Synthesis and Polymerization Behavior of 4,7-Bis[(alkylthio)cyanomethylene]-4,7-dihydrobenzofurans and 11,12-Bis(alkylthio)-11,12-dicyano-1,4-naphthoquinodimethanes

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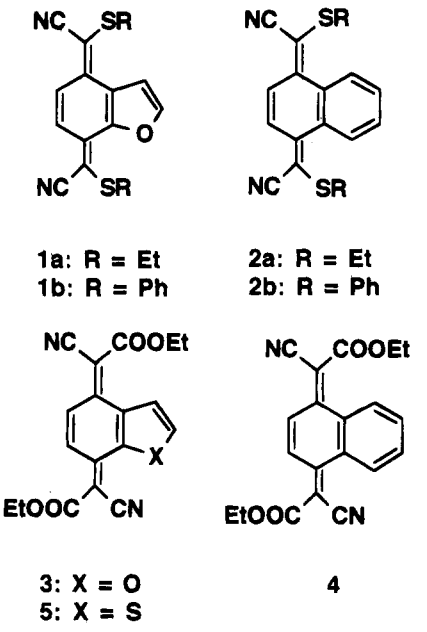
ABSTRACT: As stable quinonoid compounds of the benzofuran and the naphthalene, 4,7-bis[cyano(ethylthio)methylene]- and 4,7-bis[cyano(phenylthio)methylene]-4,7-dihydrobenzofurans (**1a** and **1b**) and 11,12-bis(ethylthio)- and 11,12-bis(phenylthio)-11,12-dicyano-1,4-naphthoquinodimethanes (**2a** and **2b**) were successfully prepared. When **1a**, **1b**, **2a**, and **2b** were dissolved in aprotic polar solvents such as acetonitrile, acetone, tetrahydrofuran, *N,N*-dimethylformamide, and dimethyl sulfoxide, no spontaneous homopolymerizations occurred. An anionic initiator butyllithium induced the homopolymerizations of **1a** and **1b** at 0 °C, and of **2a** and **2b** at −78 °C to give respective oligomers. A radical initiator 2,2′-azobis(isobutyronitrile) (AIBN) induced the homopolymerizations of **1a** and **1b** at 60 °C, but did not of **2a** and **2b**. Compounds **1a** and **1b** were copolymerizable with styrene in the presence of AIBN in a nearly alternating fashion to give the monomer reactivity ratios r_1(**1a**) = 0.70 ± 0.40 and r_2(styrene) = 0.02 ± 0.04 at 50 °C for the **1a**–styrene system and r_1(**1b**) = 0.80 ± 0.30 and r_2(styrene) = 0.01 ± 0.03 at 50 °C for the **1b**–styrene system and the Q and e values were Q = 9.7 and e = +1.27 for **1a** and Q = 17.4 and e = +1.40 for **1b**. However, when their copolymerizations were carried out at monomer concentrations where **1a** and **1b** are not homopolymerizable, no copolymerizations took place. The copolymerizations of **2a** and **2b** with styrene in the presence of AIBN at 50 °C did not occur.

Introduction

The 7,8-dicyano-1,4-benzoquinodimethanes such as 7,8-bis(alkoxycarbonyl)-7,8-dicyano-1,4-benzoquinodimethanes,[1–4] 7,8-diacyl-7,8-dicyano-1,4-benzoquinodimethanes,[5,6] and 7,8-bis(alkylthio)-7,8-dicyano-1,4-benzoquinodimethanes[7,8] were obtainable as crystals at room temperature and homopolymerizable spontaneously and also with radical and ionic initiators. Moreover, the homopolymerizations of these 7,8-dicyano-1,4-benzoquinodimethanes with radical initiators were typical equilibrium polymerizations and in their copolymerizations with styrene in the presence of a radical initiator they exhibited the different polymerization behaviors above and below equilibrium monomer concentrations.[1,8,9] At above equilibrium monomer concentrations, all 7,8-dicyano-1,4-benzoquinodimethanes were copolymerizable with styrene in a random fashion,[1,8,9] and at below equilibrium monomer concentrations, the captively substituted 7,8-dicyano-1,4-benzoquinodimethanes such as 7,8-dicyano-7,8-bis(alkoxycarbonyl)-1,4-benzoquinodimethanes and 7,8-diacyl-7,8-dicyano-1,4-benzoquinodimethanes were copolymerizable with styrene in a perfectly alternating fashion, but the captodatively substituted 7,8-dicyano-1,4-benzoquinodimethanes such as 7,8-bis(alkylthio)-7,8-dicyano-1,4-benzoquinodimethanes were not and reacted as inhibitors of the polymerization.[8,9] It was found that the polymerization behaviors of the 7,8-dicyano-1,4-benzoquinodimethanes might change greatly depending upon the nature of the substituents at the 7 and 8 positions.

Previously, the synthesis of the captively substituted quinodimethanes of benzofuran, naphthalene, and benzothiophene such as 4,7-bis[cyano(ethoxycarbonyl)-methylene]-4,7-dihydrobenzofuran (**3**),11,12-bis(ethoxycarbonyl)-11,12-dicyano-1,4-naphthoquinodimethane (**4**), and 4,7-bis[cyano(ethoxycarbonyl)methylene]-4,7-dihydrobenzothiophene (**5**) and their polymerization behaviors were reported.[10] We are interested in the polymerization behavior of the captodatively substituted quinodimethanes of benzofuran and naphthalene in comparison with those of **3**–**5** because the polymerization behavior might greatly change depending on the substituents at the exocyclic positions, as pointed out in the polymerizations of 7,8-dicyano-1,4-benzoquinodimethanes.



In this work are described the syntheses and the polymerizations of 4,7-bis[cyano(ethylthio)methylene]-

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and 4,7-bis[cyano(phenylthio)methylene]-4,7-dihydrobenzofurans (**1a** and **1b**) and 11,12-bis(ethylthio)- and 11,12-bis(phenylthio)-11,12-dicyano-1,4-naphthoquinodimethanes (**2a** and **2b**) as the captodatively substituted quinodimethanes of benzofuran and naphthalene.

