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Amphoteric Behavior of Substituted *p*-Benzoquinone Diimines in Alternating Copolymerization

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Introduction

Substituted *p*-benzoquinodimethanes bearing cyano, alkoxycarbonyl, and acyl electron-withdrawing groups at the 7 and 8 positions such as 7,7,8,8-tetracyanoquinodimethane (**1a**),[1] 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethanes (**1b**),[2,3] 7,8,8-tris(alkoxycarbonyl)-8-cyanoquinodimethanes (**1c**),[4] 7,7,8,8-tetrakis(alkoxycarbonyl)quinodimethanes (**1d**),[5,6] and 7,8-diacyl-7,8-dicyanoquinodimethanes (**1e**)[7,8] greatly change their polymerization behavior depending upon the nature and number of substituents and substitution mode. Compounds **1b** and **1e** are easily homopolymerizable and copolymerizable with a donor monomer styrene in random fashion.[2,3,7,8] Compounds **1a**, **1c** carrying bulky substituents such as a *tert*-butyl group, and **1d** are poorly or not homopolymerizable but they are copolymerizable with styrene in perfectly alternating fashion.[1,4–6] Moreover, both **1c** and **1d** among these substituted *p*-benzoquinodimethanes could copolymerize with a more electron-accepting monomer **1a** in perfectly alternating fashion. Both **1c** and **1d** are interesting monomers in that they show amphoteric behavior in alternating copolymerization. It was pointed out that their amphoteric behavior might occur when they are poorly or not homopolymerizable, and also the gaps in π-electron density between the *p*-benzoquinodimethanes and a donor monomer styrene or an acceptor monomer **1a** are large enough to give rise to a charge-transfer interaction.[6]

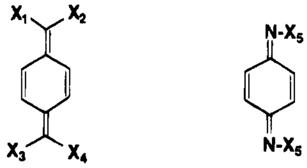
Unsubstituted *p*-benzoquinone diimine (**2a**),[9] being a member of the quinonoid family, is unstable at room temperature, and it polymerizes easily like an unsubstituted *p*-benzoquinodimethane (**1f**).[10] However, introduction of electron-withdrawing groups on the exocyclic nitrogen atom made **2a** less reactive and isolable as a crystalline material at room temperature. Many isolable *p*-benzoquinone diimines with alkylsulfonyl, arylsulfonyl, acyl, aroyl, and alkoxycarbonyl electron-withdrawing substituents on their exocyclic nitrogen atoms have been successfully prepared by Adams *et al.*,[10–15] who vigorously studied their addition reactions with halogens, hydrogen halides, dienes, and so on. However, the polymerization behavior of such isolable electron-accepting substituted *p*-benzoquinone diimines has rarely been reported except for *N,N′*-bis(phenylsulfonyl)-*p*-benzoquinone diimine (**2b**), which copolymerizes with donor monomers such as styrene or acenaphthylene in the presence of α,α′-azobis(isobutyronitrile) (AIBN) in perfectly alternating fashion.[16] As the electron-accepting substituted *p*-benzoquinodimethanes exhibit different polymerization behavior depending upon the nature and number of substituents and substitution mode as mentioned above, we are interested in the polymerization behavior of substituted *p*-benzoquinone diimines carrying electron-withdrawing substituents other than **2b**. Moreover, if there is a significant gap in polarity between substituted *p*-benzoquinone diimines and styrene or **1a**, such substituted *p*-benzoquinone diimines would be expected to show amphoteric polymerization behavior as well as **1c** and **1d** in previous works.[4–6]

Table 1. First Reduction Potentials of the Substituted *p*-Benzoquinodimethanes (1a, 1c, and 1d) and *p*-Benzoquinone Diimines (2b–d)

compd	1st red. pot,[a] V
1a	+0.16
2b (X = SO_2Ph)	+0.04
2d (X = COPh)	−0.24
2c (X = COOEt)	−0.46
1c (R = *t*-Bu)	−0.50
1d (R = Et)	−0.86

[a] Solvent, dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L); reference electrode, Ag/AgCl; scanning rate, 100 mV/s; relative error, ±0.01 V.

