initiator were placed in an ampule, which was degassed completely by the freeze–thaw method (three times) and sealed. It was set in a bath held at 60 °C during polymerization and then opened. The reaction mixture was poured into excess hexane to precipitate the copolymer. The copolymers of 1 and 2 with TCNQ were repeatedly washed with acetonitrile. The copolymers of 1 and 2 with Manh, BCQ, BzCQ, and ESCQ were dissolved in a small amount of dichloromethane, and the resulting solution was poured into excess hexane to precipitate the copolymer again. This procedure was repeated three times. The copolymer was dried under reduced pressure to constant weight.

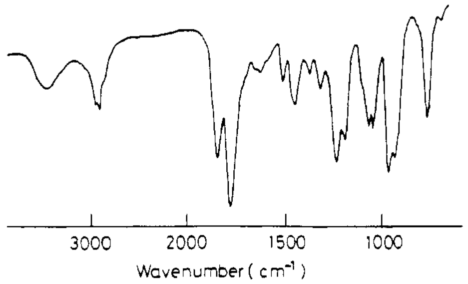

Figure 3. IR spectrum of the copolymer of 1 with Manh.

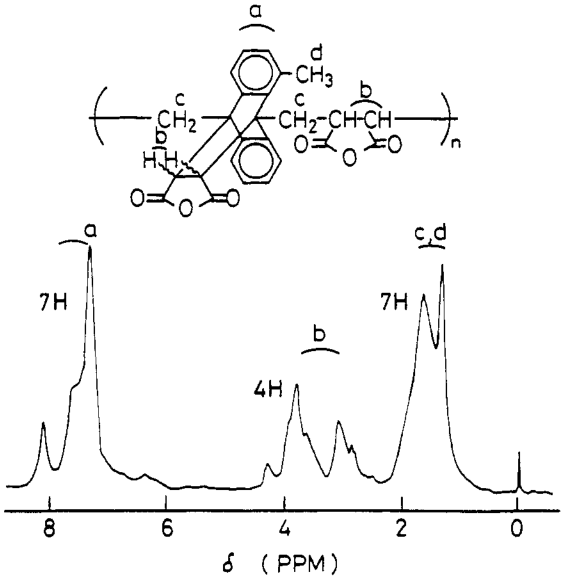

Figure 4. ¹H NMR spectrum of the copolymer of 1 with Manh in chloroform-*d*.

Characterization. Copolymer composition was established by elemental analysis. The number-average molecular weight ($\bar{M}_n$) of the copolymers was determined by GPC with a series of columns, TOSOH, G2500H, and G3000H, using THF as an eluent and standard polystyrenes as references without further calibration.

Results and Discussion

Electron-Donating Character of 1 and 2. The experimental values of the first oxidating potential for 1 and 2 are listed in Table I, together with that of anthracene for comparison. Both 1 and 2 are more electron donating than anthracene, probably owing to the existence of two exocyclic methylene moieties and methyl groups with electron-donating character. The fact that 2 is more electron donating than 1 can be explained in terms of the number of methyl substituents. These observations correspond well with the two following facts:[16] (1) The first ionization potentials of tetralin and methylenetetralin are 8.45 and 7.90 eV, respectively. (2) The first

Table III
Copolymerization[a] of 1 with Manh in Benzene at 60 °C

run	monomer 1	feed, mg Manh	amt of 1, mol %	conv, %	anal. % H	anal. % C	copolym comp[b] 1, mol %	$\bar{M}_n$[c]
1	52.60	92.69	20.3	3.2	5.26	74.04	36.6	
2	73.64	76.11	30.3	4.7	5.16	74.96	38.6	1300
3	84.16	58.26	39.4	5.4	4.94	74.66	37.9	
4	105.20	47.55	49.9	1.9	5.24	75.60	40.0	
5	115.72	34.88	59.8	3.0	5.02	75.62	40.0	
6	136.76	17.01	78.4	1.3	5.36	74.98	38.6	

[a] AIBN, 3.0 mg; solvent, 5 mL; time, 20 h. [b] Calcd from % C. [c] Determined by GPC.