Experimental Section

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 tetrahydrofuran (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 of **1a**, **1b**, **2a**, and **2b** were determined by the voltammetric measurement using dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L) as a solvent and an Ag/AgCl electrode, a glassy carbon electrode, and a platinum wire as reference, working, and third electrodes, respectively. A Büchi capillary melting point apparatus was used for the melting point measurement, a JEOL JNM-EX270 FT NMR spectrometer for ^{1}H NMR spectroscopy, a JASCO IR-700 and JASCO UVIDEC-430B spectrometers for infrared and UV–vis spectroscopy, respectively, a Yanaco CHN Corder MT-3 for elemental analysis, a gel permeation chromatography Tosoh HLC-803D with a series of two columns (Tosoh G2000H and G2500H) for measuring the number-average molecular weight, and a Yanaco New Cyclic Voltammetric Analyzer VMA-010 for measuring the first reduction potentials, respectively.

Preparation of 4,7-Bis[(alkylthio)cyanomethylene]-4,7-dihydrobenzofurans (1a,b). 4,7-Benzofurandicarbaldehyde (7). 4,7-Bis(bromomethyl)benzofuran (**6**)[10] (8.60 g, 28.3 mmol) and 15.86 g (113.1 mmol) of hexamethylenetetramine in 160 mL of a mixture solution of water and acetic acid (1:1 by volume) were refluxed for 45 min, into the reaction mixture was added 38.4 mL of concentrated hydrochloric acid, and the mixture was refluxed for 10 min. The resulting mixture was cooled to room temperature and extracted three times with 100 mL of chloroform. The extracts were combined, washed three times with 100 mL of water and 200 mL of 10% sodium carbonate aqueous solution, and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove volatile materials to obtain a pale yellow solid as the residue, which was dissolved in 3 mL of chloroform, and then, the resulting solution was passed through a silica gel column using chloroform as the eluent. The pale yellow elution band portion was collected and placed under reduced pressure to remove the solvent to give 1.71 g (34.7% yield) of **4** as a pale yellow solid: mp 154.0–155.8 °C; IR (KBr) ν_{C-H} 2842, $\nu_{C=O}$ 1686, ν_{C-O} 1131 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.62 (d, J = 2.4 Hz, 1H), 7.94 (s, 3H), 10.31 (s, 1H), 10.62 (s, 1H). Anal. Calcd for $C_{10}H_6O_3$: H, 3.47; C, 68.97; O, 27.56. Found: H, 3.30; C, 68.69.

4,7-Bis[bis(alkylthio)methyl]benzofurans (8a,b). Compound **7** (9.6 mmol) and 40 mmol of an alkanethiol were dissolved in 40 mL of chloroform, and the solution was cooled to 0 °C. Into this solution was added 0.3 mL of boron trifluoride etherate, and the mixture was stirred for 17 h. The reaction mixture was washed twice with 100 mL of 5% sodium hydroxide aqueous solution and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove volatile materials to give a pale yellow oil, which was dissolved in 2 mL of benzene, and then, the resulting solution was passed through a silica gel column using benzene as the eluent. The second elution band was collected and placed under reduced pressure to remove the solvent to give **8a,b**.

4,7-Bis[bis(ethylthio)methyl]benzofuran (8a). Compound **8a** was prepared as a colorless oil in 89.3% yield from **7** and ethanethiol: IR (NaCl) ν_{C-H} 2926, ν_{C-O} 1122, ν_{C-S} 731 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.67 (d, J = 1.2 Hz, 1H), 7.37 (d, J = 3.0 Hz, 2H), 7.12 (d, J = 1.2 Hz, 1H), 5.59 (s, 1H), 5.21 (s, 1H), 2.66 (q, J = 6.6 Hz, 4H), 2.54 (q, J = 6.6 Hz, 4H), 1.23 (t, J = 7.2 Hz, 12H). Anal. Calcd for $C_{18}H_{26}OS_4$: H, 6.79; C, 55.90; O, 4.14; S, 33.17. Found: H, 6.81; C, 55.82; S, 33.20.

4,7-Bis[bis(phenylthio)methyl]benzofuran (8b). Compound **8b** was prepared as a pale yellow solid in 87.8% yield from **7** and thiophenol: mp 79–82 °C; IR (KBr) ν_{C-H} 3014, ν_{C-O} 1122, ν_{C-S} 723 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.60 (d, J = 2.7 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.16–7.28 (m, 20H), 7.00 (d, J = 2.7 Hz, 1H), 6.02 (s, 1H), 5.59 (s, 1H). Anal. Calcd for $C_{34}H_{26}OS_4$: H, 4.54; C, 70.54; O, 2.76; S, 22.16. Found: H, 4.44; C, 70.78; S, 21.88.

4,7-Bis[(alkylthio)cyanomethyl]benzofurans (9a,b). Anhydrous stannous chloride (8.1 mmol) was added into 8.3 mmol of **8a,b** and 27.3 mmol of trimethylsilyl cyanide in 70 mL of dichloromethane at 0 °C and stirred for 4 h. Into the reaction mixture was added 100 mL of ice water, and the organic phase was separated, washed twice with 100 mL of water and 100 mL of 5% sodium bicarbonate aqueous solution, and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove volatile materials to obtain a pale yellow oil as the residue, which was dissolved in 2 mL of benzene, and then, the resulting solution was passed through a silica gel column using benzene as the eluent. The pale yellow elution band portion was collected and placed under reduced pressure to remove the solvent to give **9a,b**. Compound **9a** was recrystallized from a mixture solution of benzene and hexane. **9b** hardly crystallized.

4,7-Bis[cyano(ethylthio)methyl]benzofuran (9a): yield 73.7%; pale yellow needles; mp 78.5–80.5 °C; IR (KBr) ν_{C-H} 2932, ν_{CN} 2220, ν_{C-O} 1122, ν_{C-S} 736 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.77 (d, J = 1.2 Hz, 1H), 7.44 (d, J = 3.0 Hz, 2H), 7.07 (d, J = 1.2 Hz, 1H), 5.31 (s, 1H), 5.05 (s, 1H), 2.61–2.95 (m, 4H), 1.33 (t, J = 7.2 Hz, 6H). Anal. Calcd for $C_{16}H_{16}N_2OS_2$: H, 5.11; C, 60.72; N, 8.85; O, 5.06; S, 20.27. Found: H, 5.10; C, 61.32; N, 8.72; S, 20.31.

4,7-Bis[cyano(phenylthio)methyl]benzofuran (9b): yield 70.0%; pale yellow oil; IR (NaCl) ν_{C-H} 3016, ν_{CN} 2220, ν_{C-O} 1123, ν_{C-S} 734 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.77 (d, J = 2.7 Hz, 1H), 7.42 (d, J = 1.8 Hz, 2H), 7.35 (s, 10H), 7.02 (d, J = 2.7 Hz, 1H), 5.44 (s, 1H), 5.16 (s, 1H). Anal. Calcd for $C_{24}H_{16}N_2OS_2$: H, 3.92; C, 69.87; N, 6.79; O, 3.88; S, 15.55. Found: H, 3.95; C, 69.70; N, 6.90; S, 15.34.