In this work we describe the polymerization behavior of *N,N′*-bis(ethoxycarbonyl)-*p*-benzoquinone diimine (**2c**) and *N,N′*-dibenzoyl-*p*-benzoquinone diimine (**2d**).



1a: $X_1 = X_2 = X_3 = X_4 = CN$
1b: $X_1 = X_4 = COOR$
$X_2 = X_3 = CN$
1c: $X_1 = X_2 = X_3 = COOR$
$X_4 = CN$
1d: $X_1 = X_2 = X_3 = X_4 = COOR$
1e: $X_1 = X_4 = CN$
$X_2 = X_3 = COR$
1f : $X_1 = X_2 = X_3 = X_4 = H$

2a: $X_5 = H$
2b: $X_5 = SO_2Ph$
2c: $X_5 = COOEt$
2d: $X_5 = COPh$

Results and Discussion

Electron-Accepting Character. The electron-accepting character of **2c** and **2d** was evaluated as the values of the first reduction potential, E_1, by cyclic voltammetry. The values for **2c** and **2d** are summarized in Table 1, together with those of **1a** and **1c** carrying a *tert*-butyl group, **1d** carrying an ethyl group, and **2b** for comparison. It is obvious from the table that both **2c** and **2d** are much weaker in electron-accepting character than **1a** and **2b** but stronger than **1d** carrying an ethyl group. Also **2c** has a value (−0.46 V) close to that of **1c** (−0.50 V). The electron-accepting property of **2b**, **2c**, and **2d** can be well explained in terms of Taft's polar substituent constant values,[17] σ_p*, for the phenylsulfonyl (3.55), ethoxycarbonyl (2.12), and benzoyl (2.2) groups. Here, as **2c** has a value close to that of **1c**, **2c** is expected to show an amphoteric polymerization behavior similar to that of **1c**, which could copolymerize not only with sytrene but also with **1a** in perfectly alternating fashion.[4–6]

Polymerization. Homopolymerizations of **2c** and **2d** were attempted with the radical initiator AIBN, the anionic initiation butyllithium, and the cationic initiator boron trifluoride etherate in order to investigate their homopolymerizabilities. Also homopolymerization of **2b** was attempted with the same initiators for comparison. The results of these polymerizations are summarized in Table 2. All reaction products (oligomers) were obtained as white powders, which were soluble in chloroform, dichloromethane, tetrahydrofuran (THF), and acetone but insoluble in hexane and isopropyl ether.

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Table 2. Homopolymerizations of 2b–d

run no.	monomer, mg	initiator	[**2b**, **2c**, or **2d**]/[initiator]	solvent (mL)	temp, °C	time, h	conv, %	M_n[a]
				2b (X = SO_2Ph)				
1	100.1	AIBN	10	benzene (2)	60	48	0	
2	60.2	BuLi	10	THF (2)	0	24	0	
3	58.3	$BF_3{\cdot}Et_2O$	10	CH_2Cl_2 (2)	0	24	0	
				2c (X = COOEt)				
4	100.8	AIBN	13	benzene (2)	60	48	0	
5	58.1	BuLi	10	THF (2)	0	24	0	
6	61.2	$BF_3{\cdot}Et_2O$	10	CH_2Cl_2 (2)	0	24	0	
				2d (X = COPh)				
7	98.6	AIBN	10	benzene (2)	60	96	16.8	860
8	48.4	AIBN	5	benzene (50)	60	96	0	
9	59.9	BuLi	10	THF (2)	0	24	40.7	1200
10	61.8	$BF_3{\cdot}Et_2O$	10	CH_2Cl_2 (2)	0	24	0	

[a] Determined by GPC using THF as an eluent and standard polystyrenes as a reference.

