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Synthesis of 11,12-Bis(alkylthio)-11,12-dicyano-2,6-naphthoquinodimethanes and Their Equilibrium Polymerization Behavior

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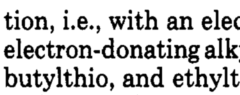
ABSTRACT: Attempts were made to prepare 2,6-naphthoquinodimethanes with different substituents such as cyano and alkylthio groups at the 11 and 12 positions, 11,12-bis(alkylthio)-11,12-dicyano-2,6-naphthoquinodimethanes (**2a–e**). Compounds **2a–e** could not be obtained as isolable crystals at room temperature but as their oligomers. It was found that when their oligomers were warmed in benzene, the oligomers depolymerized to give monomeric compounds and on cooling the monomeric compounds polymerized to form oligomers. Moreover, in the range of 20–40 °C polymerization–depolymerization equilibrium was found to be set up without side reaction. On the basis of analysis of the equilibrium polymerization behavior, thermodynamic parameters for the polymerizations of **2a–e** were determined. Their values were compared with the substituent parameters of the alkyl groups of the alkylthio substituents by means of linear free energy relationships, which exhibited that their enthalpy changes of polymerization are predominantly related with Taft's E_s values of the alkyl groups of alkylthio substituents and independent of their σ^* values ($\rho^* = 0$), indicating that homopolymerizabilities of **2a–e** are determined exclusively by a steric hindrance effect of the alkylthio substituents.

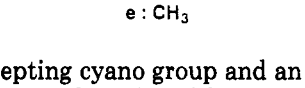
Introduction

Previously we reported the preparation of isolable 1,4-benzoquinodimethanes (**1a–c**) with captodative substitution, i.e., with an electron-accepting cyano group and an electron-donating alkylthio group such as phenylthio, *tert*-butylthio, and ethylthio at each of the 7 and 8 positions and their polymerization behavior.[1,2] Compound **1** bearing a bulky *tert*-butylthio group as an alkylthio group, 7,8-bis(*tert*-butylthio)-7,8-dicyano-1,4-benzoquinodimethane (**1b**), did not homopolymerize with any initiators, but compound **1** bearing phenylthio and ethylthio groups, 7,8-bis(phenylthio)- and 7,8-bis(ethylthio)-7,8-dicyano-1,4-benzoquinodimethanes (**1a** and **1c**), were homopolymerizable with radical and anionic initiators[1] and their homopolymerizations with a radical initiator were found to be typical equilibrium polymerizations. With the study of their equilibrium polymerization behavior, the thermodynamic parameters for their polymerizations were obtained.[2]



1

a : C_6H_5
b : t-C_4H_9
c : C_2H_5



2

a : C_4H_9
b : s-C_4H_5
c : i-C_3H_7
d : C_2H_5
e : CH_3

As to the 11,12-disubstituted 2,6-naphthoquinodimethanes, only 11,11,12,12-tetracyano-2,6-naphthoquinodimethane (TNAP)[3,4] and 11,11,12,12-tetraphenyl-2,6-naphthoquinodimethane (TPNQ)[5] carrying the same substituents at each of the 11 and 12 positions are known to be obtainable as crystals. 2,6-Naphthoquinodimethanes with a substitution mode other than TNAP and TPNQ have not been prepared yet. As 1,4-benzoquinodimethanes with captodative substitution were obtainable as crystals, we attempted to synthesize 2,6-naphthoquinodimethanes with captodative substitution, 11,12-bis(alkylthio)-11,12-dicyano-2,6-naphthoquinodimethanes (**2a–e**) bearing alkylthio groups such as butylthio, *s*-butylthio, isobutylthio, ethylthio, and methylthio. Compounds **2a–e** could not be obtained as monomeric crystals at room temperature but as their polymers (oligomers) instead. However, we found that when their oligomers were warmed in benzene, their oligomers dissociated easily to monomeric compounds and, when cooled, the monomeric compounds returned to their oligomers again, indicating that a polymerization–depolymerization equilibrium is set up between oligomer and monomer.

In this work, the polymerization–depolymerization equilibrium behavior was studied in detail to obtain the equilibrium monomer concentrations and the thermodynamic parameters such as enthalpy and entropy changes for the polymerizations of **2a–e** and moreover their polymerizabilities were discussed through analysis of these data by means of a linear free energy relationship.

Experimental Section

The number-average molecular weights, M_n, of the oligomers were determined by gel permeation chromatography (GPC) using standard polystyrene as a reference and tetrahydrofuran as an eluent without correction. ^{1}H NMR measurement was carried out in chloroform-*d* with tetramethylsilane as an internal standard. Determination of the melting points was carried out on a Büchi capillary melting point apparatus. ^{1}H NMR spectra were taken on a JEOL JNM-EX270 FT NMR spectrometer. Infrared and UV–vis measurements were made on JASCO IR-700 and UVIDEC-430B spectrometers, respectively. Elemental analysis was performed by a Yanako CHN corder MT-3. The number-average molecular weights (M_n) of the polymers were measured on a Tosoh HLC-803D with a series of two columns, Tosoh G2500H and G2000H.

Materials. Benzene (bp 80 °C) was washed in sequence with concentrated sulfuric acid, water, a 5% aqueous sodium hydroxide solution, and again water, dried over anhydrous calcium chloride, refluxed over metal sodium for 12 h, and then distilled. Chloroform (bp 61 °C) and dichloromethane (bp 40 °C) were refluxed over calcium hydride for 12 h and then distilled.

[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1994.