4,7-Bis[(alkylthio)cyanomethylene]-4,7-dihydrobenzofurans (1a,b). Activated manganese dioxide (41 mmol) was added into 4.1 mmol of **9a,b** in 70 mL of chloroform, and the mixture was refluxed with stirring under nitrogen for 2 h. The reaction mixture was filtered to remove insoluble solids to give a red solution, which was placed under reduced pressure to remove the solvent to give a dark red solid as the residue. The red solid was dissolved in 2 mL of benzene, and the resulting solution was passed through a silica gel column using benzene as the eluent. The red elution band portion was collected and placed under reduced pressure to remove the solvent to give a red solid, which was recrystallized from a mixture solution of benzene and hexane to give **1a,b** as deep red needles.

4,7-Bis[cyano(ethylthio)methylene]-4,7-dihydrobenzofuran (1a): yield 67.1%; mp 122.5–125.0 °C; UV ($CHCl_3$) 475 ($\epsilon = 6.0 \times 10^4$) nm; IR (KBr) ν_{C-H} 2934, ν_{CN} 2172, $\nu_{C=C}$ 1503, 1467, ν_{C-O} 1121, ν_{C-S} 722 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.11–7.74 (m, 1H), 3.22 (q, J = 7.2 Hz, 2H), 3.12 (q, J = 7.2 Hz, 2H), 1.47 (t, J = 7.2 Hz, 3H), 1.39 (t, J = 7.2 Hz, 3H). Anal. Calcd for $C_{16}H_{14}N_2OS_2$: H, 4.50; C, 61.11; N, 8.90; O, 5.09; S, 20.40. Found: H, 4.38; C, 60.72; N, 8.95; S, 20.36.

4,7-Bis[cyano(phenylthio)methylene]-4,7-dihydrobenzofuran (1b): yield 43.5%; mp 101.5–103.5 °C; UV ($CHCl_3$) 477 ($\epsilon = 5.24 \times 10^4$) nm; IR (KBr) ν_{C-H} 3014, ν_{CN} 2176, $\nu_{C=C}$ 1450, ν_{C-O} 1119, ν_{C-S} 732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.11–7.82 (m). Anal. Calcd for $C_{24}H_{14}N_2OS_2$: H, 3.44; C, 70.21; N, 6.82; O, 3.90; S, 15.62. Found: H, 3.35; C, 69.76; N, 6.52; S, 15.70.

Preparation of 11,12-Bis(alkylthio)-11,12-dicyano-1,4-naphthoquinodimethanes (2a,b). 1,4-Naphthalenedicarbaldehyde (11). 1,4-Bis(bromomethyl)naphthalene (**10**)[10] (10.2 g, 32.5 mmol) and 18.2 g (130 mmol) of hexamethylenetetramine in 200 mL of a mixture solution of water and acetic acid (1:1 by volume) were refluxed for 2 h, into the reaction mixture was added 80 mL of concentrated hydrochloric acid, and the mixture was refluxed for 15 min. The resulting

mixture was cooled to room temperature and extracted three times with 150 mL of diethyl ether. The extracts were combined, washed three times with 100 mL of water and 200 mL of 10% sodium carbonate aqueous solution, and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove volatile materials to give a brown solid as the residue, which was recrystallized from a mixture solution of chloroform and hexane to obtain 4.0 g (67.0% yield) of **11** as pale yellow needles: mp 120–121 °C; IR (KBr) ν_{C-H} 2840, $\nu_{C=O}$ 1690, ν_{C-O} 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.58 (s, 2H), 9.17–9.33 (m, 2H), 8.16 (s, 2H), 7.70–7.86 (m, 2H). Anal. Calcd for $C_{12}H_8O_2$: H, 4.39; C, 78.24, O, 17.37. Found: H, 4.40; C, 78.33.

1,4-Bis[bis(alkylthio)methyl]naphthalenes (12a,b). Compound **11** (11 mmol) and 50 mmol of an alkanethiol were dissolved in 100 mL of dichloromethane and cooled to 0 °C. Into the resulting solution was added 0.8 mL of boron trifluoride etherate, and the mixture was stirred for 12 h. The reaction mixture was washed twice with 100 mL of saturated sodium bicarbonate aqueous solution and dried over anhydrous magensium sulfate. The filtrate was placed under reduced pressure to remove volatile materials to give a colorless viscous oil, which was dissolved in 2 mL of benzene, and then, the resulting solution was passed through a silica gel column using benzene as the eluent. The second elution band portion was collected and placed under reduced pressure to remove the solvent to give **12a,b**.

1,4-Bis[bis(ethylthio)methyl]naphthalene (12a). Compound **12a** was prepared as a colorless oil in 92% yield from **11** and ethanethiol: IR (NaCl) ν_{C-H} 3040–3080, ν_{C-H} 2830–2975, ν_{C-S} 1420 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.24–8.41 (m, 2H), 7.82 (s, 2H), 7.42–7.63 (m, 2H), 5.71 (s, 2H), 2.55 (q, J = 7.2 Hz, 8H), 1.20 (t, J = 7.2 Hz, 12H). Anal. Calcd for $C_{20}H_{28}S_4$: H, 7.13; C, 60.54; S, 32.33. Found: H, 6.87; C, 60.52; S, 32.61.

1,4-Bis[bis(phenylthio)methyl]naphthalene (12b). Compound **12b** was prepared as white needles in 93% yield from **11** and thiophenol: mp 105–106 °C; IR (KBr) ν_{C-H} 3020–3075 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.22–8.32 (m, 2H), 7.56 (m, 4H), 7.24 (s, 20H), 6.16 (s, 2H). Anal. Calcd for $C_{36}H_{28}S_4$: H, 4.80; C, 73.42; S, 21.78. Found: H, 4.78; C, 73.00; S, 22.22.

1,4-Bis[(alkylthio)cyanomethyl]naphthalenes (13a,b). Anhydrous stannous chloride (17.4 mmol) was added into 17.4 mmol of **12a,b** and 63.6 mmol of trimethylsilyl cyanide in 100 mL of dichloromethane at 0 °C, and the mixture was stirred for 12 h. Into the reaction mixture was added 200 mL of ice water, and the organic phase was separated, washed twice with 100 mL of water and 100 mL of 5% sodium bicarbonate aqueous solution, and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove volatile materials to obtain a pale yellow solid as the residue, which was dissolved in 2 mL of benzene, and then, the resulting solution was passed through a silica gel column using benzene as the eluent. The second elution band portion was collected and placed under reduced pressure to remove the solvent to give a white solid, which was recrystallized from a mixture solution of dichloromethane and hexane to give **13a,b** as white needles.