Table 3. Copolymerizations[a] of Styrene with 2c and with 2d in Benzene at 60 °C

	monomer feed							anal.		copolym compn	
run no.	**2c** or **2d**, mg	styrene, mg	**2c** or **2d**, mol %	solv, mL	AIBN, mg	time, h	conv, %	% C	% N	**2c** or **2d**, mol %	M_n[b]/10^3
					2c (X = COOEt)						
1	104.4	382.9	10.2	5	5.1	4	4.1	71.06	7.27	42.5	6.2
2	151.7	245.2	20.6	7.5	7.1	12	9.5	67.85	7.87	49.7	4.0
3	203.2	194.4	30.2	10	8.4	16	8.6	67.72	7.89	49.8	2.9
4	202.1	120.5	41.1	10	9.7	30	9.7	67.10	7.84	49.3	2.4
5	253.2	105.0	50.0	12.5	11.7	69	9.7	66.35	8.10	52.1	2.3
6	303.2	91.8	57.9	15	15.4	144	6.6	64.73	8.44	56.1	1.7
7	302.4	57.0	68.8	15	15.3	168	1.7	66.96	7.86	49.5	1.7
8	301.9	31.6	80.1	15	14.5	255	2.8	66.98	8.01	51.2	1.2
					2d (X = COPh)						
9	107.1	315.6	10.1	2	3.6	6	3.4	80.42	6.66	49.5	3.0
10	158.7	203.7	20.5	3	4.5	15	5.9	79.86	6.97	54.4	2.3
11	208.7	162.2	29.9	4	5.6	20	6.7	79.61	7.11	56.8	1.7
12	209.6	101.0	40.8	4	6.0	24	9.1	79.18	7.35	61.0	1.6
13	263.5	87.0	50.1	5	6.9	32	8.9	78.95	7.49	64.6	1.5
14	262.5	60.5	59.0	5	7.6	36	6.9	78.55	7.71	68.1	1.3
15	313.9	28.3	78.5	6	8.9	48	4.1	77.53	8.28	81.4	1.3

[a] [**2c**] = 0.08 mol/L and [**2d**] = 0.17 mol/L. [b] Determined by GPC using THF as an eluent and standard polystyrenes as a reference.

They could not be cast into films, probably due to their low molecular weights. Compounds **2b** and **2c** were not homopolymerizable with any initiator (run nos. 1–6). On the other hand, **2d** polymerized with AIBN at a monomer concentration of 0.15 mol/L at 60 °C (run no. 7) and with butyllithium at 0 °C (run no. 9) to give oligomers with molecular weights of 860 in 16.8% yield and of 1200 in 40.7% yield, respectively, but did not with boron trifluoride etherate at 0 °C (run no. 10). When the polymerization of **2d** was carried out with AIBN at a monomer concentration as low as 0.003 mol/L at 60 °C, no polymerization occurred (run no. 8). The highest electron-accepting monomer **2b** (E_1 = +0.04 V) and the lowest one **2c** (E_1 = −0.46 V) were not homopolymerizable with butyllithium initiator, but the intermediate one **2d** (E_1 = −0.24 V) was homopolymerizable. This difference in their polymerization behaviors could not be explained reasonably on the basis of only the difference in electron-accepting properties of **2b–d** toward nucleophilic anionic species, suggesting a contribution of some factors other than the electron-accepting property to their polymerizations. For example, the contribution of the equilibrium polymerizability observed in the polymerizations of substituted *p*-benzoquinodimethanes[8] is strongly supported by the finding that no polymerization of **2d** with AIBN took place at a monomer concentration as low as 0.003 mol/L.