Table IV
Copolymerizations of 1 and 2 with TCNQ in Acetonitrile at 60 °C

run	monomer feed, mg monomer	monomer feed, mg TCNQ	amt of TCNQ, mol %	solvent, mL	time, h	conv, %	anal. % H	anal. % C	anal. % N	copolym comp TCNQ, mol %	η_{sp}/c[a]
					1						
1	11.1	96.6	90.3	20	1	18.2	4.09	80.49	12.72	48.0	
2	26.6	58.5	70.1	10	1.5	44.8	4.25	81.39	12.63	47.8	
3	48.2	45.5	50.2	10	2	90.0	4.19	82.14	13.10	49.4	1.1
4	121.6	48.8	30.0	10	1	49.1	4.36	82.31	12.93	48.8	1.3
5	152.0	25.4	15.1	5	1.5	25.6	4.45	81.89	12.31	47.5	
					2						
6	20.3	71.2	79.9	5	12	12.0	4.07	79.66	11.93	46.7	
7	21.1	40.5	68.7	5	44	14.3	4.17	80.02	12.48	48.8	
8	44.0	38.5	49.9	5	21	18.5	3.38	81.62	12.15	47.5	0.11
9	60.8	24.9	31.8	5	20	17.5	4.12	81.54	12.71	49.5	0.11
10	72.2	14.8	19.0	5	12	23.1	4.16	81.21	11.74	46.0	

[a] Solvent, concentrated H_2SO_4; c = 0.1 g/dL.

Table V
Copolymerizations[a] of 1 with BCQ, BzCQ, and ESCQ in Chloroform at 60 °C

run	monomer feed, mg 1	monomer feed, mg comonomer	amt of 1, mol %	solvent, mL	time, h	conv, %	anal. % H	anal. % C	anal. % N	copolym comp 1,[b] mol %	$10^{-4}\bar{M}_n$[c]
						BCQ					
1	7.4	99.3	10.7	30[d]	60[e]	6.3	6.04	70.78	5.61	39.9	
2	11.0	100.1	15.1	30[d]	90[e]	11.3	5.99	69.35	5.60	40.0	15
3	11.5	100.1	15.6	30[d]	6[e]	0.5	6.43	68.94	5.49	41.6	
4	14.8	100.0	19.3	30[d]	15[e]	5.4	5.91	69.80	5.48	41.8	
5	22.0	100.3	26.3	30[d]	15[e]	4.7	6.57	77.37	5.17	46.2	
6	34.4	99.7	35.8	30[d]	10[e]	13.5	6.17	73.63	5.14	46.6	
7	51.7	99.7	45.7	30[d]	10[e]	30.6	6.40	77.01	5.05	47.8	
8	74.6	100.3	54.7	30[d]	5[e]	24.5	6.42	77.14	5.01	48.4	
						BzCQ					
9	16.5	247.5	9.9	15[d]	4	4.3	4.33	80.68	5.14	45.5	
10	27.5	106.9	29.9	7[d]	3	7.5	4.75	82.84	4.92	48.6	
11	30.0	114.2	30.3	7[d]	3	1.3	4.44	75.02	4.84	49.7	
12	44.0	109.3	40.0	7[d]	3	14.3	4.08	78.28	5.03	47.1	0.3
13	74.9	95.7	56.5	6[d]	1	14.6	4.41	79.99	4.72	51.4	
14	104.8	72.4	70.5	5[d]	1	13.8	4.85	85.00	4.96	48.1	
						ESCQ					
15	14.8	126.2	12.8	20	45	11.3	5.00	61.60	9.52	8.3	
16	24.9	62.5	33.3	10	21	12.8	5.46	63.95	8.45	20.7	
17	44.4	62.8	46.9	10	20	8.7	5.07	63.38	7.90	26.8	
18	49.8	62.6	50.0	10	13	8.5	5.43	67.77	7.64	19.7	
19	111.0	62.6	69.0	10	20	9.2	6.03	72.08	6.53	41.4	
20	192.4	41.8	85.2	7	20	12.9	5.40	68.87	6.40	42.8	5.7

[a] AIBN, 0.5 mg. [b] Calcd from % N. [c] Determined by GPC. [d] Containing 2 drops of AcOH. [e] In min.

ionization potentials of benzene and toluene are 9.24 and 8.82 eV, respectively.