1,4-Bis[(ethylthio)cyanomethyl]naphthalene (13a): yield 53%; mp 151–152 °C; IR (KBr) ν_{C-H} 3020–3075, ν_{C-H} 2890–2930, ν_{CN} 2240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.23–8.07 (m, 2H), 7.80 (s, 2H), 7.76–7.59 (m, 2H), 5.44 (s, 2H), 2.82 (q, J = 7.2 Hz, 4H), 1.33 (t, J = 7.2 Hz, 6H). Anal. Calcd for $C_{18}H_{18}N_2S_2$: H, 5.56; C, 66.22; N, 8.58; S, 19.64. Found: H, 5.53; C, 66.74; N, 8.51; S, 19.22.

1,4-Bis[(phenylthio)cyanomethyl]naphthalene (13b): yield 69%; mp 158–159 °C; IR (KBr) ν_{C-H} 3072–3020, ν_{CN} 2230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.25–8.13 (m, 2H), 7.85–7.81 (m, 2H), 7.37 (s, 10H), 7.23 (s, 2H), 5.59 (s, 2H). Anal. Calcd for $C_{26}H_{18}N_2S_2$: H, 4.29; C, 73.90; N, 6.63; S, 15.18. Found: H, 4.26; C, 73.95; N, 6.76; S, 15.03.

11,12-Bis(alkylthio)-11,12-dicyano-1,4-naphthoquinodimethanes (2a,b). *N*-chlorosuccinimide (NCS) (3.0 mmol) was added into 1.5 mmol of **13a,b** in 30 mL of chloroform at 0 °C, and the mixture was stirred for 10 min. Into the resulting solution was added 3.0 mmol of triethylamine, and the mixture was stirred for 3 min. The reaction mixture was washed twice with 50 mL of water and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove volatile materials to give a red-orange solid, which was dissolved in 2 mL of benzene, and then, the resulting solution was passed through a silica gel column using benzene as the eluent. The red-orange elution band portion was collected and placed under reduced pressure to remove the solvent to give a red-orange solid, which was recrystallized from a mixture solution of dichloromethane and hexane to give **2a,b** as orange needles.

11,12-Bis(ethylthio)-11,12-dicyano-1,4-naphthoquinodimethane (2a): yield 71%; mp 70–71 °C; UV ($CHCl_3$) 445 ($\epsilon = 3.79 \times 10^4$) nm; IR (KBr) ν_{C-H} 3070–3040, ν_{C-H} 2975–2840, ν_{CN} 2200, $\nu_{C=C}$ 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.71–8.57 (m, 1H), 8.33–8.20 (m, 1H), 7.63–7.44 (m, 4H), 3.17 (q, J = 7.2 Hz, 4H), 1.40 (t, J = 7.2 Hz, 6H). Anal. Calcd for $C_{18}H_{16}N_2S_2$: H, 4.98; C, 66.62; N, 8.63; S, 19.77. Found: H, 4.92; C, 66.20; N, 8.54; S, 20.34.

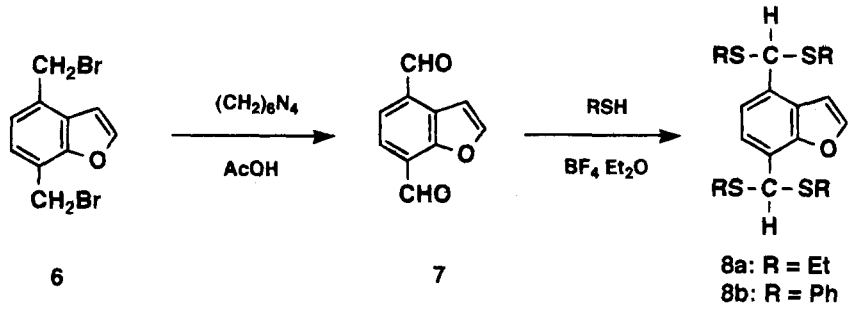
11,12-Bis(phenylthio)-11,12-dicyano-1,4-naphthoquinodimethane (2b): yield 84%; mp 123–124 °C; UV ($CHCl_3$) 445 ($\epsilon = 4.34 \times 10^4$) nm; IR (KBr) ν_{C-H} 3014, ν_{CN} 2176, $\nu_{C=C}$ 1450, ν_{C-O} 1119, ν_{C-S} 732 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.67 (m, 1H), 8.12 (m, 1H), 7.81 (s, 2H), 7.65 (m, 2H), 7.49 (s, 10H). Anal. Calcd for $C_{26}H_{16}N_2S_2$: H, 3.84; C, 74.25; N, 6.66; S, 15.25. Found: H, 3.75; C, 74.36; N, 6.81; S, 15.08.

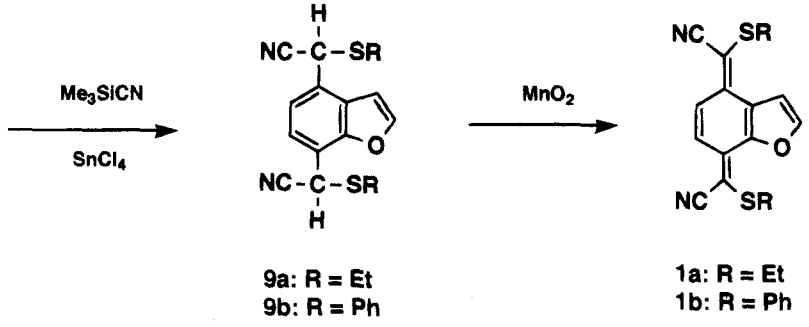
Other Materials. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Boron trifluoride etherate was distilled under reduced pressure in an atmosphere of nitrogen. Commercial butyllithium (1.6 M in hexane) and activated manganese dioxide (both Aldrich Co.) were used without further purification. Boron trifluoride etherate [bp 50 °C (50 mmHg)] was distilled under reduced pressure under nitrogen. Styrene was washed with 2% sodium hydroxide aqueous solution and water and dried over anhydrous magnesium sulfate for 1 day. Its supernatant was dried again over calcium hydride with stirring at room temperature for 12 h and distilled under reduced pressure. Chloroform (bp 61 °C), acetonitrile (bp 82 °C), acetone (bp 56 °C), and dichloromethane (bp 40 °C) were refluxed over calcium hydride for 12 h and then distilled. Tetrahydrofuran (THF) (bp 66 °C) was refluxed over lithium aluminum hydride for 12 h and then distilled. Dimethyl sulfoxide (DMSO) [bp 68 °C (10 mmHg)] and *N,N*-dimethylformamide (DMF) [bp 70 °C (10 mmHg)] were dried over 3A molecular sieves for 1 day and then distilled under reduced pressure. Tetrabutylammonium perchlorate was dried under reduced pressure at 150 °C for 12 h.