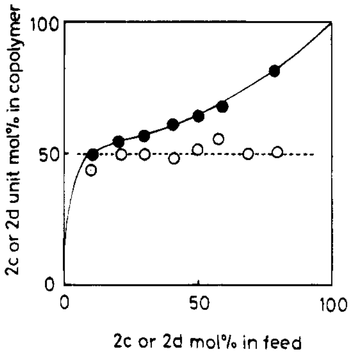

Figure 1. Composition diagrams of the copolymerizations for (○) the **2c**–styrene system with the concentration of **2c** of 0.08 mol/L and (●) the **2d**–styrene system with the concentration of **2d** of 0.17 mol/L in benzene at 60 °C.

The copolymerizations of styrene with **2c** and with **2d** in the presence of AIBN were carried out in benzene at 60 °C with given monomer concentrations of 0.08 mol/L for **2c** and 0.17 mol/L for **2d**. All copolymers were obtained as white powders, which were soluble in benzene, dichloromethane, chloroform, acetone, ethyl acetate, acetonitrile, and THF but insoluble in hexane, isopropyl ether, and methanol. The results of the copolymerizations are summarized in Table 3, and their composition diagrams are shown in Figure 1. The copolymers for the **2c**–styrene system were always composed of about 50 mol % of the **2c** unit regardless of the monomer feed ratios. In the IR spectrum, **2c** shows an absorption peak at 1575 cm^{-1} due to the stretching vibration of the imine group, but the copolymer does not. The ^1H NMR spectrum in chloroform-*d* of a copolymer of **2c** with styrene is shown in Figure 2, where each peak is assignable to the respective protons

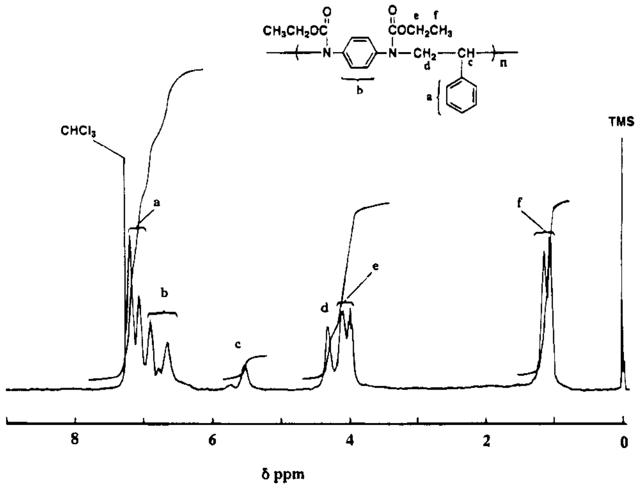

Figure 2. ^{1}H NMR spectrum for the copolymer (run no. 2 in Table 3) of **2c** with styrene in chloroform-*d*.

of the chemical structure illustrated therein. The methine and methylene protons of the styrene unit of the copolymer appear in the 5.5 and 4.3 ppm regions, respectively, indicating that they are much more subject to deshielding than the corresponding ones of polystyrene, generally appearing at the 1−2 ppm region. Presumably, the deshielding arises from an electron withdrawal by the neighboring (ethoxycarbonyl)amino group when the styrene unit is sandwiched between **2c** units in the copolymer. It is concluded, therefore, that **2c** copolymerizes with styrene in perfectly alternating fashion, and it reacts at the exocyclic nitrogen sites. Compound **2d** copolymerized with styrene in moderately alternating fashion, and the results for the **2d**−styrene system were rationally analyzed according to the intersection[18] and Kelen−Tüdös[19] methods to obtain monomer reactivity ratios of r_1(**2d**) = 0.86 ± 0.06 and r_2(styrene) = 0.012 ± 0.027 at 60 °C. The Alfrey−Price Q and e values of **2d** were calculated on the basis of the monomer reactivity ratios to be 15.0 and +1.34, respectively, indicating that **2d** is highly conjugative and electron-accepting as well as **1b**,[2,3] **1c**,[4] and **1e**.[7,8] Although both **2c** and **2d** reacted as acceptor monomers toward a donor monomer styrene, their copolymerization fashions were different, probably due to the difference in their homopolymerizabilities such that **2d** is homopolymerizable and **2c** is nonhomopolymerizable. This can be explained in terms of our mechanism of alternating copolymerization in connection with equilibrium polymerization behavior.[8]