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Butanethiol, 2-butanethiol, 2-propanethiol, ethanethiol, methanethiol, 2,6-dimethylnaphthalene, *N*-bromosuccinimide (NBS) (all from Wako), and activated manganese dioxide (for organic oxidations, from Aldrich) were used without further purification. 11,11,12,12-Tetracyano-2,6-naphthoquinodimethane (TNAP) was prepared according to the methods of Diekman et al.[3] and Sandman et al.[4]

Syntheses of 11,12-Bis(alkylthio)-11,12-dicyano-2,6-naphthoquinodimethanes. 2,6-Bis(dibromomethyl)naphthalene (4). 2,6-Dimethylnaphthalene (3; 10.0 g, 64 mmol), 46.0 g (258 mmol) of *N*-bromosuccinimide (NBS), and 40 mg of benzoyl peroxide in 200 mL of carbon tetrachloride were refluxed with stirring under nitrogen for 4 h, and then 100 mg of α,α'-azobis(isobutyronitrile) was added and the solution was refluxed for an additional 24 h. The reaction mixture was cooled to 0 °C to deposit a solid which was collected by filtration. The filter cake was dissolved in 100 mL of chloroform, and the resulting solution was washed three times with 100 mL of water and dried over anhydrous magnesium sulfate. Then the filtrate was placed under reduced pressure to remove volatile materials to give a pale yellow solid, which was recrystallized from acetone to give 27.9 g (92.4% yield) of 4 as white needles: mp 158–159 °C; IR (KBr) ν_{CH} 3006, $\nu_{C=C}$ 1504 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.87 (m, 6H), 6.80 (s, 2H). Anal. Calcd for $C_{12}H_8Br_4$: C, 30.52; H, 1.71; Br, 67.74. Found: C, 30.48; H, 1.77; Br, 67.75.

2,6-Naphthalenedicarbaldehyde (5). Compound 4 (13.7 g, 29.1 mmol) in 100 mL of acetic acid was refluxed for 24 h and cooled to room temperature. Into the reaction mixture were added 300 mL of water and 2 mL of 2% hydrochloric acid, and the resulting mixture was stirred for an additional 1 h to deposit brown solid which was collected by filtration. The filter cake was dissolved in 100 mL of benzene, and the resulting solution was passed through a silica gel column using benzene as an eluent. The second elution band portion was collected and placed under reduced pressure to remove solvent to obtain a pale yellow solid, which was recrystallized from acetone to give 3.06 g (57.1% yield) of 5 as white needles: mp 169–170 °C (lit.[6] mp 173–174 °C); IR (KBr) ν_{CH} 3050–3300, $\nu_{C=O}$ 1700, $\nu_{C=C}$ 1531 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 10.23 (s, 2H), 8.28 (s, 2H), 8.10 (s, 4H).

2,6-Bis[bis(alkylthio)methyl]naphthalenes (6a–e). Zinc chloride (0.4 g) was added into **5** (0.8 g, 4.3 mmol) and 20 mmol of the respective alkanethiol in 30 mL of chloroform, and then hydrogen chloride gas was bubbled through the solution at room temperature for 10 min and stirred for an additional 2 h. The reaction mixture was washed five times with 20 mL of water and twice with 20 mL of a 10% sodium carbonate aqueous solution and dried over anhydrous magnesium sulfate. Then the filtrate was placed under reduced pressure to remove volatile materials to obtain a pale yellow viscous oil as the residue, which was dissolved in a small amount of chloroform, and then the resulting solution was passed through a silica gel column using benzene as an eluent. The second elution band portion was collected and placed under reduced pressure to remove solvent to give **6a–e**, which were recrystallized from carbon tetrachloride.

2,6-Bis[bis(butylthio)methyl]naphthalene (**6a**). Compound **6a** was prepared in 84.6% yield from **5** and butanethiol: mp 65–66 °C; IR (KBr) ν_{CH} 2922, 2832, $\nu_{C=C}$ 1571, 1476 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.78 (m, 4H), 7.61 (m, 2H), 5.01 (s, 2H), 2.57 (m, J = 7.4 Hz, 8H), 1.55 (m, J = 7.4 Hz, 8H), 1.39 (m, J = 7.3 Hz, 8H), 0.87 (t, J = 7.3 Hz, 12H). Anal. Calcd for $C_{28}H_{44}S_4$: C, 66.12; H, 8.72; S, 25.16. Found: C, 65.90; H, 8.72; S, 25.38.

2,6-Bis[bis(*s*-butylthio)methyl]naphthalene (**6b**). Compound **6b** was prepared in 77.1% yield from **5** and 2-butanethiol: mp 65–66 °C; IR (KBr) ν_{CH} 2924, 2884, $\nu_{C=C}$ 1571, 1475 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.78 (m, 4H), 7.68 (m, 2H), 5.08 (s, 2H), 2.81 (m, 2H), 2.70 (m, 2H), 1.57 (m, J = 4.2 Hz, 8H), 1.24 (t, J = 4.0 Hz, 12H), 0.91 (t, J = 4.0 Hz, 12H). Anal. Calcd for $C_{28}H_{44}S_4$: C, 66.12; H, 8.72; S, 25.16. Found: C, 65.72; H, 8.71; S, 25.57.

2,6-Bis[bis(isopropylthio)methyl]naphthalene (**6c**). Compound **6c** was prepared in 56.5% yield from **5** and 2-propanethiol: mp 113–114 °C; IR (KBr) ν_{CH} 2920, 2826, $\nu_{C=C}$ 1573, 1432 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.80 (m, 4H), 7.67 (m, 2H), 5.09 (s, 2H), 2.94 (q, J = 6.6 Hz, 4H), 1.24 (t, J = 6.6 Hz, 24H). Anal. Calcd for $C_{24}H_{36}S_4$: C, 63.70; H, 8.02; S, 28.28. Found: C, 63.76; H, 8.15; S, 28.09.

2,6-Bis[bis(ethylthio)methyl]naphthalene (**6d**). Compound **6d** was preapred in 60.4% yield from **5** and ethanethiol: mp 122–124 °C; IR (KBr) ν_{CH} 2922, 2832, $\nu_{C=C}$ 1571, 1476 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.79 (m, 4H), 7.64 (m, 2H), 5.09 (s, 2H), 2.46 (q, J = 7.2 Hz, 8H), 1.24 (t, J = 7.2 Hz, 12H). Anal. Calcd for $C_{20}H_{28}S_4$: C, 60.54; H, 7.13; C, 32.33. Found: C, 60.34; H, 7.46; S, 32.20.