Homopolymerizations of 1 and 2. The results of the homopolymerizations of 1 and 2 with anionic, cationic, and radical initiators are summarized in Table II. 2 is not homopolymerizable with any initiator, and 1 is homopolymerizable only with boron trifluoride etherate to give a yellow polymeric material, which is insoluble in solvents such as chloroform, ethyl acetate, THF, and DMSO. Figure 1 illustrates IR spectra of 1 and its polymeric material. 1 shows absorption peaks at 1620 and 1645 cm^{-1} due to stretching of the exocyclic carbon–carbon double bond and at 890 cm^{-1} due to out-of-plane bending of the carbon–hydrogen bond of exocyclic methylene group (Figure 1a). On the other hand, the polymeric material of 1 no longer shows these absorptions (Figure 1b), suggesting that 1 undergoes 1,6-polymerizations at its exocyclic methylene sites.

Copolymerizations of 1 and 2 with Vinyl and Related Monomers. Copolymerizations of 1 and 2 with styrene (St), methyl methacrylate (MMA), acryronitrile (AN), and maleic anhydride (Manh) were carried out in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) at 60 °C. 2 was found not to be copolymerizable with any of these comonomers since the comonomers were recovered in quantitative amounts. 1 was not copolymerizable with St, MMA, and

Table VI
Copolymerizations[a] of 2 with BCQ, BzCQ, and ESCQ in Chloroform at 60 °C

run	monomer feed, mg		amt of 2, mol %	solvent, mL	time, h	conv, %	anal.			copolym comp 2,[b] mol %	$10^{-4}\bar{M}_n$[c]
	2	comonomer					% H	% C	% N		
BCQ											
1	20.1	200.1	13.2	20^d	10^e	3.6	5.73	63.43	6.26	28.6	3.2
2	32.5	198.8	19.9	20^d	15^e	3.8	5.96	65.16	5.85	34.8	6.8
3	28.9	99.5	30.6	10^d	25^e	12.1	5.95	67.94	5.55	39.2	8.3
4	44.2	98.0	40.6	10^d	22^e	12.3	5.91	67.41	5.20	44.2	10.5
5	63.5	100.2	49.1	10^d	15^e	7.0	6.01	70.14	5.20	44.2	3.2
6	152.7	98.8	70.1	10^d	15^e	13.5	6.45	74.99	4.96	47.5	20
7	197.4	99.6	75.1	10^d	50^e	15.2	6.40	74.91	4.92	48.0	12
8	373.9	100.0	85.0	10^d	10^e	14.7	6.46	76.06	4.84	49.1	8.6
BzCQ											
9	30.0	149.4	23.8	10^d	3	9.2	3.95	75.17	6.48	23.1	0.2
10	39.6	105.4	36.8	7^d	5	9.1	4.07	76.95	6.13	28.9	0.2
11	43.3	61.9	52.1	4^d	5	13.4	4.71	82.64	5.49	38.9	0.8
12	60.0	51.1	64.6	3^d	8	16.6	4.79	83.07	5.19	43.3	0.2
13	75.5	26.8	81.4	2^d	8	14.8	4.91	83.50	4.85	48.8	0.6
ESCQ											
14	17.4	118.6	14.7	10	43	9.0	5.62	63.42	10.07	1.6	
15	50.4	59.4	50.1	5	26	6.2	5.05	60.83	9.57	7.3	
16	75.6	60.0	59.7	5	27	5.5	4.96	60.61	9.30	10.3	0.5
17	117.9	59.9	69.9	5	24	5.5	4.93	63.57	8.78	16.1	
18	203.3	59.0	80.2	5	27	2.2	6.33	64.39	8.02	24.3	

[a] AIBN, 0.5 mg. [b] Calcd from % N. [c] Determined by GPC. [d] Containing 2 drops of AcOH. [e] In min.

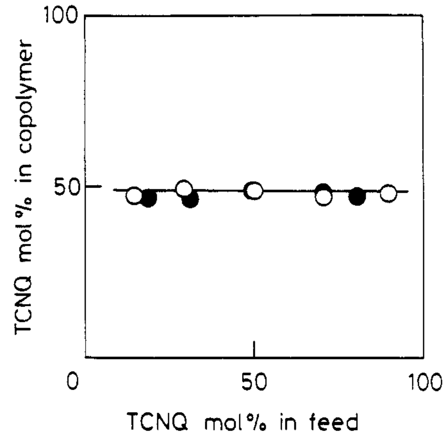

Figure 5. Composition diagrams for the copolymerizations of (○) 1 and (●) 2 with TCNQ at 60 °C.