Polymerization Procedure. Spontaneous Polymerization. Compounds **1a,b** and **2a,b** (about 2 mg) were dissolved in 2 mL of a solvent such as acetone, acetonitrile, THF, DMSO, and DMF. After standing 5 days at room temperature, an aliquot of the solution was taken out by syringe and was subjected to gel permeation chromatography to determine whether polymerization occurred or not.

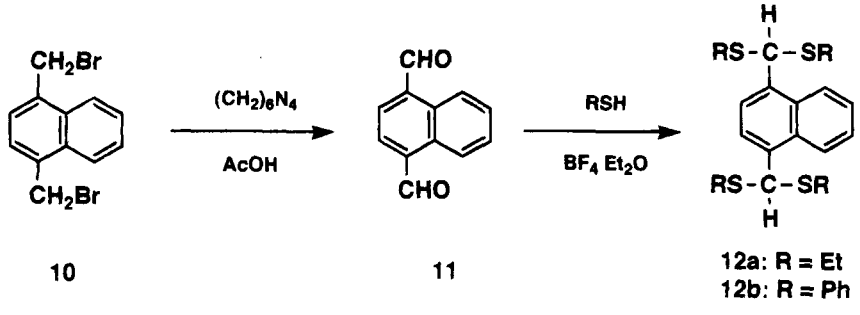
Ionic Polymerization. The polymerization was carried out with the apparatus reported previously.[2] A given amount of **1a**, **1b**, **2a**, or **2b** as a monomer was placed in the apparatus, which was filled with nitrogen gas. Into it was introduced a given amount of solvent by syringe. After the resulting solution was degrassed 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 or −78 °C and a fixed amount of butyllithium or boron trifluoride etherate was injected into it by syringe. After a given time of the reaction, the reaction mixture was poured into excess hexane 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. When no polymeric product was deposited in this process, the hexane solution was placed under reduced pressure to remove volatile materials. The remaining residue was dissolved in a small amount of dichloromethane and the resulting solution was passed through a silica gel column to separate it into two portions: the colored band as unreacted monomer and the colorless band as a reaction product. The latter was placed under reduced pressure to leave an oligomeric reaction product. An aliquot of the reaction mixture was taken out of the

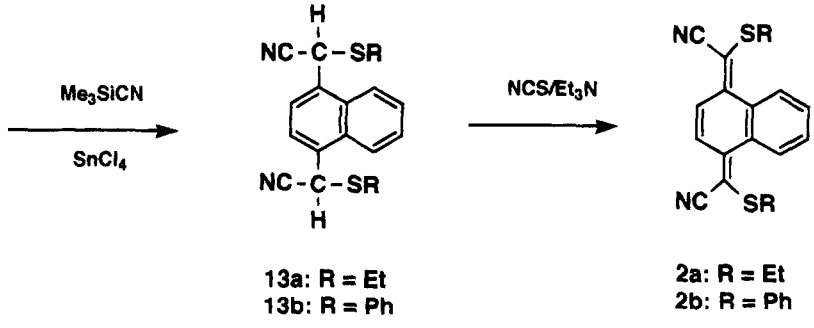
Scheme 1





Scheme 2





apparatus and added to excess THF. The resulting THF solution was subjected to GPC to determine the molecular weight of the products in the reaction mixture.

Radical Polymerization. Given amounts of a monomer (**1a**, **1b**, **2a**, or **2b**), styrene as a comonomer if necessary, chloroform 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 50 or 60 °C for the time of the polymerization and then opened. The rest of the procedure was carried out similarly to the above-mentioned ionic polymerization.

Results and Discussion

Syntheses of 1a, 1b, 2a, and 2b. 4,7-Bis[cyano(ethylthio)methylene]- and 4,7-bis[cyano(phenylthio)methylene]-4,7-dihydrobenzofurans (**1a** and **1b**) and 11,12-bis(ethylthio)- and 11,12-bis(phenylthio)-11,12-dicyano-1,4-naphthoquinodimethanes (**2a** and **2b**) were successfully prepared according to Schemes 1 and 2, respectively.

The bromomethyl groups of 4,7-bis(bromomethyl)benzofuran (**5**) and 1,4-bis(bromomethyl)naphthalene (**10**) were converted easily to the formyl ones by the Sommelet reaction[11] to give 4,7-benzofurandicarbalde-

Table 1. First Reduction Potentials, E_1, of 1a, 1b, 2a, 2b, 3, and 4[a]

compd	E_1N	compd	E_1N
3	−0.14	**4**	−0.29
1b	−0.63	**2b**	−0.72
1a	−0.88	**2a**	−1.03

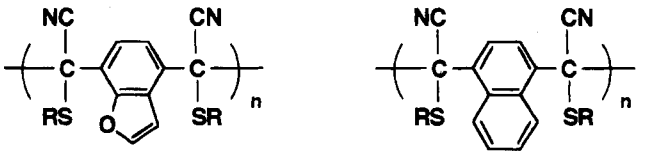
[a] Solvent, dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L); reference electrode, Ag/AgCl; scanning rate, 100 mV/s; relative error, ±0.01 V.

hyde (**7**) and 1,4-naphthalenedicarbaldehyde (**11**) in moderate yields, respectively. The reactions of **7** and **11** with alkanethiols under an acidic condition gave the respective thioacetals, 4,7-bis[bis(alkylthio)methyl]benzofurans (**8a,b**) and 1,4-bis[bis(alkylthio)methyl]naphthalenes (**12a,b**), in high yields. The reactions of **8a,b** and **12a,b** with about 4 times the molar quantity of the trimethylsilyl cyanide in the presence of the anhydrous stannous tetrachloride allowed one alkylthio group of each thioacetal group to be substituted with a cyano group to give 4,7-bis[(alkylthio)cyanomethyl]benzofurans (**9a,b**) and 1,4-bis[(alkylthio)cyanomethyl]naphthalenes (**13a,b**), respectively, in moderate yields. However, in the use of double the molar quantity of the trimethylsilyl cyanide, only one alkylthio group among the four alkylthio groups of **8a,b** and **12a,b** was substituted with a cyano group. And also the cyanation of thioacetal **8a** with a mercury(II) cyanide and iodine[12] reagent gave 4-formyl-7-(ethylthio)cyanomethylbenzofuran in good yield instead of desired compound **9a**. Compounds **9a,b** were readily oxidized with an activated manganese dioxide in chloroform to give 4,7-bis[(alkylthio)cyanomethylene]-4,7-dihydrobenzofurans (**1a,b**) as deep red needles and the compounds **13a,b** were reacted with NCS/triethylamine to give 11,12-bis(alkylthio)-11,12-dicyano-1,4-naphthoquinodimethanes (**2a,b**) as orange needles in good yields. Their IR and ^{1}H NMR spectra and elemental analysis strongly supported their chemical structures. The total yields of **1a,b** and of **2a,b** in four steps were 9−15% and 23−36%, respectively.