2,6-Bis[bis(methylthio)methyl]naphthalene (**6e**). Compound **6e** was prepared in 81.8% yield from **5** and methanethiol: mp 181–182 °C; Ir (KBr) ν_{CH} 2934, 2872, $\nu_{C=C}$ 1569, 1473 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.80 (m, 4H), 7.57 (m, 2H), 4.93 (s, 2H), 2.12 (s, 12H). Anal. Calcd for $C_{16}H_{20}S_4$: C, 56.42; H, 5.92; S, 37.60. Found: C, 56.66; H, 6.07; S, 37.27.

2,6-Bis[1-(alkylthio)-1-cyanomethyl]naphthalenes (7a–e). Anhydrous stannous chloride (1.50 g, 5.6 mmol) was added into **6a–e** (2.4 mmol) and 0.90 g (9.0 mmol) of trimethylsilyl cyanide in 20 mL of dichloromethane at room temperature and stirred for 2 h. Into the reaction mixture was added 100 mL of water, and the organic phase was separated, washed twice with 100 mL of water and 100 mL of a 5% sodium bicarbonate aqueous solution, and dried over anhydrous magnesium sulfate. Then the filtrate was placed under reduced pressure to remove volatile materials to obtain a pale yellow solid or viscous oil as the residue, which was dissolved in 5 mL of a mixture solution of chloroform and hexane (1:1 by volume), and then the resulting solution was passed through a silica gel column using a mixture solution of chloroform and hexane (1:1 by volume) as an eluent. The third elution band portion was collected and placed under reduced pressure to remove solvent to give **7a–e**, where were recrystallized from carbon tetrachloride except for **7b**. **7b** hardly crystallized.

2,6-Bis[1-(butylthio)-1-cyanomethyl]naphthalene (**7a**): yield 43.8%; white needles; mp 116–118 °C; ν_{CH} 2914, 2888, $\nu_{C\equiv N}$ 2218, $\nu_{C=C}$ 1576, 1476 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.91 (m, 4H), 7.58 (m, 2H), 4.95 (s, 2H), 2.82 (m, J = 7.2 Hz, 2H), 2.62 (m, J = 7.2 Hz, 2H), 1.61 (m, J = 7.3 Hz, 4H), 1.41 (m, J = 7.3 Hz, 4H), 0.86 (t, J = 7.3 Hz, 6H). Anal. Calcd for $C_{22}H_{26}N_2S_2$: C, 69.07; H, 6.85; N, 7.32; S, 16.76. Found: C, 68.86; H, 6.93; N, 6.98; S, 17.23.

2,6-Bis[1-(*s*-butylthio)-1-cyanomethyl]naphthalene (**7b**): yield 66.4%; colorless oil; IR (NaCl) ν_{CH} 2926, 2890, $\nu_{C\equiv N}$ 2218, $\nu_{C=C}$ 1574, 1478 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.86 (m, 4H), 7.58 (m, 2H), 4.97 (s, 2H), 3.03 (m, J = 6.6 Hz, 2H), 1.76 (m, J = 6.9 Hz, 2H), 1.67 (m, J = 6.9 Hz, 2H), 1.42 (t, J = 6.6 Hz, 3H), 1.24 (t, J = 6.8 Hz, 3H), 0.97 (m, J = 6.9 Hz, 6H). Anal. Calcd for $C_{22}H_{26}N_2S_2$: C, 69.07; H, 6.85; N, 7.32; S, 16.76. Found: C, 69.07; H, 6.83; N, 7.07; S, 17.07.

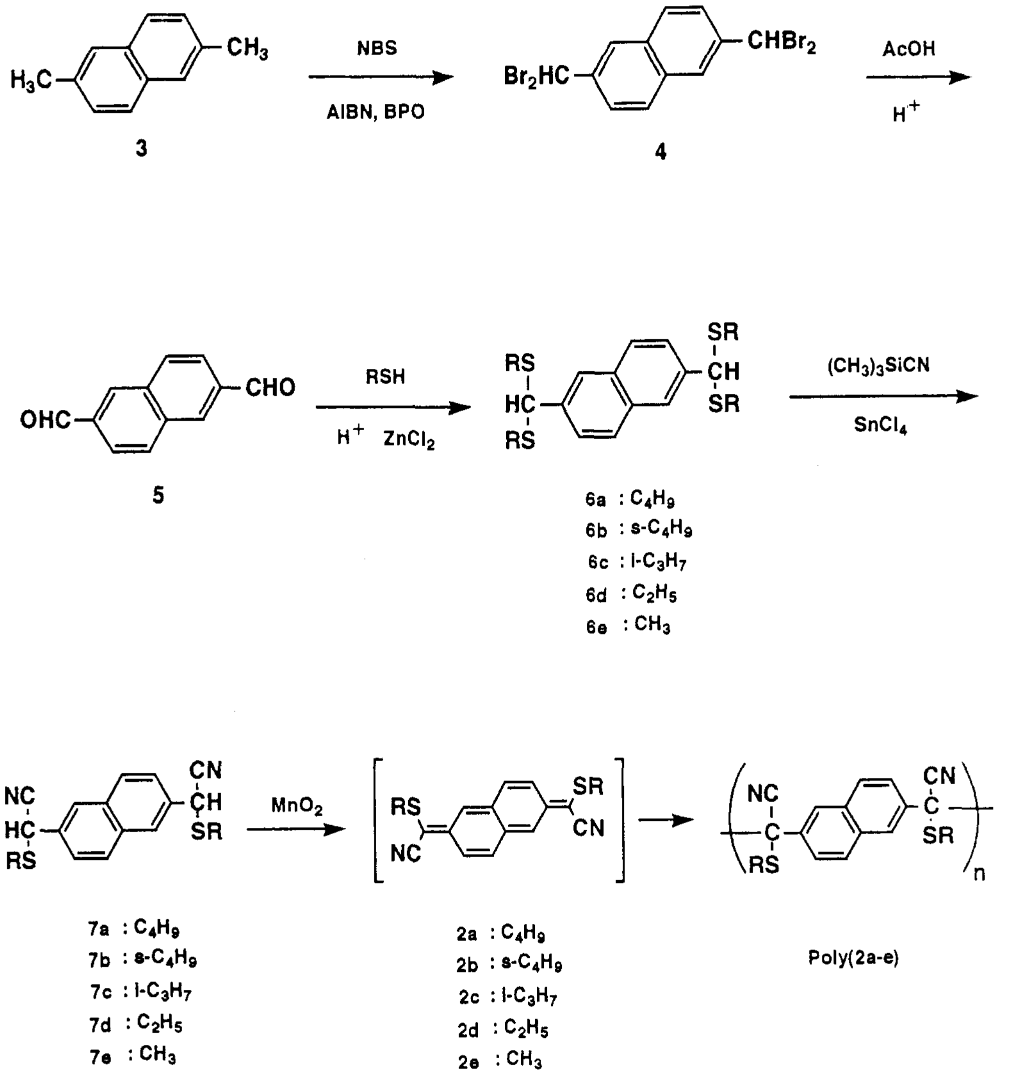
2,6-Bis[1-cyano-1-(isopropylthio)methyl]naphthalene (**7c**): yield 42.0%; pale yellow needles; mp 115–116 °C; IR (KBr) ν_{CH} 2924, $\nu_{C\equiv N}$ 2216, $\nu_{C=C}$ 1575, 1478 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.91 (m, 4H), 7.62 (m, 2H), 4.97 (s, 2H), 3.24 (m, J = 6.6 Hz, 2H), 1.45 (d, J = 6.6 Hz, 6H), 1.29 (d, J = 6.6 Hz, 6H). Anal. Calcd for $C_{20}H_{22}N_2S_2$: C, 68.68; H, 6.35; N, 7.70; S, 17.09. Found: C, 68.76; H, 6.25; N, 7.70; S, 17.29.