The copolymerizations of **1a** with **2c** and with **2d** in the presence of AIBN were carried out in acetonitrile at 60 °C. Copolymers were obtained for the **1a**−**2c** system but not for the **1a**−**2d** system. All reaction products for the **1a**−**2c** system were obtained as off-white powders, which were partially soluble in dichloromethane, THF, acetonitrile, dimethyl sulfoxide, and *N,N*-dimethylformamide, and insoluble in hexane, methanol, and isopropyl ether. The results of the copolymerization for the **1a**−**2c** system are summarized in Table 4, and the composition diagram is shown in Figure 3. The obtained copolymers are always composed of about 50 mol % of the **2c** unit regardless of the monomer feed ratios. The IR spectrum exhibited absorption peaks at 2230 cm^{-1} due to the nitrile group and at 1693 cm^{-1} due to the ester group, indicating the incorporation of **2c** and **1a** units into the copolymer. It is considered that **2c** copolymerizes as a donor monomer with the more electron-accepting monomer **1a** in alternating fashion. However, the copolymerization of **2d** with **1a** did not take place. Previously, in the mechanism[8] of the alternating copolymerizations related to substituted *p*-benzoquinodimethanes, it was pointed out that the polar character of the polymer radical and the monomer plays an important role in the addition reaction; that is, the polymer radical undergoes cross propagation under favor of strong charge-transfer interaction with comonomer due to a great difference in polarity between the two reacting species. As the E_1 values obtained in the previous section indicate that **2d** is stronger in electron-accepting property than **2c**, the gap in polarity between **2d** and **1a** should be smaller than that between **2c** and **1a**. It is considered, therefore, that no copolymerization of **2d** with **1a** is attributable to the smaller gap in polarity between **2d** with **1a** compared to that between **2c** and **1a**. Moreover, UV−vis spectral measurement was carried out in acetonitrile at a **2c** concentration of 3 × 10^{-3} mol/L and a **1a** concentration of 5 × 10^{-4} mol/L. The charge-transfer band appeared in the 480−580 nm region though it was very weak, supporting a contribution of the charge-transfer interaction to the cross-propagation step. It is interesting that amphoteric behavior in alternating copolymerization like that observed for substituted *p*-benzoquinodimethanes[4-6] such as **1c** and **1d** was also found in substituted *p*-benzoquinone diimines such as **2c**.

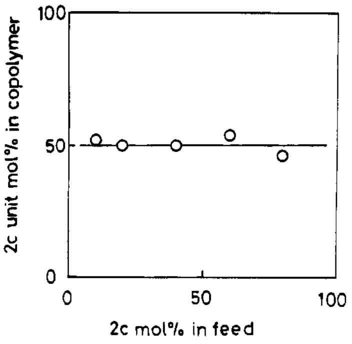

Figure 3. Composition diagram of the copolymerization for the **2c**−**1a** system in acetonitrile at 60 °C.

In summary, **2c** is not homopolymerizable with any initiator, whereas **2d** is homopolymerizable with AIBN and butyllithium initiators but not with boron trifluo-

Table 4. Copolymerizations[a] of 2c with 1a in Acetonitrile at 60 °C

run no.	monomer feed: 2c, mg	monomer feed: 1a, mg	monomer feed: 2c, mol %	solv, mL	time, h	conv, %	anal.: % C	anal.: % N	copolym compn 2c, mol %	M_n[b,c]/10^3
1	31.8	219.9	10.6	15	96	5.6	63.18	18.18	51.9	1.3
2	50.8	163.5	20.2	8	168	6.3	63.42	18.48	50.1	1.7
3	99.2	122.6	39.7	6	168	7.9	63.43	18.49	50.0	1.9
4	151.1	81.6	60.2	4	168	5.3	62.92	17.86	53.9	2.0
5	201.5	40.5	80.3	2	168	8.1	63.88	19.06	46.5	2.5