Electron-Accepting Characteristics of 1a, 1b, 2a, and 2b. The values of the first reduction potentials, E_1, for **1a**, **1b**, **2a**, and **2b** are summarized in Table 1, together with those of **3** and **4** for comparison. It is obvious that the captodatively substituted quinodimethanes, **1a**, **1b**, **2a**, and **2b**, have much weaker electron-accepting properties than **3** and **4**, indicating that the substitution of the ethoxycarbonyl group in **3** and **4** with a dative group such as an ethylthio or a phenylthio group makes the quinodimethane compounds more neutral in polarity. Moreover, the electron-accepting properties of **1a** and **2a** are weaker than those of respective **1b** and **2b**. The Hammett substitution constant values, σ_p, for the ethylthio and phenylthio groups are reported to be +0.03[13] and +0.29,[14] respectively, indicating that the electron-accepting property of the phenylthio group is stronger than that of the ethylthio one. Therefore, the difference in the electron-accepting properties between **1a** and **1b** and between **2a** and **2b** could be explained well by the difference in the substitution constant values of the dative groups.

Homopolymerizations of 1a, 1b, 2a, and 2b. The polymerization behavior of **1a**, **1b**, **2a**, or **2b** dissolved in basic aprotic polar solvents such as acetonitrile, acetone, THF, DMSO, and DMF was examined. When **1a**, **1b**, **2a**, or **2b** was dissolved in these solvents, the red to orange color of the resulting solutions remained almost unchanged for 10 days and each GPC chromatogram showed only a peak as the monomer state, indicating that **1a**, **1b**, **2a**, and **2b** are not homopolymerizable in those basic aprotic solvents. When **3** and **4** were dissolved in the same solvents, **3** was homopolymerizable in more basic polar solvents such as DMSO and DMF, but not in less basic polar solvents such as acetonitrile, acetone, and THF, and **4** was not homopolymerizable in the five such solvents.[10] The polymerization behaviors of **1a**, **1b**, **2a**, and **2b** in these basic aprotic polar solvents were similar to that of **4**. As **1a**, **1b**, **2a**, and **2b** became more neutral in polarity compared with **3** and **4** because of the captodative substitution, it is considered that spontaneous polymerizations of **1a**, **1b**, **2a**, and **2b** cannot take place in these basic aprotic polar solvents.

The homopolymerizations of **1a**, **1b**, **2a**, and **2b** were attempted with AIBN, butyllithium, and boron trifluoride etherate in order to investigate their polymerizability. The results are summarized in Table 2. All reaction products (oligomers) were soluble in dichloromethane, chloroform, THF, and ethyl acetate, but insoluble in hexane. Unfortunately, they could not be cast into films, probably due to their low molecular weights. When the polymerizations of **1a** and **1b** with AIBN were carried out in chloroform in a monomer concentration range of 0.16−0.32 mol/L at 60 °C, the polymerizations of **1a** and **1b** took place to give their oligomers with molecular weights of 300−5600 in 3−7% yields, but when the polymerizations were carried out at a lower monomer concentration of 0.011 mol/L at 60 °C, no polymerizations took place. These polymerization behaviors of **1a** and **1b** were similar to that of **3**, where **3** polymerized at a high monomer concentration of 0.16 mol/L at 60 °C to give an oligomer with the molecular weight of 9000 in 9.2% yield but did not at a lower monomer concentration of 0.026 mol/L.[10] When the polymerizations of **1a** and **1b** were carried out in THF with strong anionic initiator butyllithium at a monomer concentration of 0.032 mol/L at 0 °C for 24 h, **1a** and **1b** polymerized to give their oligomers with molecular weights of 300−4700 in 7−10% yields, in contrast to the yields and the molecular weights of the polymers obtained for the polymerization of **3**, where **3** polymerized in THF with butyllithium at a monomer concentration of 0.011 mol/L at 0 °C for 1 h to give a polymer with the molecular weight of 15 000 in yields as high as 87%. This indicates that **1a** and **1b** are less reactive in the polymerizations than **3**, probably arising from the much weaker electron-accepting property of **1a** and **1b** compared with **3**, as shown in their E_1 values. Polymerizations of benzoquinodimethanes are known to occur through the exocyclic methylene groups or the disubstituted methylene ones with reversion of the ring to the stable aromatic structure.[4,15−18] It is considered therefore that the oligomers obtained with AIBN and butyllithium initiators have the following structures:



When the polymerizations of **2a** and **2b** were carried out in the presence of AIBN at a monomer concentration range of 0.098−0.44 mol/L, similar to the monomer concentration range for the polymerization of **1a,b** with AIBN at 60 °C, no polymerizations occurred and the