2,6-Bis[1-cyano-1-(ethylthio)methyl]naphthalene (**7d**): yield 41.4%; pale yellow needles; mp 83–84 °C; ν_{CH} 2930, $\nu_{C\equiv N}$ 2216, $\nu_{C=C}$ 1575, 1478 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.90 (m, 4H), 7.61 (m, 2H), 4.98 (s, 2H), 2.85 (m, 2H), 2.65 (m, J = 7.2 Hz, 2H), 1.30 (t, J = 7.2 Hz, 6H). Anal. Calcd for $C_{18}H_{18}N_2S_2$: C, 66.29; H, 5.56; N, 8.59; S, 19.56. Found: C, 67.01; H, 5.61; N, 8.49; S, 18.89.

2,6-Bis[1-cyano-1-(methylthio)methyl]naphthalene (**7e**): yield 67.1%; pale yellow needles; mp 133–134 °C; IR (KBr) ν_{CH} 3010, 2882, $\nu_{C\equiv N}$ 2218, $\nu_{C=C}$ 1574, 1478 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.92 (m, 4H), 7.61 (m, 2H), 4.94 (s, 2H), 2.22 (m, 6H). Anal. Calcd for $C_{16}H_{14}N_2S_2$: C, 64.47; H, 4.73; N, 9.39; S, 21.41. Found: C, 64.43; H, 4.71; N, 9.34; S, 21.48.

11,12-Bis(alkylthio)-11,12-dicyano-2,6-naphthoquinodimethanes (8a–e). Activated manganese dioxide (0.5 g) was added into **7a–e** (0.1 g) in 50 mL of chloroform and refluxed with stirring under nitrogen for 1 h. The reaction mixture was filtered to remove insoluble solid to give a pale purple to orange solution, the color of which gradually faded with evaporation of chloroform and, on complete evaporation of solvent, to give the pale yellow solid. The residue solid was dissolved in about 1 mL of dichloromethane chilled to 0 °C as soon as possible, and the resulting solution was poured into an excess of methanol chilled to 0 °C to deposit product, which was collected by the centrifugation method. The product was purified in three or more cycles of a redissolution–reprecipitation method using dichloromethane as solvent and methanol as precipitant and dried under reduced pressure until a constant weight was reached. All products were

Scheme 1



obtained as a white powder. The products obtained were characterized as follows.

11,12-Bis(butylthio)-11,12-dicyano-2,6-naphthoquinodimethane (**8a**): yield 63.0%; number-average molecular weight (M_n) = 4300; IR (KBr) ν_{CH} 2924, 2890, $\nu_{C\equiv N}$ 2214, $\nu_{C=C}$ 1567, 1472 cm^{-1}. Anal. Calcd for $(C_{22}H_{24}N_2S_2)_n$: C, 69.43; H, 6.39; N, 7.36; S, 16.85. Found: C, 69.44; H, 6.57; N, 7.30; S, 16.69.

11,12-Bis(*s*-butylthio)-11,12-dicyano-2,6-naphthoquinodimethane (**8b**): yield 63.0%; M_n = 2600; IR (KBr) ν_{CH} 2924, 2890, $\nu_{C\equiv N}$ 2216, $\nu_{C=C}$ 1569, 1472 cm^{-1}. Anal. Calcd for $(C_{22}H_{24}N_2S_2)_n$: C, 69.43; H, 6.36; N, 7.36; S, 16.85. Found: C, 69.25; H, 6.53; N, 7.26; S, 16.96.

11,12-Bis(isopropylthio)-11,12-dicyano-2,6-naphthoquinodimethane (**8c**): yield 88.4%; M_n = 2500; IR (KBr) ν_{CH} 2924, 2888, $\nu_{C\equiv N}$ 2220, $\nu_{C=C}$ 1566, 1472 cm^{-1}. Anal. Calcd for $(C_{20}H_{20}N_2S_2)_n$: C, 68.14; H, 5.72; N, 7.94; S, 18.20. Found: C, 68.02; H, 5.75; N, 7.80; S, 18.43.

11,12-Bis(ethylthio)-11,12-dicyano-2,6-naphthoquinodimethane (**8d**): yield 76.0%; M_n = 6400; IR (KBr) ν_{CH} 3016, 2930, $\nu_{C\equiv N}$ 2214, $\nu_{C=C}$ 1566, 1472 cm^{-1}. Anal. Calcd for $(C_{18}H_{16}N_2S_2)_n$: C, 66.70; H, 4.98; N, 8.63; S, 19.69. Found: C, 67.34; H, 5.63; N, 8.63; S, 18.80.