[a] AIBN, 15 mg. [b] Determined by using THF as an eluent and standard polystyrenes as a reference. [c] Molecular weights of THF-soluble parts were measured.

ride etherate. Equilibrium polymerizability was suggested in the polymerizations of substituted *p*-benzoquinone diimines like the polymerizations of substituted *p*-benzoquinodimethanes. Compound **2c** could copolymerize not only with the donor monomer styrene but also with the more electron-accepting monomer **1a** in perfectly alternating fashion, indicating that **2c** exhibited amphoteric behavior in alternating copolymerization. Compound **2d** copolymerized with styrene in moderately alternating fashion to obtain monomer reactivity ratios of r_1(**2d**) = 0.86 ± 0.06 and r_2(styrene) = 0.012 ± 0.027 at 60 °C and Q and e values of Q = 15.0 and e = +1.34, indicating that **2d** is highly conjugative and electron-accepting, but did not copolymerize with **1a**. Amphoteric behavior was observed in alternating copolymerizations of substituted *p*-benzoquinone diimines as well as substituted *p*-benzoquinodimethanes, and it was pointed out that this behavior might take place when quinonoid compounds are poorly or not homopolymerizable and there is a large gap in polarity between the compounds.

Experimental Section

Materials. *N,N'*-Bis(phenylsulfonyl)-*p*-benzoquinone diimine (**2b**), *N,N'*-bis(ethoxycarbonyl)-*p*-benzoquinone diimine (**2c**), and *N,N'*-dibenzoyl-*p*-benzoquinone diimine (**2d**) were prepared according to the methods reported by Adams *et al.*[10,11] and Pinkus *et al.*[20]

2b: mp 164−166 °C; IR (KBr) ν_{CH} 3200, $\nu_{C=N}$ 1530, ν_{SO_2} 1296, 1141 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.14−8.00 (m, 6H), 7.76−7.56 (m, 6H), 6.92 (d, J = 10 Hz, 2H). Anal. Calcd for $C_{18}H_{14}O_4N_2S_2$: C, 55.94; H, 3.66; N, 7.25; O, 16.56; S, 16.59. Found: C, 55.89; H, 3.58; N, 7.18; S, 16.62.

2c: mp 75.3−76.6 °C; IR (KBr) ν_{CH} 3010, 2954, $\nu_{C=O}$ 1672, $\nu_{C=N}$ 1575, ν_{C-O} 1224 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.88 (br s, 4H), 4.36 (q, J = 7.2 Hz, 4H), 1.38 (t, J = 7.2 Hz, 6H). Anal. Calcd for $C_{12}H_{14}O_4N_2$: C, 57.59; H, 5.65; N, 11.19; O, 25.57. Found: C, 57.94; H, 5.81; N, 11.23.

2d: mp 139.7−141.2 °C; IR (KBr) ν_{CH} 3018, $\nu_{C=O}$ 1633, $\nu_{C=N}$ 1568 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.92 (d, J = 7.26 Hz, 4H), 7.62 (t, J = 7.26 Hz, 2H), 7.48 (t, J = 7.43 Hz, 4H), 6.92 (s, 4H). Anal. Calcd for $C_{20}H_{14}N_2O_2$: C, 76.42; H, 4.49; N, 8.91; O, 10.18. Found: C, 76.71; H, 4.41; N, 8.80.