Table 2. Homopolymerizations of 1a, 1b, 2a, and 2b with Various Initiators

run no.	amt of **1** or **2**/mg	initiator	[**1** or **2**]/[initiator]	solv, vol/mL	[**1** or **2**]/mol/L	temp/°C	time/h	conv/%	M_n[a]
				1a					
1	50.1	AIBN	20	$CHCl_3$, 15	0.011	60	24	0	
2	50.1	AIBN	20	$CHCl_3$, 1	0.16	60	24	5.6	300–1500
3	50.1	AIBN	20	$CHCl_3$, 0.5	0.32	60	24	7.0	300–1500
4	50.0	BuLi	10	THF, 5	0.032	0	24	7.8	300–2050
5	50.0	BF_3·Et_2O	10	CH_2Cl_2, 5	0.032	0	24	0	
				1b					
6	66.2	AIBN	20	$CHCl_3$, 15	0.011	60	24	0	
7	66.0	AIBN	20	$CHCl_3$, 1	0.16	60	24	3.0	300–1500
8	65.4	AIBN	20	$CHCl_3$, 0.5	0.32	60	24	3.1	300–5600
9	65.8	BuLi	10	THF, 5	0.032	0	24	10.3	300–4700
10	65.8	BF_3·Et_2O	10	CH_2Cl_2, 5	0.032	0	24	0	
				2a					
11	70.4	AIBN	32	$CHCl_3$, 1	0.217	60	24	0	
12	42.8	AIBN	20	$CHCl_3$, 0.3	0.44	60	27	0	
13	68.2	BuLi	13	toluene, 2	0.105	0	23	0	
14	43.0	BuLi	8	THF, 2	0.066	−78	7.5	6.0	370–580
15	41.5	BF_3·Et_2O	5	CH_2Cl_2, 1	0.128	0	24	0	
				2b					
16	41.2	AIBN	16	$CHCl_3$, 1	0.098	60	25	0	
17	43.1	AIBN	14	$CHCl_3$, 0.5	0.205	60	24	0	
18	80.6	BuLi	12	toluene, 4	0.048	0	17	0	
19	39.2	BuLi	6	THF, 2	0.047	−78	7.5	4.1	480–880
20	42.6	BF_3·Et_2O	13	CH_2Cl_2, 1	0.101	0	22	0	

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

Table 3. Copolymerizations[a] of 1a and 1b with Styrene in Chloroform at 50 °C

	monomer feed						copolym compn				
							anal.				
run no.	amt of **1a** or **1b**/mg	amt of styrene/mg	concn of **1a** or **1b**/mol %	vol of solv/mL	time/h	conv/%	% H	% C	% N	concn of **1a** or **1b**/mol %	10^{-4} M_n[b]
					1a						
1	30.8	206.8	4.7	0.26	40	11.1	5.66	69.64	6.48	46.8	2.06
2	31.5	94.0	10.0	0.36	40	14.6	5.49	70.05	6.36	45.2	1.05
3	62.8	83.6	19.9	0.84	45	4.9	4.81	67.61	7.06	55.7	1.04
4	92.5	74.4	29.2	1.32	72	13.1	5.18	67.27	7.15	57.4	1.90
5	124.6	63.1	39.5	1.80	90	8.2	5.37	66.86	7.27	59.5	1.90
6	157.2	52.5	49.8	2.27	92	5.1	4.91	66.02	7.51	64.0	1.08
7	188.4	44.0	58.7	2.74	100	6.8	4.81	65.97	7.53	64.3	1.06
					1b						
8	41.3	198.1	5.02	0.23	12	10.4	4.45	74.60	5.47	50.6	1.62
9	82.0	189.2	9.91	0.70	15	8.9	4.31	74.51	5.49	51.2	1.50
10	164.7	166.5	20.1	1.63	17	3.6	4.04	73.64	5.77	58.1	1.50
11	246.3	143.9	30.3	2.57	51	11.5	4.06	73.70	5.75	57.5	1.33
12	328.6	126.4	39.7	3.50	51	3.1	4.23	73.47	5.82	59.5	1.50
13	410.2	105.3	49.9	4.42	53	2.4	4.12	73.00	5.97	63.8	1.43
14	572.2	96.8	60.0	6.37	60	2.9	4.10	72.86	6.01	65.1	1.27

[a] [**1a**] = [**1b**] = 0.2 mol/L, AIBN = 5 mg. [b] Determined by GPC using THF as an eluent and standard polystyrenes as the reference.

unreacted **2a** and **2b** were recovered in quantitative yields. The polymerizations of **2a** and **2b** with butyllithium in toluene at 0 °C with monomer concentrations of **2a** of 0.105 mol/L and of **2b** of 0.048 mol/L, respectively, did not take place, but **2a** and **2b** polymerized in THF at a lower temperature of −78 °C with monomer concentrations of **2a** of 0.066 mol/L and of **2b** of 0.047 mol/L to give oligomers with molecular weights of 370–880 in 4–6% yields, suggestive of the equilibrium polymerization behavior in the polymerizations of **2a** and **2b** with butyllithium. Polymerization behaviors of **2a** and **2b** with both initiators were very similar to that of **4** reported previously.[10] When the polymerization behaviors of **1a** and **1b** with AIBN were compared with those of **2a** and **2b**, the former two compounds polymerized and the latter ones did not despite the similar polymerization conditions. The difference of these polymerization behaviors suggests that **2a** and **2b** have larger equilibrium monomer concentrations at 60 °C compared with **1a** and **1b**.

Compounds **1a**, **1b**, **2a**, and **2b** were not polymerizable with boron trifluoride etherate under the experimental conditions shown in Table 2, as well as **3** and **4** reported previously.[10]

Copolymerizations of 1a, 1b, 2a, and 2b with Styrene. The copolymerizations of styrene with **1a** and with **1b** in the presence of AIBN were carried out in chloroform at 50 °C with monomer concentrations of **1a** and **1b** of 0.2 mol/L. All copolymers were obtained as white powders, which were soluble in chloroform, dichloromethane, THF, acetone, and ethyl acetate, but insoluble in hexane and methanol. The results of the copolymerizations are summarized in Table 3, and the copolymerization composition curves for the **1a**–styrene and **1b**–styrene systems are shown in Figures 1 and 2, respectively. The results for the **1a**–styrene and **1b**–styrene systems are rationally analyzed according to the intersection[19] and Kelen–Tüdös[20] methods to obtain the monomer reactivity ratios r_1(**1a**) = 0.70 ± 0.40 and r_2(styrene) = 0.02 ± 0.04 at 50 °C for the **1a**–styrene

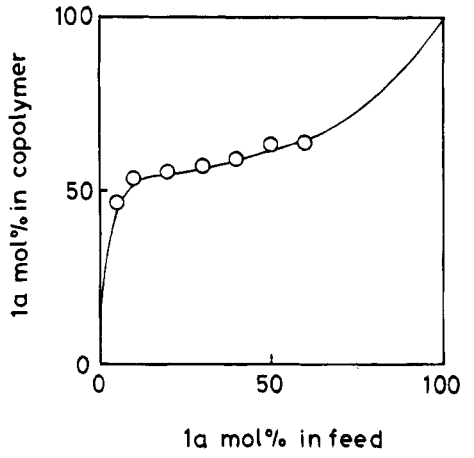


Figure 1. Copolymerization composition diagram for the **1a**–styrene system in chloroform at 50 °C.