11,12-Bis(methylthio)-11,12-dicyano-2,6-naphthoquinodimethane (**8e**): yield 78.0%; M_n = 5500; IR (KBr) ν_{CH} 2882, $\nu_{C\equiv N}$ 2214, $\nu_{C=C}$ 1567, 1473 cm^{-1}. Anal. Calcd for $(C_{16}H_{12}N_2S_2)_n$: C, 64.90; H, 4.09; N, 9.48; S, 21.53. Found: C, 65.02; H, 4.09; N, 9.31; S, 21.58.

UV–Vis Spectral Measurement. A given amount of polymer (oligomer) such as poly(**2a**), poly(**2b**), poly(**2c**), poly(**2d**), or poly(**2e**) was weighed out in a 20-mL volumetric flask which was filled up to its meniscus with benzene to prepare its solution. An aliquot of the resulting solution was pipetted into a 100-mL volumetric flask and diluted with benzene to prepare a solution of poly(**2**) with a known concentration. A total of 4 mL of the solution was pipetted into an ampule with a quartz window cell (cell length: 1 cm), which was saturated with nitrogen gas and sealed. The ampule was set in a thremostated bath at the respective temperatures. The absorbance of the solution at wavelengths of 524 nm for poly(**2a**) and poly(**2b**), of 522 nm for poly(**2c**), or of 520 nm for poly(**2d**) and poly(**2e**) was measured spectrometrically as a function of time. The values of the molar absorption coefficient were determined by using solutions of poly(**2a–e**) with concentrations of 1.03 × 10^{-6} unit mol/L for poly(**2a**), 4.99 × 10^{-7} unit mol/L for poly(**2b**), 8.47 × 10^{-7} unit mol/L for poly(**2c**), 6.17 × 10^{-7} unit mol/L for poly(**2d**), and 7.65 × 10^{-7} unit mol/L for poly(**2e**). The values of the equilibrium monomer concentration at the respective temperature were determined by using solutions of poly(**2a–e**) with different concentrations such as 1.04 × 10^{-6}, 3.94 × 10^{-5}, 7.01 × 10^{-5}, 1.09 × 10^{-4}, and 3.64 × 10^{-4} unit mol/L for poly(**2a**), 1.59 × 10^{-4}, 2.50 × 10^{-4}, and 4.33 × 10^{-4} unit mol/L for poly(**2b**), 1.59 × 10^{-4}, 1.69 × 10^{-4}, and 2.83 × 10^{-4} unit mol/L for poly(**2c**), 2.33 × 10^{-5}, 4.67 × 10^{-5}, and 6.17 × 10^{-5} unit mol/L for poly(**2d**), and 7.65 × 10^{-6}, 1.09 × 10^{-5}, and 1.53 × 10^{-5} unit mol/L for poly(**2e**).

Results and Discussion

Syntheses of 11,12-Bis(alkylthio)-11,12-dicyano-2,6-naphthoquinodimethanes (2a–e). Attempts were made to prepare 11,12-bis(alkylthio)-11,12-dicyano-2,6-naphthoquinodimethanes (**2a–e**) with five kinds of alkylthio groups such as butylthio, *s*-butylthio, isobutylthio, ethylthio, and methylthio via the reaction route shown in Scheme 1.

Two methyl groups of 2,6-dimethylnaphthalene (**3**) were converted easily to dibromomethyl groups by the bromination reaction of **3** with NBS in the presence of radical

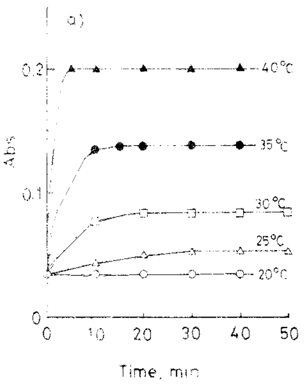


Figure 1. Time dependence of the absorbance of solutions of poly(**2a**) in benzene at a wavelength of 524 nm at 20, 25, 30, 35, and 40 °C: (a) [poly(**2a**)] = 3.94×10^{-5} unit mol/L; (b) [poly(**2a**)] = 1.04×10^{-6} unit mol/L.

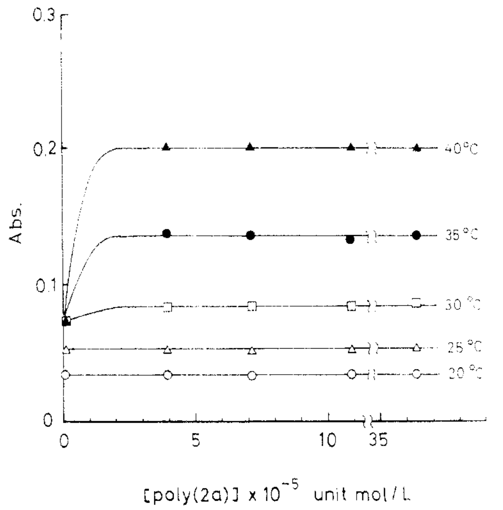


Figure 2. Plots of absorbances at a wavelength of 524 nm after 1 h versus concentrations of solutions of poly (**2a**) in benzene at 20, 25, 30, 35, and 40 °C.

initiator to give 2,6-bis(dibromomethyl)naphthalene (**4**) in high yield. The dibromomethyl groups in **4** were converted to formyl groups by the reaction of **4** with acetic acid followed by a hydrolysis reaction with hydrochloric acid to give 2,6-naphthalenedicarbaldehyde (**5**) in moderate yield. The reaction of **5** with alkanethiols under acidic conditions gave the respective thioacetals, 2,6-bis[bis(alkylthio)methyl]naphthalenes (**6a–e**), in high yield. The reactions of **6a–e** with trimethylsilyl cyanide in the presence of anhydrous stannous tetrachloride allowed one alkylthio group of each thioacetal group at the 2 and 6 positions of **6a–e** to be substituted with a cyano group to give 2,6-bis[1-(alkylthio)-1-cyanomethyl]naphthalenes (**7a–e**) in moderate yield. The oxidation reactions of **7a–e** with activated manganese dioxide in chloroform gave pale purple to orange solutions. However, the color of the solutions faded away on removal of chloroform as the solvent, and pale yellow solids were obtained as the residue in the bottom of the flask. The residue solids were dissolved in a small amount of dichloromethane chilled to 0 °C, and the resulting solutions were poured into an excess of methanol chilled to 0 °C to give white solids. The molecular weights of the white solids obtained were found to be several thousands by GPC measurement, and also their elemental analysis values were in good agreement with the calculated ones for monomeric **2a–e**. It is concluded, therefore, that the white solids obtained by this method were polymers (oligomers) with low molecular weights (poly(**2a–e**)) instead of monomeric **2a–e**.