Commercial 7,7,8,8-tetracyanoquinodimethane (**1a**) was recrystallized twice from acetonitrile. Styrene [bp 52 °C (30 mmHg)] was washed with 2% aqueous sodium hydroxide solution and water, dried over anhydrous magnesium sulfate, stirred over calcium hydride, and then distilled under reduced pressure. Acetonitrile (bp 82 °C) and dichloromethane (bp 40 °C) were refluxed over calcium hydride for 12 h and then distilled. THF (bp 66 °C) was refluxed over lithium aluminum hydride for 12 h and distilled, and then the distillate was distilled again over benzophenone−sodium. Benzene (bp 80 °C) was washed with sulfuric acid, water, 5% aqueous sodium hydroxide solution, and again water, dried over sodium metal chips, and distilled. Boron trifluoride etherate [bp 50 °C (50 mmHg)] was distilled under reduced pressure under nitrogen. α,α'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Commercial butyllithium solution in hexane (1.6 mol/L) was used without further purification. Commercial tetrabutylammonium perchlorate was dried under reduced pressure at 150 °C for 12 h.

Polymerization Procedure. For radical polymerization, given amounts of **2c** or **2d**, styrene or **1a** as a comonomer if necessary, benzene or acetonitrile as a solvent, and AIBN as a radical initiator were placed in a glass ampule, which was degassed by the freeze−thaw method (repeated three times) and sealed. The ampule was placed in a bath thermostated at 60 °C for the time of polymerization and then opened. The reaction mixture was poured into an excess of hexane or isopropyl ether to deposit a polymeric product, which was purified in three or more redissolution−reprecipitation cycles. Dichloromethane and hexane were used as a solvent and a precipitant, respectively, for the homopolymerizations of **2c** and **2d** and for the copolymerizations of the **2c**−styrene and **2d**−styrene systems. The copolymers of the **2c**−**1a** system were washed repeatedly with a mixture solution of acetonitrile and methanol.

For ionic polymerization, the polymerization was carried out with the apparatus reported previously.[3] A given amount of **2c** or **2d** as a monomer was placed in the apparatus, which was filled with nitrogen. Into it was introduced a given amount of THF or dichloromethane as a solvent by a syringe. After the resulting solution was degassed by the freeze−thaw method (repeated twice), the apparatus was filled with nitrogen and sealed. Then it was set in a bath thermostated at 0 °C, and a fixed amount of butyllithium or boron trifluoride etherate as an ionic initiator was injected into it by a syringe. After a given time of reaction, the reaction mixture was poured into an excess of hexane to deposit a polymeric product. The precipitated polymeric product was dissolved again in a small amount of dichloromethane, and the resulting solution was poured into hexane for purification. When no polymeric product was deposited in this process, the hexane solution was placed under reduced pressure to remove volatile materials. An aliquot of the residue was dissolved in a small amount of THF, and the resulting THF solution was subjected to GPC to check whether the polymerization took place or not.

Characterization. Copolymer compositions were established by elemental analysis. The number-average molecular weights, M_n, of homopolymers and copolymers were determined by gel permeation chromatography (GPC) using standard polystyrenes as a reference and THF as an eluent without correction. ^{1}H NMR measurement was carried out in chloroform-*d* with tetramethylsilane as an internal standard. The first reduction potentials were determined by voltammetric measurement at room temperature at a scanning rate of 100 mV/s using dichloromethane as the solvent containing tetrabutylammonium perchlorate (0.1 mol/L) as a supporting electrolyte, and a Ag/AgCl electrode, a glassy carbon electrode, and a platinum wire were used as reference, working, and third electrodes, respectively. A Yanaco MT-3 CHN Corder was used for elemental analysis, a Tosoh HLC-803D gel permeation chromatograph with a series of two columns (Tosoh G2000H and G2500H) was used for measuring the number-average molecular weight, a JEOL JNM-EX 270 FT NMR spectrometer was employed for ^{1}H NMR spectroscopy, a JASCO IR-700 spectrometer was used for infrared spectroscopy, and a Yanaco VMA-010 New Cyclic Voltammetric Analyzer was used for measuring the first reduction potentials.

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