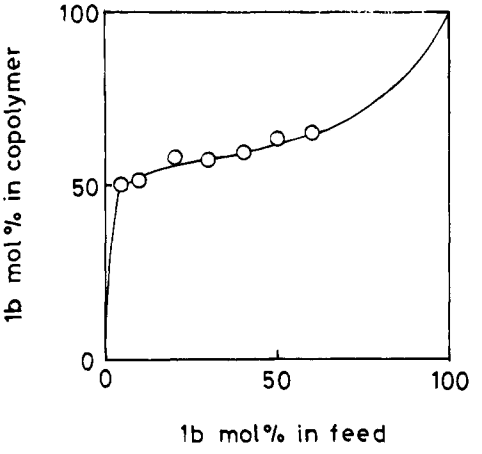


Figure 2. Copolymerization composition diagram for the **1b**–styrene system in chloroform at 50 °C.

system and r_1(**1b**) = 0.80 ± 0.30 and r_2(styrene) = 0.01 ± 0.03 at 50 °C for the **1b**–styrene system, respectively. The Alfrey–Price Q and e values of **1a** and **1b** were calculated on the basis of the monomer reactivity ratios to be Q = 9.7 and e = +1.27 for **1a** and Q = 17.4 and e = +1.40 for **1b**, respectively, indicating that **1a** and **1b** are highly conjugative and electron-accepting monomers. Previously, the monomer reactivity ratios for the copolymerization of the **3**–styrene system were reported to be r_1(**3**) = 0.18 ± 0.055 and r_2(sytrene) = 0.065 ± 0.025 at 50 °C.[10] The relative reactivity of **1a**, **1b**, and **3** toward the polymer radical with the styrene terminal unit was estimated from the comparison with the reciprocal of the monomer reactivity ratio, $1/r_2$, to be given as **1b** (100) > **1a** (50) > **3** (15), indicating that **1a** and **1b** are more reactive than **3**. This is considered to be due to a larger resonance stabilization of a polymer radical with the **1a** or **1b** terminal unit by the captodative substituent effect[21] compared to that with the **3** or **4** terminal unit. When the copolymerizations of **1a** and **1b** with styrene were attempted at 50 °C in chloroform at monomer concentrations of **1a** and **1b** of 0.01 mol/L, where they were not homopolymerizable, no copolymerizations took place. When the copolymerization was carried out at lower monomer concentrations of **1a** and **1b**, they lose the homopolymerizability and at the same time react as an inhibitor of the polymerization in contrast to the copolymerization of **3** with styrene, where **3** was copolymerizable with styrene in a perfectly alternating fashion.[10]

For the copolymerizations of styrene with **2a** and with **2b**, when the copolymerizations of the **2a**–styrene system with a monomer feed **2a**/styrene ratio of 45.5/153.3 in milligrams and of the **2b**–styrene system with a monomer feed **2b**/styrene ratio of 41.0/166.2 in milligrams were attempted in 1 mL of chloroform in the presence of 1.5 mg of AIBN at 50 °C for 24 h, no copolymerizations occurred and the unreacted monomers **2a** and **2b** were recovered in quantitative yields, in contrast to the copolymerization of **4** with styrene, where **4** was copolymerizable with styrene in a perfectly alternating fashion.[10] Previously, it was reported that when the copolymerization of 7,8-bis(ethylthio)-7,8-dicyanoquinodimethane (ESCQ) with styrene was carried out in chloroform at a monomer concentration below an equilibrium monomer concentration of ESCQ, no polymerization took place and ESCQ might react as an inhibitor of the polymerization.[6] The behaviors of the copolymerizations of styrene with **2a** and **2b** as well as with **1a** and **1b** under such experimental conditions that **1a** and **1b** cannot homopolymerize were very similar to that of the copolymerization of ESCQ with styrene below an equilibrium monomer concentration of ESCQ. When **1a**, **1b**, **2a**, and **2b** were not homopolymerizable owing to a significant participation of the depolymerization, they reacted as inhibitors of the polymerization. On the other hand, more electron-accepting **3** and **4** compared with **1a**, **1b**, **2a**, and **2b** were copolymerizable with styrene in a perfectly alternating fashion.[10] This indicates that the charge-transfer interaction between the polymer radical with the terminal quinodimethane unit and the comonomer styrene plays an important role in the rate-determining step of the alternating copolymerization mechanism[9] proposed previously, that is, in the addition step of the least reactive polymer radical to the least reactive monomer styrene. In other words, as **1a**, **1b**, **2a**, and **2b** have much weaker electron-accepting properties compared with **3** and **4**, the addition reactions of polymer radicals with **1a**, **1b**, **2a**, and **2b** units to a styrene cannot take place because of a weaker charge-transfer interaction.

In summary, 4,7-bis[cyano(ethylthio)methylene]- and 4,7-bis[cyano(phenylthio)methylene]-4,7-dihydrobenzofurans (**1a** and **1b**) and 11,12-bis(ethylthio)- and 11,12-bis(phenylthio)-11,12-dicyano-1,4-naphthoquinodimethanes (**2a** and **2b**) were successfully prepared as pure, isolable deep red crystals and orange crystals, respectively. When **1a**, **1b**, **2a**, and **2b** were dissolved in aprotic polar solvents such as acetonitrile, acetone, THF, DMF, and DMSO, no spontaneous homopolymerizations occurred. Compounds **1a,b** and **2a,b** were homopolymerizable with radical and anionic initiators, but not with a cationic initiator. Compounds **1a** and **1b** were copolymerizable with styrene in the presence of AIBN to give the monomer reactivity ratios r_1(**1a**) = 0.70 ± 0.40 and r_2(styrene) = 0.02 ± 0.04 at 50 °C for the **1a**–styrene system and r_1(**1b**) = 0.80 ± 0.30 and r_2(styrene) = 0.01 ± 0.03 at 50 °C for the **1b**–styrene system and the Q and e values of Q = 9.7 and e = +1.27 for **1a** and Q = 17.4 and e = +1.40 for **1b**, indicating that **1a** and **1b** were highly conjugative and electron-accepting. When the copolymerizations of **1a** and **1b** with styrene were carried out at lower monomer concentrations where **1a** and **1b** are not homopolymerizable, no copolymerizations took place and both **1a** and **1b** reacted as inhibitors of the polymerization. The copolymerizations of **2a** and **2b** with styrene in the presence of AIBN at 50 °C did not take place. It is considered that the lower polymerizability of **1a,b** and **2a,b** compared with that of **3** and **4** is probably due to

weaker electron-accepting properties of **1a,b** and **2a,b** caused by the captodative substitution.

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