Equilibrium Polymerization Behavior. When about 2 mg of the white solids were dissolved in 10 mL of benzene and warmed to 50 °C, the solutions developed color of pale purple to orange. The UV–vis spectra of these colored solutions exhibited absorption maxima (λ_{max}) at 524 nm for poly(**2a**), 524 nm for poly(**2b**), 522 nm for poly(**2c**), 520 nm for poly(**2d**), and 520 nm for poly(**2e**). As the UV–vis spectrum of the solution of TNAP in benzene showed an absorption maximum at 491 nm ($\epsilon_{\lambda_{max}} = 5.10 \times 10^4$), these absorption maxima observed for solutions of poly(**2a–e**) were regarded to be characteristic for monomeric substituted 2,6-naphthoquinodimethane. Therefore, it may be presumed that when solutions of poly(**2a–e**) in benzene were warmed to 50 °C, depolymerizations of poly(**2a–e**) took place to form monomeric **2a–e**.

The time dependence of the absorbances of solutions of poly (**2a**) in benzene with two different concentrations of 3.94×10^{-5} and 1.04×10^{-6} unit mol/L at a wavelength of 524 nm was measured at temperatures of 20, 25, 30, 35, and 40 °C. The results with concentrations of 3.94×10^{-5} and 1.04×10^{-6} unit mol/L are shown in parts a and b of Figure 1, respectively. At 20 °C, the absorbance of the solution of poly(**2a**) with a concentration of 3.94×10^{-5} unit mol/L is not variable regardless of time. When the solution was warmed to 25 °C, the absorbance increased gradually with time to reach a constant value in about 30 min, which was retained hereinafter. Similarly, when warmed to 30, 35, or 40 °C, their absorbances increased with time to reach the respective constant values in a much shorter time than 30 min, which were retained afterward. The higher the temperature, the shorter the time to reach constant values. It is obvious that when the solution of poly(**2a**) in benzene is kept at respective temperatures more than 1 h, the absorbances may reach respective constant values. The time dependence for the solution of poly(**2a**) with a concentration of 1.04×10^{-6} unit mol/L was similar to that with a concentration of 3.94×10^{-5} unit mol/L except for 30 and 40 °C where the absorbances were the same values. Solutions of poly(**2a**) with five different kinds of concentrations such as 1.04×10^{-6}, 3.94×10^{-5}, 7.10×10^{-5}, 1.09×10^{-4}, and 3.64×10^{-4} unit mol/L were kept at temperatures of 20, 25, 30, 35 and 40 °C for 1 h, and their absorbances were measured. The result is shown in Figure 2. Absorbances of the solutions with concentrations above 3.94×10^{-5} unit mol/L had almost the same values at the respective temperatures regardless of their concentrations. On the other hand, the absorbance of the solution with a concentration as low as 1.04×10^{-6} unit mol/L had lower values at temperatures above 30 °C compared with those of solutions with concentrations above 3.94×10^{-5} unit mol/L. Moreover, when the solution with a concentration of 1.04×10^{-6} mol/L was warmed to 40 °C, the increase in the absorbance was no longer observed. Therefore, it can be regarded that poly(**2a**) dissociated completely into monomeric **2a** at a temperature above 30 °C. If solutions of poly (**2a–e**) with a low concentration were warmed to higher temperature and the absorbance values no longer increased, the monomer molar absorption coefficient ($\epsilon_{\lambda_{max}}$) of **2a–e** may be determined. By application of this method for poly(**2a–e**), the values of $\epsilon_{\lambda_{max}}$ for **2a–e** were obtained as follows: 7.02×10^4 for **2a**, 4.18×10^4 for **2b**, 8.74×10^4 for **2c**, 5.67×10^4 for **2d**, and 5.36×10^4 for **2e**, respectively, which are presumably reasonable values from analogy with the $\epsilon_{\lambda_{max}}$ value (5.1×10^4) of TNAP.

The time dependence of the absorbance at a wavelength of 524 nm on three cycles of the warming–cooling process between 20 and 40 °C and between 20 and 60 °C was measured using the solution of poly(**2a**) in benzene with a concentration of 3.94×10^{-5} unit mol/L. The results for the cycles of the warming–cooling process between 20 and 40 °C and between 20 and 60 °C are shown in parts a and

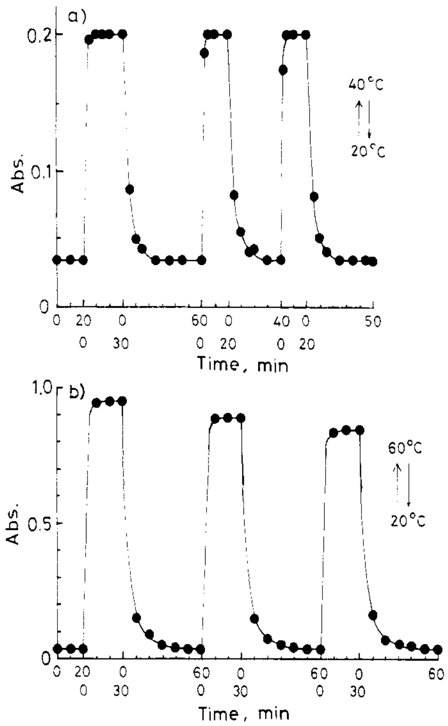


Figure 3. Time dependence of the absorbance at a wavelength of 524 nm of the solution of poly(**2a**) in benzene with a concentration of 3.94×10^{-5} unit mol/L on cycles of the warming–cooling process in the temperature ranges (a) between 20 and 40 °C and (b) between 20 and 60 °C.