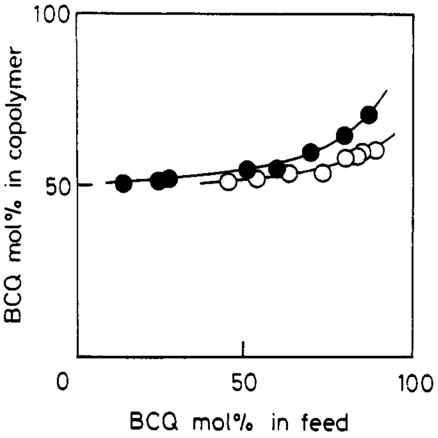

Figure 6. Composition diagrams for the copolymerizations of (○) 1 and (●) 2 with BCQ at 60 °C.

AN but was with Manh, the copolymer of which was obtained as yellow powder. The results of the copolymerization of 1 with Manh are summarized in Table III, and its copolymerization diagram is shown in Figure 2. Obviously, the resulting copolymers are always composed of about 38 mol % of the 1 unit regardless of monomer feed ratios, indicating that the monomer unit ratios of the copolymer, 1–Manh, are not 1:1 but 1:2. Figures 3 and 4 show the IR and ^{1}H NMR spectra of the copolymer, respectively. Its IR spectrum shows absorptions at 1850, 1780, and 2980 cm^{-1}, assigned to the carbonyl groups of Manh and the methyl group of 1, respectively, but shows no peaks at 1645, 1620, and 890 cm^{-1} assignable to the exocyclic methylene groups of 1. The ^{1}H NMR spectrum exhibits absorption peaks at 2.5–4 ppm assigned to methine protons and peaks at 1–2 ppm assigned to methyl and methylene protons, but none in the 5.4 and 5.6 ppm regions assignable to the exocyclic vinylidene protons of 1. It is conceivable therefore that 1 copolymerizes with Manh in an alternating fashion, and then the anthracene ring of the resulting alternating copolymer further undergoes a Diels–Alder cycloaddition reaction with Manh to give the 1:2 copolymer as shown in Figure 4, which corresponds well with the fact[17] that anthracene reacts with Manh to give *cis*-9,10-dihydroanthracene-9,10-*endo*-succinic anhydride.

Copolymerization of 1 and 2 with 7,8-Disubstituted Quinodimethanes. Since both 1 and 2 are highly conjugative, electron-donating quinodimethane monomers, highly conjugative but oppositely polar monomers were chosen as the comonomers such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ), 7,8-dibenzoyl-7,8-dicyanoquinodimethane (BzCQ), and 7,8-bis(ethylthio)-7,8-dicyanoquinodimethane (ESCQ). Table IV summarizes the results of the copolymerizations of 1 and 2 with TCNQ, which is very powerfully electron accepting and not homopolymerizable. Figure 5 shows their composition diagrams, indicating a typical profile of an alternating copolymerization. The alternating copolymers, obtained as yellow powders, are insoluble in THF, acetone, and DMSO but soluble in sulfuric acid.

Tables V and VI summarize the results of the copolymerizations of 1 or 2 with either BCQ, BzCQ, or ESCQ as homopolymerizable quinodimethane monomers, respectively. Figures 6–8 show each of those copolymerization composition diagrams, whose profiles indicate that all of the copolymerizations took place in random fashion. Their results were able to be successfully analyzed by the Kelen–Tüdös[20] and the cross-section[21] methods to obtain the monomer reactivity ratios (MRR) summarized in Table VII, where M_1 monomers refer to 1 and 2. The r_2 values

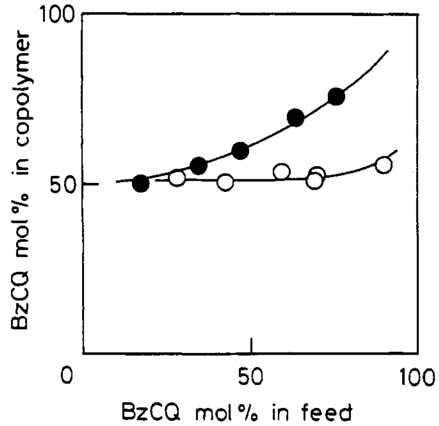

Figure 7. Composition diagrams for the copolymerizations of (○) 1 and (●) 2 with BzCQ at 60 °C.