Table 1. Equilibrium Monomer Concentrations, $[M]_e$, at Various Temperatures[a]

	$[M]_e \times 10^6$, mol/L				
temp, °C	**2a** (Bu)	**2b** (*s*-Bu)	**2c** (*i*-Pr)	**2d** (Et)	**2e** (Me)
20	0.50	14.5	3.55	0.42	0.33
25	0.75	22.3	5.48	0.65	0.53
30	1.20	33.6	8.42	1.04	0.84
35	1.94	49.0	12.8	1.68	1.28
40	2.86	68.0	19.5	2.56	2.11

[a] Equilibrium monomer concentrations were determined by using solutions of poly(**2a–e**) with the following concentrations: 1.04×10^{-6}, 3.94×10^{-5}, 7.01×10^{-5}, 1.09×10^{-4}, and 3.64×10^{-4} unit mol/L for poly(**2a**); 1.59×10^{-4}, 2.50×10^{-4}, and 4.33×10^{-4} unit mol/L for poly(**2b**); 1.59×10^{-4}, 1.69×10^{-4}, and 2.83×10^{-4} unit mol/L for poly(**2c**); 2.33×10^{-5}, 4.67×10^{-5}, and 6.17×10^{-5} unit mol/L for poly(**2d**); 7.65×10^{-6}, 1.09×10^{-5}, and 1.53×10^{-5} unit mol/L for poly(**2e**).

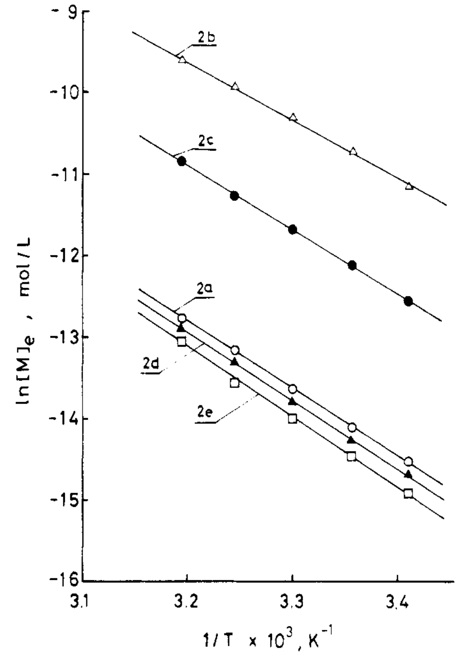


Figure 4. Plots of ln $[M]_e$ versus $1/T$ for polymerizations of **2a–e**.

Table 2. Enthalpy Changes (ΔH), Entropy Changes (ΔS), and Substituent Constants for Polymerizations of 2a–e

monomer	$-\Delta H$, kJ/mol	$-\Delta S$, J/K·mol	σ^{*10}	E_s^{10}	σ^{10}	$\Delta\Delta H$	$\Delta\Delta H - 10E_s$
2a (Bu)	67.3	109.1	−0.13	−0.39	−0.151	−2.5	+1.4
2b (*s*-Bu)	58.9	108.8	−0.21	−1.13	−0.12	−10.9	+0.4
2c (*i*-Pr)	64.6	116.1	−0.19	−0.47	−0.197	−5.2	−0.5
2d (Et)	69.4	114.5	−0.10	−0.07	−0.151	−0.4	+0.3
2e (Me)	69.8	114.0	0.0	0.0	−0.17	0	0

b of Figure 3, respectively. At 20 °C, absorbance of the solution of poly(**2a**) showed a constant value. When the solution was warmed to 40 °C, the absorbance increased rapidly to reach a given value in about 10 min, which no longer increased afterward. Subsequently, when the solution kept at 40 °C was cooled to 20 °C, the absorbance decreased slowly with time to return to the previous value at 20 °C in 30 min, which was retained hereinafter. Even though the cycle of the warming–cooling process between 20 and 40 °C was repeated three times, the constant values of the absorbances at temperatures of 20 and 40 °C observed on the first cycle were almost the same as the corresponding values observed on the third cycle, indicating that the polymerization–depolymerization equilibrium reaction between poly(**2a**) and **2a** took place without side reaction. However, when the cycles of the warming–cooling process of this solution were repeated between 20 and 60 °C, the value of absorbance at 60 °C decreased every each cycle at a low level (Figure 3b), indicating that, at a temperature as high as 60 °C, side reaction took place gradually in the solution. Similar behaviors also were observed for the same measurements at wavelengths of 524 nm for poly(**2b**), 522 nm for poly(**2c**), 520 nm for poly(**2d**), and 520 nm for poly(**2e**), respectively.

Equilibrium Monomer Concentrations and Thermodynamic Parameters for the Polymerization. The equilibrium monomer concentrations of **2a–e** in the range of 20–40 °C without side reaction were determined from the absorbance values after attainment of equilibrium and the values of $\epsilon_{\lambda_{max}}$ for each monomer obtained in the previous section. The values of equilibrium monomer concentrations, $[M]_e$, at temperatures of 20, 25, 30, 35, and 40 °C determined by using three or five different kinds of poly(**2a–e**) concentrations are summarized in Table 1. It is known that a log value of $[M]_e$ is related to a ceiling temperature, T_c, of polymerization according to 1[8]

$$\ln [M]_e = \Delta H/RT_c - \Delta S/R \qquad (1)$$

where ΔH and ΔS are enthalpy and entropy changes for the polymerization, respectively, and R is the gas constant. Plots of log values of $[M]_e$ versus the reciprocal of the absolute polymerization temperature, $1/T$, for poly(**2a–e**) are shown in Figure 4 to give good straight lines, the slopes and the intercepts of which give the ΔH and ΔS values for polymerizations of **2a–e**. ΔH and ΔS values for polymerizations of **2a–e** are summarized in Table 2. The ΔH values for the polymerization vary with the alkylthio groups of **2a–e**, whereas their ΔS values are almost constant within the −109 to −115 J/K·mol range and also are almost the same as the corresponding values (−110 to −130 J/K·mol)[8] for vinyl and related monomers. These ΔS values for polymerizations of **2a–e** are greatly different from the corresponding values for the previously reported equilibrium-polymerizable 1,4-benzoquinodimethanes such as 7,8-bis(butoxycarbonyl)-7,8-dicyano-1,4-benzoquinodimethane (ΔH = −26.4 kJ/mol, ΔS = −36.8 J/K·mol),[9] 7,8-