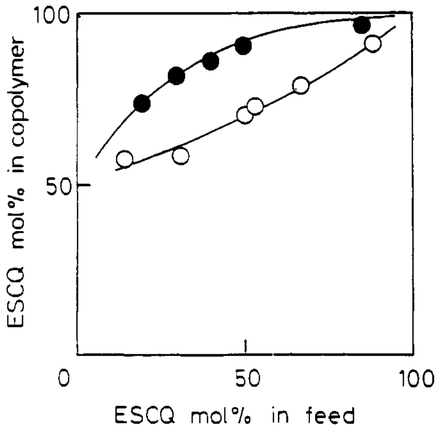

Figure 8. Composition diagrams for the copolymerizations of (○) 1 and (●) 2 with ESCQ at 60 °C.

Table VII
Monomer Reactivity Ratios of the Copolymerizations between 1 or 2 and 7,7,8,8-Tetrasubstituted Quinodimethanes

		M_2 monomer		
M_1 monomer		BCQ	BzCQ	ESCQ
1	r_1	0.0	0.0	0.0
	r_2	0.074 ± 0.029	0.021 ± 0.002	1.4 ± 0.43
2	r_1	0.0	0.0	0.0
	r_2	0.22 ± 0.10	0.70 ± 0.15	9.9 ± 1.5

Table VIII
Q–e Values of 1 and 2[a]

pairs of comonomers	1	2
ESCQ BCQ	$Q = 0.65$ $e = -5.8$	$Q = 0.04$ $e = -8.0$
ESCQ BzCQ	$Q = 1.95$ $e = -3.2$	$Q = 0.6$ $e = -1.2$
BCQ BzCQ	$Q = 31.4$ $e = -0.9$	$Q = 890$ $e = 4.64$

[a] BCQ, $Q = 9.28$, $e = +0.8$;[18] BzCQ, $Q = 9.28$, $e = +1.24$;[18] ESCQ, $Q = 12.42$, $e = +0.42$.[19]

for copolymerizations of 1 are always smaller than the corresponding ones for those of 2, indicating that 1 is more reactive than 2 toward any polymer radicals with either a terminal BCQ, BzCQ, or ESCQ monomer unit. This difference in reactivity between 1 and 2 does not correspond to the difference in electron-donating character between 1 and 2 but it does correspond well to the number of methyl groups at the peri position with respect to the reactive methylene groups, suggesting strong participation of a steric hindrance effect of those methyl groups on their reactivity.

Alfrey-Price's Q–e values for 1 and 2 were calculated from their monomer reactivity ratios as listed in Table VIII. Estimation of these values was carried out from the MRRs of a pair of copolymerization systems because 1 and 2 ($r_1 = 0$) were not homopolymerizable. Apparently, Q–e values for 1 and 2 seriously depend upon combination of the copolymerization systems. Such a situation is often encountered when a copolymerization deviates greatly from an ideal copolymerization.

Finally, 9,10-anthraquinodimethane is so reactive that it cannot be isolated in monomer form. When methyl groups are introduced at the peri position with respect to the reactive methylene groups, it decreases in reactivity and becomes obtainable as stable crystals. Compound 1 with a methyl group at the peri position is homopolymerizable with a cationic initiator and copolymerizable with maleic anhydride in an alternating fashion. Compound 2, carrying two methyl groups at the peri position, is not homopolymerizable with any initiator and not copolymerizable with vinyl monomers. Compounds 1 and 2 are copolymerizable with highly conjugative, electron-accepting quinodimethanes in a random fashion. The difference in the polymerizability (reactivity) between 1 and 2 does not correspond to their polar character but reasonably corresponds to a steric hindrance effect of the methyl groups at the peri position with respect to the reactive methylene groups.

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Registry No. 1, 63557-91-5; 1 (homopolymer), 131457-73-3; (1)(Manh) (alternating copolymer), 131457-74-4; (1)(TCNQ) (copolymer), 131457-75-5; (1)(BCQ) (copolymer), 131457-77-7; (1)(BzCQ) (copolymer), 131457-78-8; (1)(ESCQ) (copolymer), 131457-79-9; 2, 63557-86-8; (2)(TCNQ) (copolymer), 131457-76-6; (2)(BCQ) (copolymer), 131457-80-2; (2)(BzCQ) (copolymer), 131457-81-3; (2)(ESCQ) (copolymer), 131457-82-4; AIBN, 78-67-1; BCQ, 99214-01-4; BzCQ, 110458-74-7; ESCQ, 131457-67-5; BF_3OEt_2, 109-63-7.