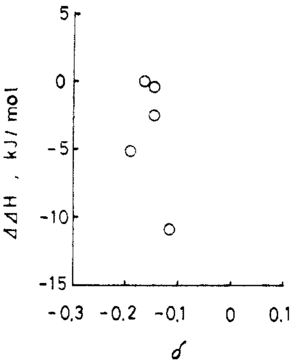


Figure 5. Hammett plot of $\Delta\Delta H$ versus σ for polymerizations of **2a–e**.

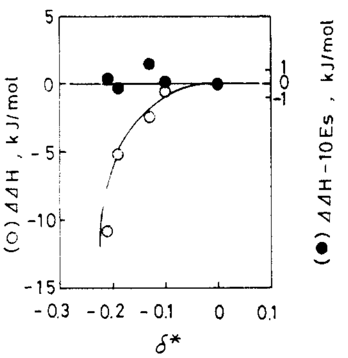


Figure 6. Hammett plot of $\Delta\Delta H$ versus σ^* (○) and Taft plot of $\Delta\Delta H - 10E_s$ versus σ^* (●) for polymerizations of **2a–e**.

diacetyl-7,8-dicyano-1,4-benzoquinodimethane ($\Delta H = -25.4$ kJ/mol, $\Delta S = -36.9$ J/K·mol),[9] 7,8-dibenzoyl-7,8-dicyano-1,4-benzoquinodimethane ($\Delta H = -21.4$ kJ/mol, $\Delta S = -37.5$ J/K·mol),[9] **1a** ($\Delta H = -23.5$ kJ/mol, $\Delta S = -33.8$ J/K·mol),[2] and **1c** ($\Delta H = -23.4$ kJ/mol, $\Delta S = -31.0$ J/K·mol).[2] The equilibrium monomer concentrations in polymerizations of **2a–e** were measured on the oligomer–monomer equilibrium state, while the equilibrium monomer concentrations in the polymerizations of polymerizable 1,4-benzoquinodimethanes were measured by the kinetic method on the basis of polymerization rate measurement. Unfortunately, at present, there is no reason to judge whether the difference of the ΔS value for the polymerizations of the quinodimethane monomers is induced by the difference in the measurement methods or by the difference in the structure between 2,6-naphthoquinodimethane and 1,4-benzoquinodimethane.

Linear Free Energy Relationship. Influence of alkylthio groups at the 11 and 12 positions on the polymerizability of 2,6-naphthoquinodimethanes with captodative substitution was studied. The enthalpy changes, ΔH, for polymerizations of **2a–e** were analyzed by means of the linear free energy relationships such as the Hammett[10] and Taft[10] equations:

$$\text{Hammett equation} \qquad \Delta H = \rho\sigma \tag{2}$$

and

$$\text{Taft equation} \qquad \Delta H = \rho^*\sigma^* + \delta E_s \tag{3}$$

where ρ is a constant for the specific reaction, σ is a polar substituent constant, generally referred to as the Hammett substituent constant, ρ^* is a constant giving the susceptibility of the reaction to the polar effect, σ^* is a polar substituent constant of the substituent group to the methyl group, E_s is a steric effect parameter of a substituent, and δ is a constant giving the susceptibility of the reaction to the steric effect. In the Table 2 are listed values of σ, σ^*, and E_s[10] for the alkyl groups (R) of the alkylthio (RS) substituents at the 11 and 12 positions of the substituted 2,6-naphthoquinodimethanes. Here, for polymerization of **2a–e**, the ΔH value for **2e**, which has a methyl group as the alkyl group of the alkylthio substituent, was taken as a standard and differences between ΔH values for **2e** and ΔH values for **2a**, **2b**, **2c**, and **2d** were given as $\Delta\Delta H$ values. As shown in Figure 5, $\Delta\Delta H$ are not found to be correlated with σ values of the R group. Also, as shown in Figure 6, the plot (○) between $\Delta\Delta H$ and σ^* is not found to be a good linear relationship. On the other hand, if the steric hindrance is taken into account by subtracting $10E_s$ from $\Delta\Delta H$, the plot (●) between $\Delta\Delta H - 10E_s$ and σ^* becomes a straight line with zero slope; i.e., $\rho^* = 0$. It is concluded, therefore, that the free energy change of polymerization for **2** is dependent only on the steric hindrance of the substituents and is no more influenced by the polar effect of the substituents. This is another example supporting the steric hindrance effect of substituents on the polymerizabilities of quinodimethane monomers obtained from polymerizations of 7,8-diacyl-7,8-dicyano-1,4-benzoquinodimethanes.[11]

In summary, 11,12-bis(alkylthio)-11,12-dicyano-2,6-naphthoquinodimethanes (**2a–e**) are so reactive that they polymerized during preparation to give their oligomers instead of monomeric crystals. When the oligomers were warmed in benzene, the oligomers depolymerized to yield monomeric compounds, and on cooling the monomeric compounds polymerized to give oligomers. Moreover, it was found that perfect polymerization–depolymerization equilibrium is set up without side reaction in the range of 20–40 °C. On the basis of analysis of the equilibrium polymerization behavior, ΔH and ΔS values for polymerizations of **2a–e** were determined. It was found that ΔS for polymerizations of **2a–e** were almost constant regardless of alkylthio substituents and polymerizabilities of **2a–e** were significantly dependent on the ΔH values. ΔH values were analyzed by means of the linear free energy relationship such as the Taft equation. It was concluded that polymerizabilities of **2a–e** are dependent only on a steric hindrance of the substituents and independent of their polar effect.

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